GEOCHEMICAL CONTRIBUTIONS TO PROBLEMS OF PETROGENESIS

By

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INTRODUCTION

INTRODUCTION

The foundations of our knowledge concerning the trace-element contents of minerals and rocks and the principles of their distribution are based mainly on the well known geochemical studies of V.M. Goldschmidt. During recent years, a beginning has been made in applying trace-element data to attempts to solve some of the numerous problems of petrogenesis. Such studies have already shown that this line of research is likely to be very fruitful in contributing towards our understanding of the natural history of rocks. Impressed by the very promising possibilities and also by the paucity of data concerning suites of geochemically related rocks of various kinds, the writer decided a few years ago to devote himself to a systematic programme of geochemical research, and to this end he was most fortunate in being awarded a Farouk I Fellowship by the Egyptian Government, and in being granted study leave from the University of Alexandria for a period of two years.

This period has been spent at (a) the Grant Institute of Geology, University of Edinburgh, under the stimulating influence of Professor Arthur Holmes and Dr D.L. Reynolds, and (b) the Macaulay Institute for Soil Research at Aberdeen with its fully equipped spectrochemical laboratories, where the most outstanding British work on the determination of trace elements has been carried out.

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The choice of rocks for investigation was controlled by the availability of powders or specimens of rocks already analysed chemically for petrographic purposes. A few of these the writer was able to contribute himself, but most of the material studied was furnished from research collections of the Grant Institute, representing series of rocks of petrogenetic significance already fully described from a petrographic standpoint.

In all, 22 trace elements have been determined spectrographically in number chemically analysed rocks. The suites represented comprise:

(a) Metamorphic-metasomatic types from Co. Donegal, Ireland (7).

(b) Regional metamorphic rocks from the Scottish Highlands (5)

(c) Granitic and related rocks from the complexes of Loch Doon (12) and Spango (5).

(d) Perthite pegmatites from the Black Hills, South Dakota (23)

(e) Magmatic rocks, forming a well established differentiation series, from the Braefoot Outer sill, Fife, Scotland (10)

(f) Volcanic ultrabasic potassic types from South-west Uganda and the adjoining part of the Belgian Congo (29)

(g) Carbonatites (4) and limestones (2) of different occurrences.

The determined trace elements are: Rb, Li, Ba, Sr, Cr, Co, Ni, Zr, La, Y, Cu, V, Ga, Tl, Sn, Pb, Sc, Mo, Ge, Be, Ag and In. The distribution of each element in the various suites of rocks is discussed and the petrogenetic significance of their trace-element constitution is considered.

The Thesis now presented contains the following papers:

(I) Behaviour of the trace elements in a front of metasomatic-metamorphism in the Dalradian of Co. Donegal; published in Geochimica et Cosmochimica Acta, 1952, Vol. 2, pp. 170-184.

The epidiorite and quartzite of the Malin Head district (Ireland), are considered by Holmes and Reynolds (Comm. geol. Finlande Bull. 140, 1947, pp. 25-65) to be metasomatically transformed into skarn-rocks and mica-schist respectively. In this transformation process, it has been found that the trace elements follow the major elements for which they can substitute in favourable crystal lattices. Rb, Ba and probably Pb and Ag follow and substitute for K; Sr and Y for Ca and probably K; Li, Cr, Ni, Co, V, Cu, Sc, Sn and Mo for Mg, Fe^2 and Fe^3; and Ga for Al.

(II) The distribution and significance of the trace elements in the Braefoot Outer sill, Fife; published in Trans. Edin. Geol. Soc., 1952, Vol. 15, pp. 150-186.

The trace-element contents of the differentiated rocks of the Braefoot Outer sill indicate that certain elements concentrate at particular stages of magmatic crystallisation. The stages of crystallisation are classified into early (accumulative intermediate and late on the basis of the ratio $(FeO+Fe_2O_3)/(MgO+FeO+Fe_2O_3)$, which increases from early to late. The distribution of the trace elements is found to depend mainly on the amount and type of the minerals of the discontinuous and continuous reaction series predominating in the rock. Cr and Ni concentrate in the early types, rich in olivines and/or pyroxenes. /

pyroxenes. Co, V, Cu and Sr are relatively enriched in rocks of the intermediate stage, rich in pyroxenes, amphiboles and calc-alkalic plagioclases. Li, Rb, Ba, Ga, La, Y and Be concentrate in rocks of the late stage of magmatic crystallisation, rich in biotites and potash feldspars.

The early and intermediate stages are characterised by having the inter-relationship Cr > Ni > Co and Sr > Ba whereas the late stage has Ni > Co > Cr and Ba > Sr. The relative proportions of (Cr+Ni+Li) : (Co+V) : (Rb+Ba) in the different stages show a trend similar to that of $MgO:FeO:(Na_2O+K_2O)$.

There are certain ratios which attain their highest values at particular stages. The most important of these are $(Mg+Fe^2+Fe^3)/(Na+K+Ca)$ and $(Cr+Co+Ni+V+Cu)/(Rb+Ba+Sr)$ in the early stage; Fe^2/Mg and $(V+Co)/(Cr+Ni)$ in the intermediate stage and $(FeO+Fe_2O_3)/(MgO+FeO+Fe_2O_3)$, Li/Mg, Rb/Ba, Rb/K and Ga/Al in the late stage.

(III) A geochemical study of the regional metamorphic zones of the Scottish Highlands; presented at the Inter. Geol. Cong., XIXme Sess., 1952, Algiers, Algeria.

The grades of regional metamorphism are conveniently divided into low, medium and high, comprising rocks of the chlorite zone (green schist facies), the biotite and garnet zones (epidote-amphibolite facies) and the staurolite and sillimanite zones (amphibolite facies) respectively. It is found that the ratios $(FeO+Fe_2O_3)/(MgO+FeO+Fe_2O_3)$ and K_2O/Al_2O_3 do not substantially differ in the three grades. Fe_2O_3/MgO and Fe^3/Fe^2 show a regular increase from low to high. The geochemical changes involved during the development of the rocks of the different grades seem to have been (a) decrease in Al and K, and a slight increase in the total of Mg, Fe^2 and Fe^3 in the low grade; (b) decrease in Al, Ca and $(Mg+Fe^2+Fe^3)$, and increase in K in the medium grade; and (c) very slight decrease in K, and increase in Al, Ca and $(Mg+Fe^2+Fe^3)$ in the high grade.

The behaviour of the trace elements resembles that of those major elements which have approximately the same ionic radii. The trace elements, therefore, culminate in the rocks which show culmination of certain major elements. Ga culminates with /

with Al; Ti, Mn, Li, Cr, Ni, Co and V with Mg, Fe^2 and Fe^3; Sr, Y and La with Ca; and Rb, Ba and Pb with K. Similar inter-relationships between certain trace elements are found in all three grades of metamorphism; e.g. the distribution of Cr, Ni and Co in the three grades is $Cr > Ni > Co$ and that of Ba and Sr is $Ba > Sr$ corresponding to the distribution of these elements in average shale.

(IV) Petrogenesis of perthite pegmatites of the Black Hills, South Dakota; published in Jour. Geology, 1949, Vol. 57, pp. 555-581.

Some pegmatitic perthites of the Glendale area of the Black Hills of South Dakota were chemically analysed and microscopically studied in order to provide evidence bearing on the origin of the perthites of this area. The textures of the perthites and the microscopic features of the country rocks seem to be inconsistent with a magmatic origin; rather they suggest metasomatic activities. Evidence of metasomatic derivation of the perthites is given in the discussion of their petrochemistry. The feldspar equilibrium diagram is shown to be inconsistent with the actual composition of the perthites. The schists grade into feldspar-rich types, the country schists having been chemically reactivated. The feldspathic materials are thought to be endogenetically derived from the schist. Perthitisation was partial in some parts of the country rock, where perthite-schists were developed. In other parts of the country rock, perthitisation was complete because of favourable conditions of temperature, pressure and structure, and thus perthitic pegmatite bodies formed. In still other parts of the country rock the conditions assisted both in the trapping of some elements and in the action of certain reaction processes which gave rise to the formation of shells or zones composed essentially of definite minerals characteristic of such conditions. The perthite zone of certain pegmatites is considered to be one of these zones.

It is suggested that the formation of perthite was a complex metasomatic process which took place in various stages. The following stages are believed to have been passed during the evolution of the perthites studied: (1) endogenetic development of homogeneous potash-soda feldspathic material by metamorphic differentiation of the country rocks; (2) exchange of Na /

Na and K and diffusion of the Na into preferred parts of the structure of the homogeneous material to form the string and film types; (3) further migration of Na from the schist to form albite which, (4) replaces microcline of the film and string types of perthite by reaction metasomatism, thereby giving rise to perthite of the vein and patch types.

(V) Observations on the distribution of trace elements in the perthite pegmatites of the Black Hills, South Dakota; to be published in American Mineralogist, 1952, Vol. 37.

The trace-element contents of the Black Hills perthites have been determined spectrographically. Their chief trace elements are found to be Rb, Ba and Sr. Li, Pb and Ga are fairly abundant but in amounts notably less than those of Rb, Ba and Sr. Mn, V, Cu, Be and Ge are relatively rare; and Ag, Cr, Co, Ni, Sc, Mo, La and Y are very rare. Tl is present in detectable amounts in perthites which are relatively rich in Rb. The pink and reddish perthites seem to be relatively poor in Rb but relatively rich in Ba, while the greyish types show the reverse relationship.

The distribution and relative proportions of the different trace elements are discussed. They are consistent with the metasomatic derivation of the perthites from the schists of the country rocks in which the pegmatites occur.

(VI) The trace elements of the plutonic complexes of Loch Doon and Spango (South Scotland) and their petrogenetic significance; to be submitted for publication to the Royal Society of Edinburgh.

The trace-element contents of the plutonic rocks of Loch Doon and Spango Complexes are discussed. It is found that the trace-element constitution of the granitic types of these complexes is not consistent with the magmatic mode of origin.

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During the metasomatic development of the Loch Doon and Spango granitic rocks the trace elements behave like those major elements which, respectively, have approximately the same diffusion coefficients and ionic radii, and are known to be replaced by them in favourable crystal lattices.

(VII) The trace elements of the volcanic ultrabasic potassic rocks of South-Western Uganda and the adjoining part of the Belgian Congo, and their bearing on petrogenesis; to be submitted for publication to the Geological Society of America.

The trace-element contents of different volcanic ultrabasic potassic rocks from South-western Uganda and the adjoining part of the Belgian Congo are discussed. The trace-element constitution of the types studied, supports Holmes' hypothesis of their derivation from reactions between magmatic carbonatite and sialic crustal material.

The following additional papers embodying the results of original research are included in support of the Thesis:

(VIII) Significance of the orthoclase-albite-anorthite, and the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagrams in igneous petrogeny; published in American Mineralogist, 1950, Vol. 35, pp. 1039-1048.

High temperature studies of silicate systems indicate that rocks which form at the latest stages of the differentiation of a basaltic magma should have salic normative proportions which lie in the low temperature region of the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagram. Their normative feldspar content should lie approximately on the cotectic curve of the Or-Ab-An equilibrium diagram. The chemical compositions of some potash- and soda-rich acidic rocks do not harmonise with these requirements. It is suggested, therefore, that some of these rocks may /

may have been enriched in potash or soda through metasomatic processes, while others may have been derived from the crystallisation of potash-rich "granitic" or soda-rich spilitic magmas respectively, formed, possibly, by differential remelting of the crust.

(IX) (Jointly with N.M. Shukri) Mechanical analysis of some bottom deposits of the Northern Red Sea; published in Jour. Sed. Pet., 1944, Vol. 14, pp. 43-69.

The mechanical composition of some sixty bottom samples from the Northern Part of the Red Sea, in particular from the Gulf of Suez, the Gulf of Aqaba and the Red Sea proper is discussed. The statistical constants are correlated with each other and with the contents of calcium carbonate, nitrogen and organic matter and these properties are correlated with the environmental conditions of deposition.

The irregular bottom topography gives rise to variety in the deposits. Contrasts appear between the deposits of the shallow and smooth-floored Gulf of Suez, of the deeper Gulf of Aqaba, and the very irregular Red Sea proper.

(X) (Jointly with N.M. Shukri) The mineralogy of some bottom deposits of the Northern Red Sea; published in Jour. Sed. Pet., 1944, Vol. 14, pp. 70-85.

The special character of the wind-borne Red Sea deposits is discussed. The mineralogy of the sediments is uniform over the three provinces (Gulf of Suez, Gulf of Aqaba and Red Sea proper) and thus contrasts with the variations commonly found in other basins of deposition. Local variations are, however, caused by contamination from local source-rocks or variation in the environmental conditions of deposition.

PART I

BEHAVIOUR OF THE TRACE ELEMENTS IN A FRONT OF METASOMATIC-METAMORPHISM IN THE DALRADIAN OF CO. DONEGAL.

(To be published in Geochimica et Cosmochimica Acta)

ABSTRACT

The epidiorite and quartzite of the Malin Head district (Ireland) have been found by Holmes and Reynolds (7) to be metasomatically transformed into skarn-rocks and mica-schist respectively. The trace element contents of these rocks were investigated using semi-quantitative methods in order to study the behaviour of the different trace elements during the metasomatic changes which have taken place. The determined elements are Rb, Ba, Ag and Pb; Sr, Y and La; Li, Cr, Ni, Co, V, Cu, Sc, Sn and Mo; Ga; Zr, Be, Tl, Ge and In. The trace elements follow the major elements for which they can substitute in favourable crystal lattices. The substitution is found to be in accord with Goldschmidt's rules. Rb, Ba and probably Pb and Ag follow and substitute for K; Sr and Y for Ca and probably K; Li, Cr, Ni, Co, V, Cu, Sc, Sn and Mo for Mg, Fe^{2+} and Fe^{3+}; and Ga for Al. During granitization processes the trace elements seem to culminate in rocks which show culmination of their respective interchangeable major elements.

INTRODUCTION /

INTRODUCTION

In their study of the White Cow epidiorite sills of the Malin Head district, Inishowen, Co. Donegal, Eire, in the most northerly part of Ireland, Holmes and Reynolds (7) have established the following sequence:-

$$\begin{tikzcd}
 & & & \text{lepidomelane-skarn} \\
\text{epidiorite} \arrow[r] & \text{biotite-epidiorite} \arrow[r] & \text{biotite-skarn} \arrow[ur] \arrow[dr] & \\
 & & & \text{chlorite-skarn}
\end{tikzcd}$$

They have also discovered and investigated the following transformation:-

quartzite   mica-schist.

The quartzite underlies the main White Cow and separates the latter sill from an underlying thinner epidiorite sill. For the general geology of the district and a geological map see Holmes and Reynolds (7) p. 28 & fig. 3, p. 29.

From field evidence and microscopic examination a metasomatic derivation of the skarn rocks from the epidiorite, and of the mica-schist from the quartzite is inferred. Differential atomic migration of the various elements and reorganization of the constituents of the country-rocks in the solid-state are thought to be responsible for the metasomatic changes that have taken place. Gaseous transfer is considered inade-

quate /

inadequate, since a gas phase is most likely to be acidic, whereas in the metasomatic changes under consideration introductions of alkaline materials were dominant. Moreover, hydrothermal solutions could not readily account for the transformations, since cracks, fissures and other passageways which could assist circulating solutions in penetrating rocks such as quartzite are lacking.

The metasomatic changes mentioned above are considered to be complementary to granite formation. The skarn-rocks and the mica-schist are regarded as representatives of a basic front, possibly to be correlated with the development of syntectonic migmatites elsewhere.

The chemical changes involved in the transformation processes and responsible for the change from epidiorite to skarn-rocks have been, on the whole, increase of MgO, (total FeO+MgO), K_2O, H_2O, P_2O_5 and MnO and decrease of Al_2O_3, CaO and Na_2O.

The transformation of quartzite to mica-schist seems to have resulted from similar changes to that found from development of the skarn-rocks from epidiorite; thus there seems to have been an increase of Al_2O_3, total FeO, MgO, K_2O, H_2O, TiO_2, P_2O_5 and MnO and decrease of SiO_2, Ca CO_3, CaO and Na_2O.

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The present study is an investigation of the behaviour of the trace elements during this metasomatic-metamorphism. Using spectrographic methods, the author has analysed the following rocks of the Malin Head district for their trace elements:-

epidiorite (No. 94);
biotite-epidiorite (No. 350);
biotite-skarn (No. 92);
lepidomelane-skarn (No. 381) and chlorite-skarn (No. 353);
quartzite (No. 394) and mica-schist (No. 395).

Petrographic descriptions and chemical analyses of these rocks are given by Holmes and Reynolds and their exact location is illustrated (7, fig. 4, p. 30 & fig. 6, p. 34).

ANALYTICAL METHODS

Portions of the powders used for the chemical analyses were kindly provided by Professor A. Holmes and Dr D.L. Reynolds. The spectrographic analyses were made at the Macaulay Institute for Soil Research at Aberdeen.

The semi-quantitative analytical method adopted in this study has already been described in detail by Mitchell (9).

The determined elements, the respective wave lengths of /

of their diagnostic lines and the sensitivity of each element are listed in Table 1.

RESULTS

The percentages of the major oxides determined chemically, quoted from Holmes and Reynolds (7), as well as those of the different trace elements are recorded in Table 2. The rock formula (based on a unit cell of 160 oxygen atoms) introduced by Barth (2) for metasomatic processes of each of the analysed rocks, was calculated with the results listed in Table 3. Figs. 1-5 show the significant gains and losses of the various elements involved at each stage of the transformation processes.

ALTERATIONS OF THE EPIDIORITE

(a) Alteration of epidiorite A to biotite-epidiorite B.

The unmodified epidiorite of the sill (No. 94) is formed of narrow alternating bands which differ in colour. The /

The relatively dark bands are rich in hastingsite and contain some iron-ore, sphene, a little epidote and occasional biotite. The relatively light coloured bands are composed of feldspar, small crystals of epidote and occasional garnet (7, p. 31). The biotite-epidiorite (No. 350) is composed of hastingsite, quartz, oligoclase with abundant associated sericite, finely granular epidote, relatively large flakes of biotite, and a little sphene, black iron-ore and pyrite. The biotite which is partially altered to ripidolite, replaces the original constituents of the epidiorite.

The mineralogical changes are, therefore, an increase of biotite and quartz at the expense, principally, of amphibole and sodic plagioclase. The chemical changes involved in this transformation correspond fairly closely to the changes in the mineralogical constitution.

Reference to Table 3 shows the gains and losses in the formation of the biotite-epidiorite. The most significant gains are Mg 1.06, K 0.99 and Si 0.60 and losses are Al 2.40, Na 1.48 and lesser amounts of Ca 0.74, Fe^{2+} 0.43 and Fe^{3+} 0.18.

The minor elements which were added to the epidiorite are P and Mn, while the trace elements gained are Cr, Ni, Co, Li, Cu, Mo, Sn, Rb, Ba and Pb. One minor element, Ti, was subtracted, and the trace elements 'lost' are Sr, Y, V, Ga and Ag.

There /

There are still six elements, namely La, Tl, Sc, Ge, Be and In, which if present in the epidiorite and/or its metasomatic product the biotite-epidiorite, are in amounts below the limits of sensitivity given in Table 1. Any change in these elements is, therefore, undetectable.

Table 4 shows for each of the major rock forming elements, namely Si^{4+}, Al^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Ca^{2+}, Na^{+} and K^{+} which of the minor and trace elements are believed to substitute for it, under favourable conditions of temperature and pressure and in the appropriate crystal lattices. Substitution may be by camouflage, capture or admission depending on the electrostatic charges and the radii of the elements concerned (4, 5 and 6).

It is significant that in the transformation process under review - epidiorite to biotite-epidiorite - each trace element, whether added or subtracted, follows quite closely the major element with which it can form a substituting pair. Li, Cr, Ni, Co and Cu follow Mg; Rb, Ba and Pb follow K; and Sr follows Ca.

Ferrous and ferric iron were both subtracted from the epidiorite. Neither Co nor Cr was subtracted though they have interchangeable ionic radii with Fe^{2+} and Fe^{3+} respectively. But the amount of gain in Mg is much higher than the total loss in iron. It is evident therefore, why Co and Cr which can proxy /

proxy for Mg and/or Fe^{2+} and Fe^{3+} followed Mg. V on the other hand, was subtracted, as was ferric iron. V^{3+} has an ionic radius 0.65 Å very nearly the same as that of Fe^{3+} 0.67 A°. Ti, having an ionic radius of 0.64 Å, was also subtracted, thus behaving like Fe^{3+}.

The gain in Mg is 1.06, while the total loss of both Fe^{2+} and Fe^{3+} is only 0.61. The trace elements which can substitute for Mg, Fe^{2+}, and Fe^{3+}, as shown in Table 4, are Li, Cr, Co, Ni, Cu, Sn, Mo and V. Amongst these elements, V was subtracted, whereas the others were added. The total of the added ions (0.038) exceeds that of the subtracted ions (0.001), as in the case of their respective interchangeable major elements.

Rb and Ba were added, clearly following K. Sr can substitute for both Ca and K. In this case it may be surmised that Ba and Rb, having apparently satisfied what the potassium mineral lattices could accommodate, left Sr to follow Ca. Just as the added amount of K exceeds that of the subtracted Ca, so the added Rb and Ba (0.01) is also higher than the subtracted Sr, Y and Ag (0.007). Y is known to substitute for Ca while Ag can replace both K and Ca.

Ga, following Al, was subtracted. It is not clear at this stage which trace element(s) follow Na. It can be said that /

that the loss in Na accounts for the relative impoverishment of the biotite-epidiorite in soda-plagioclase. It seems that the substitution in the feldspar lattice takes place mainly with respect to Ca and K. The ions which can substitute for Na are Co, Cu, Ni, Li and Sc. The feldspar lattice is not favourable for these ions, since they have relatively low co-ordination numbers. Moreover, they have high activation energy values (13) and therefore, can preferentially substitute in minerals formed at higher temperatures than those appropriate to the crystallization of sodic plagioclase. In soda-amphiboles and soda-pyroxenes for example, Co, Cu, Ni, Li and Sc can replace Mg and/or iron, while their substitution for Na cannot be justified. The same trace elements are commonly found in the olivines. Soda-olivines, however, are not known as natural minerals and so far have not been synthesized. It would appear that Na, which can exist in the silicon-oxygen chain structures of amphiboles and pyroxenes, cannot take part in the tetrahedral structure of olivines which, moreover, form at temperatures apparently too high for Na to play a role in their composition.

Table 5 gives the ratio of each of the trace elements to its interchangeable major element. The ratio Ga/Al, Ni/Mg and Co/Fe^{2+} are approximately the same in the epidiorite (amphibole-rich rock) and the biotite-epidiorite (biotite-rich rock).

Ga /

Ga, Ni and Co seem to enter into the amphibole and the biotite lattices with about equal ease. On the other hand, the biotite-rich rock B, has higher Li/Mg, Ba/K and (Ba+Rb)/K ratios and a lower Sr/K ratio with comparison to the amphibole-rich rock. Nockolds has mentioned similar findings (in Nockolds and Mitchell, 10, pp. 551-552) regarding the hornblendes and biotites occurring in certain Caledonian plutonic rocks which are mainly of granodioritic composition. He considered such characteristic tendencies in the ratios under discussion as an indication that hornblende crystallized from magmatic sources earlier than biotite. Supposing for the sake of argument that Nockolds is right in ascribing a magmatic origin to these minerals, one would therefore be led to the belief that the fundamental principles of replacement of the major elements by the trace elements remain essentially the same, whether the mineral concerned is formed from magmatic melts, migrating atoms or even granitizing solutions. The same mineral, so far as our knowledge goes, has the same crystal lattice and reveals essentially the same geochemical relationships in every case.

The paragenesis of minerals on the basis of the behaviour of the trace elements would not then provide conclusive evidence for a magmatic derivation. This inference is independent of the fact that the order of crystallization in magmatic rocks /

rocks can rarely be judged with adequate certainty.

Buerger and Washkin (3) show that during metamorphism a mineral will recrystallize only when it is heated above a certain critical temperature which varies with the mineral and is characteristic of it. Each of the well known facies of the metamorphic rocks forms under specific conditions of temperature and pressure. Metasomatic products also depend on the temperature prevailing during the replacement. The effect of temperature on the substitution of the trace elements for their interchangeable major elements would be the same in all the different crystalline-rock formation processes. A given trace element, whether present in the magmatic melt, in the country rocks or in the replacing materials, appears to enter into any favourable mineral lattice, following the same geochemical rules in every case.

Ahrens (1) has established that thallium and rubidium are enriched in replacement microclines. This enrichment accords well with Goldschmidt's rules for substitution. Jaffe (8) studied the trace elements of garnets from pegmatites and from metamorphic rocks, namely, schists and tactites. Again, he finds that Goldschmidt's concepts of substitution of the trace elements hold true in every case. The pegmatite garnets are manganese rich, where Y (ionic radius 0.83 Å) proxies for Mn (0.91 Å).

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The garnets of the schist are rich in magnesium and iron where Sc (0.83 Å) proxies for either Mg (0.78 Å) or Fe^{2+}(0.83 A°). The garnets of the tactites are calcium rich where Sr (1.27 Å) proxies for Ca (1.06 Å). These replacements are essentially similar to those here shown to characterise the metasomatic transformation of epidiorite to biotite-epidiorite.

(b) Alteration of biotite-epidiorite B to biotite-skarn C.

Gradation between biotite-epidiorite and skarn is found in places (7, p. 37). The significant mineralogical change in this transformation is the great increase of biotite at the expense of hastingsite.

Table 5 indicates that the biotite-epidiorite gained K 4.14, C 2.62, Fe^{2+}0.48, Fe^{3+}0.34, and lost the following: Si 2.95, Na 3,58, Ca 1.56 and Mg 0.86. The trace elements which were added are Li, V and Sc; Rb, Ba, Sr, Y and Ag. The subtracted minor and trace elements are respectively, Ti and Mn, and Cr, Co, Ni, Cu, Sn, Mo; and Pb.

It is noticeable that V and Sc followed iron. It is quite likely that V replaced Fe^{3+}, and Sc substituted for Fe^{2+} with other appropriate substitutions taking place, mainly in the biotite lattice, to balance the electrostatic charge. It might be recalled that Li was added in the replacement of hastingsite by biotite to form the biotite-epidiorite. The same happened when more biotite replaced hastingsite to give rise to the biotite-skarn /

biotite-skarn from the biotite-epidiorite. This shows the great tendency of lithium to enter the biotite lattice. Rb, Ba, Sr and Ag followed K. The amount of the K gained (4.14) is much higher than that of the Ca subtracted (1.56). It is understandable, therefore, why Sr, which can proxy for both K and Ca followed the former in this case. The total gain in combined Fe^{2+} and Fe^{3+} (0.76) is less than the loss in Mg (0.86). Correspondingly, the total gain in Li, V and Sc (0.05) is also less than the total loss in Ti, Mn, Cr, Co, Ni, Cu, Sn and Mo (0.26).

Na was lost in accord with the impoverishment in sodic plagioclase.

Ga and Al remained unchanged and therefore the ratio Ga/Al is the same. Table 7 shows that the transformation of biotite-epidiorite to biotite-skarn involved negligible change in the ratios Ni/Mg, Co/Mg and Co/Fe^{2+}. These ratios are also approximately the same in the biotite-epidiorite and the epidiorite, suggesting that Ga, Ni and Co enter into the biotite and amphibole lattices with about equal ease. The Li/Mg ratio becomes much higher in the biotite-skarn. Notable changes take place in the ratios of Ba, Rb and Sr to K. The ratio Rb/K increases markedly, Ba/K decreases slightly and (Rb+Ba)/K is higher in the biotite-skarn. Sr/K decreases but Sr/Ca increases. Rubidium is, therefore, the element which most readily replaces K in the biotite lattice.

(c) /

(c) Alteration of biotite-skarn C to lepidomelane-skarn D.

The biotite-skarn passes locally into lepidomelane-skarn. In other places, it was metasomatically transformed into chlorite-skarn.

The mica of the lepidomelane-skarn is different from that of the biotite-skarn. The lepidomelane has X = light golden yellow Y = deep gold Z = reddish gold; 2V = 20°; γ = 1.681: and marked dispersion; whereas the biotite of the biotite-skarn has X = straw yellow Y = Z = old gold to greenish brown; 2V small; and γ ranging from 1.643 to 1.645 (7, p. 41 and p. 36). In association with the 'golden' mica, the lepidomelane-skarn has a relatively small amount of biotite which is greenish brown, or distinctly green in colour, and displays optical properties resembling those of the biotite of the biotite-skarn. The textural relationship between the lepidomelane and the greenish biotite indicates that the former has developed at the expense of the latter. In places, the lepidomelane-skarn contains hastingsite relics of the original rock, that is, the epidiorite. Sphene occurs in minute granules as a minor accessory.

The dominant mineralogical change is evidently the transformation of biotite to lepidomelane.

The chemical changes in the major elements are shown in /

in Table 3. The most significant changes seem to be:- addition of

Si 2.25, Fe^{3+} 3.43, Mg 2.26 and Na 0.76

and subtraction of

Fe^{2+} 3.86, C 2.62, Ca 1.80, K 1.44 and Al 0.90.

The trace elements that increased are

Ti, Mn, Cr, Cu and Sn; Ga; Rb and Pb; and Y.

The trace elements that decreased are

V, Sc, Co and Li; Ba and Ag; and Sr.

Ti, Mn, Cr, Ni, Cu and Sn followed Mg and Fe^{3+}, while Li, V and Sc followed Fe^{2+}. Ba and Ag followed K and Sr followed Ca and possibly K. The total addition of Fe^{3+} and Mg (5.69) is higher than the total subtraction of Fe^{2+} (3.86). Concordantly, the total addition in Ti, Mn, Cr, Ni, Cu and Sn (0.3) is higher than the total subtraction of Li, Co, V and Sc (0.03). The total subtraction of Ba, Sr and Ag (0.05) exceeds that of the added Rb and Pb (0.009) in accordance with the decrease of K.

Na was added, although there was no development of soda-plagioclase. The sodium content of lepidomelane is generally higher than that of biotite. It can be present amongst the (X) group elements of the generalised mica formula (see below) or it may be replacing Fe^{3+} in the sixfold co-ordinated positions.

Ga /

Ga was added, yet Al was subtracted. This can be readily explained if we consider that the amount of the Al lost (0.90) is far less than the Fe^{3+} gained (3.43). Fe^{3+} can replace Al and Ga substitutes for both.

The transformation of biotite to lepidomelane does not involve a change in the lattice type. The general chemical formula for each of these micas is also of the same type. The formula of mica is known to be $(X)_{0-1}\ (Y)_{2-3}\ (Al, Si)_4\ O_{10}\ (OH, F)_2$, where (X) comprises K, Ca, Na, Rb, Ba and Sr; and (Y) is Al, Mg, Fe^{2+}, Fe^{3+}, Ti, Mn, Cr, Co, Ni and Li, all having co-ordination number six. The difference between lepidomelane and biotite is that the former has relatively more Fe^{3+} and less Mg and Fe^{2+}. The total amounts of these elements would be essentially the same. It is significant that the total of the ratios* (Mn+Ni+Co+Li)/Mg, $(Co+Li)/Fe^{2+}$ and Cr/Fe^{3+} in the biotite skarn and the lepidomelane-skarn are 12.65 and 13.13 respectively. Moreover, the ratios (Sr+Rb+Ba)/K are 73.25 and 73.80 respectively. The similarity of these ratios in both rocks indicates that the trace elements enter with exactly the same ease into the identical lattices of both /

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*$Li \times 1000/Fe^{2+}$ and $Mn \times 10/Mg$ of the biotite-skarn and lepidomelane-skarn are 0.92 and 0.56, and 1.00 and 0.62 respectively. Ti/Mg was not taken since Ti is also present in sphene. The other ratios are recorded in Table 7.

both biotite and lepidomelane, replacing the appropriate major elements in the favourable positions of the structure. However, Sr/Ca differs widely in the two rocks. On the one hand, calcium is not nearly so important an element in biotite and lepidomelane as K, Mg, Fe^{2+}, or Fe^{3+}. On the other hand, the minor accessories in both rocks are mainly calcium-bearing minerals, such as epidote, sphene and apatite. Moreover, CO_2 is 2.02 per cent in the biotite skarn and none in the lepidomelane-skarn, normative calcite being 4.59 in the former. Strontium, therefore, is most likely to be present in the calcite and the other calcium-bearing minor accessory minerals.

(d) Alteration of biotite-skarn C to chlorite-skarn E.

Transitional rocks between the biotite-skarn and the chlorite-skarn are found in places. The chlorite-skarn is composed of chlorite (ripidolite), epidote, quartz, feldspar which may be iso-orthoclase (intimately intergrown with chlorite), a little albite, sphene and calcite (7, p. 44).

The chemical changes (Table 5) in the major elements involve addition of

Mg 1.22, Fe^{3+} 0.26, Na 0.26 and C 0.46

and subtraction of

K 4.36, Si 2.30, Al 1.90 and Fe^{2+} 0.50.

The /

The trace elements that increased are Ti, Mn, Li, Cr, Ni, Cu, Sn and Mo. The trace elements that decreased are Rb, Ba, Sr, Y and Ag; Ga; and V and Sc.

The general behaviour which has been found in all the previous transformations is also followed in this case. Ti, Mn, Li, Cr, Ni, Cu, Sn and Mo follow Mg and Fe^{3+}. Rb, Ba, Sr, Ag and Pb follow K. Ga follows Al; and V and Sc follow Fe^{2+}. The total addition of Mg and Fe^{3+} (1.48) exceeds that of the subtracted Fe^{2+} (0.50) just as the total addition of Ti, Mn, Li, Cr, Ni, Cu, Sn and Mo (0.49) exceeds the subtraction of V and Sc (0.008). The loss in K is far greater than the added Ca, thus explaining the behaviour of Sr. Na was added in accordance with the development of albite in the chlorite-skarn.

The chlorites in general are known to have more hydroxyl and less of the alkalies, mainly K, than the micas. The chlorite-skarn is richer in H and poorer in K than both the biotite-skarn and the lepidomelane-skarn. In consequence of this, the Rb, Ba, Sr and Ag contents of the chlorite-skarn are much lower than those of the other two rocks and Pb is also very low. The main differences between the biotite-skarn on one hand, and the lepidomelane- and chlorite-skarns on the other, are (a) increase of Rb/K in the lepidomelane-skarn and its decrease in the chlorite-skarn and (b) the marked decrease of Sr/Ca, reaching its /

its lowest value in the chlorite-skarn. Li/Mg decreases in the lepidomelane-bearing rocks and is approximately the same in both the biotite- and the chlorite-bearing rocks. Cr/Fe^{3+} increases in the lepidomelane-skarn but is practically unaltered in the chlorite-skarn. Co/Fe^{2+} behaves somewhat like Cr/Fe^{3+}, but decreases more notably in the chlorite-skarn.

It is important to estimate the changes involved in the transformation of the biotite-skarn to its two metasomatic derivatives. Table 6 records the addition and subtraction of the different elements which have taken place where two "unit cells" of the biotite-skarn are assumed to have given rise to one "unit cell" of each of the lepidomelane-skarn and the chlorite-skarn. There would then be a gain of Fe^{3+}, Mg and Na, the added trace elements being Ti, Mn, Cr, Ni, Cu, Sn and Mo. There would also be a loss of Al; Fe^{2+}; Ca; and K, the subtracted trace elements being Ga; Li, Co, V and Sc; Sr and Y; and Rb, Ba and Ag. The total gain in Fe^{3+} and Mg (3.59) exceeds the loss in Fe^{2+} (2.18), corresponding to the total gains (0.39) and losses (0.02) of the trace elements which can proxy for these three interchangeable elements.

(e) /

(e) Alteration of epidiorite to skarn-rocks: General statement.

The cumulative sum of the different geochemical changes which have taken place in all the transformation processes discussed above is recorded in Table 9. On the whole, there has been increase in Mg and Fe^{3+} as well as their substituting minor and trace elements, namely, Mn, Cr, Ni, Li, Cu and Sn. K has been gained as were the trace elements which can proxy for it, namely, Rb, Ba and Pb. On the other hand, there has been decrease in Fe^{2+}, and the minor and trace which replace it, namely, Ti, Co, Sc and Mo. Al and Ga have been subtracted. Sr and Y have followed Ca. The total gain in Mg and Fe^{3+} (3.89) is higher than the loss in Fe^{2+} (2.13) in correspondence with the totals of gains (0.17) and losses (0.03) in the trace elements which can proxy for these three elements. The loss in Ca exceeds the gain in K and thus the subtraction of Sr can be explained.

H has been gained in accordance with enrichment in the hydroxyl; and Na has been lost in accordance with the impoverishment of the soda plagioclase. The trace elements which follow Na cannot be recognised precisely. There has been a gain in C in agreement with the increase of calcite.

P has increased and Zr has decreased. These two elements are found mainly in the minor accessory minerals, apatite and /

and zircon respectively. The role played by these minerals in the transformations is insignificant and therefore, P and Zr are not discussed.

The same behaviour is shown in some Finnish rocks studied by Sahama (12). At Ihovaara Hill, 'contaminated' rapakivi granite (IV) has been formed by metasomatic replacement of the mica-gneiss country-rock (I). The chemical and spectrographic analyses of his mica-gneiss (II) from the immediate vicinity of the rapakivi contact, and the contaminated rapakivi granite (IV) from the same contact are given by Sahama (13, analyses II and IV Table XI, p. 59). The mica-gneiss (II) is relatively rich in Mg, Fe^{2+} and Fe^{3+}. The corresponding trace elements which are also enriched in this rock are Ti, Mn, Li, Co, Ni, Cr and V. Ca, Sr and Y are also higher in the mica-gneiss. On the other hand, the contaminated rapakivi granite (IV) is enriched in K and the total of Rb and Ba also increases relative to the mica-gneiss (II).

Fig. 1 shows the changes in the proportions of (a) Rb, Ba and Sr, and (b) Cr+Li, Co and Ni in the different rocks of the White Cow sill near Malin Head. (a) Here the change has involved relative enrichment of both Rb and Ba, and relative impoverishment in Sr up to the biotite-skarn stage. Beyond this stage /

stage, two different alterations have taken place. The one, giving rise to lepidomelane-skarn has involved an increase in Rb relative to Sr and only a slight change in Ba. The other giving rise to chlorite-skarn has involved an increase in Ba relative to Rb and only a slight change in Sr. (b) There has been an increase in the relative proportion of the total Cr+Li and a relative decrease in Ni up to the biotite-skarn stage. Co also decreases but not so markedly as Ni. The increase in the total proportion of Cr+Li continues in the transformation of biotite-skarn to lepidomelane- and chlorite-skarns, with a relative decrease in Co in both rocks, but with a relative decrease in Ni in the lepidomelane-skarn and a relative increase in Ni in the chlorite-skarn.

ALTERATION OF QUARTZITE TO MICA-SCHIST

The quartzite (No. 394) is composed of quartz and albite with a little potash feldspar, muscovite, biotite and garnet. It is relatively rich in calcite. In comparison with the quartzite the mica schist is enriched in potash feldspar and biotite. /

biotite. It contains accessory apatite and iron-ore; calcite is absent or very scarce and garnet is found rarely.

The chemical changes expressed in terms of the "unit cells" of these rocks are given in Table 5. They involved addition of

Al 5.32, Fe^{2+} 2.18, Fe^{3+} 1.44, Mg 1.95, K 3.86 and H 8.88,

and subtraction of

Si 3.50, Ca 4.69, Na 1.16 and C 4.61.

The trace elements behave in essentially the same way as found in the transformation of the epidiorite to skarn rocks. Ti, Mn, Li, Cr, Co, Ni, V and Sc follow Mg, Fe^{2+} and Fe^{3+}. Rb and Ba follow K. Sr follows Ca and Ga follows Al. Although Cu and Sn, which usually follow Mg and iron, were subtracted, the total of the subtracted amounts of these two elements (0.014) is far less than the total amounts of the added elements (0.65) which can proxy for Mg and iron. The same is true with respect to Pb and Ag, which substitute for K.

Changes in Tl, Mo, Ge and In are not detectable, since these elements if present are found in amounts below the limits of sensitivity.

CONCLUSIONS

Holmes and Reynolds (7) believe that the transformations discussed above may be correlated with the development of migmatitic rocks such as those outcropping to the west of the Malin Head district. The skarn rocks would be of the basic front representatives of this granitization process.

The total additions and subtractions of the different elements during the transformation of epidiorite to skarn rocks as a whole, and that of quartzite to mica-schist are recorded in Table 8. The data show that K, Mg, Fe^{2+}, Fe^{3+} and Al are added, and that they culminate in the basic front rocks. The minor elements, Ti, P and Mn also culminate in the basified rocks as discovered by Reynolds. The present study shows that the trace elements which proxy for K, Mg, Fe^{2+}, Fe^{3+} and Al culminate in the same rocks as those which show culmination of the major elements. Rb and Ba culminate with K; Li, Cr and Ni with Mg and Fe^{3+}; Co and V with Fe^{2+}; and Ga with Al.

The released elements after the formation of the basified rocks are Si, Ca and one of the alkalies which is Na in this case. Sr was released in accord with Ca. There has also been release of Sn, Ag, Pb and Cu. These are elements commonly found /

found in the ore-deposits associated with granitic rocks. If the hypothesis of the metasomatic derivation of granitic rocks is true, it might be suspected that ore-deposits composed of Sn, Ag, Pb and Cu could be obtained from the country-rock material. Further geochemical work is needed in order to establish the quantitative validity of this assumption.

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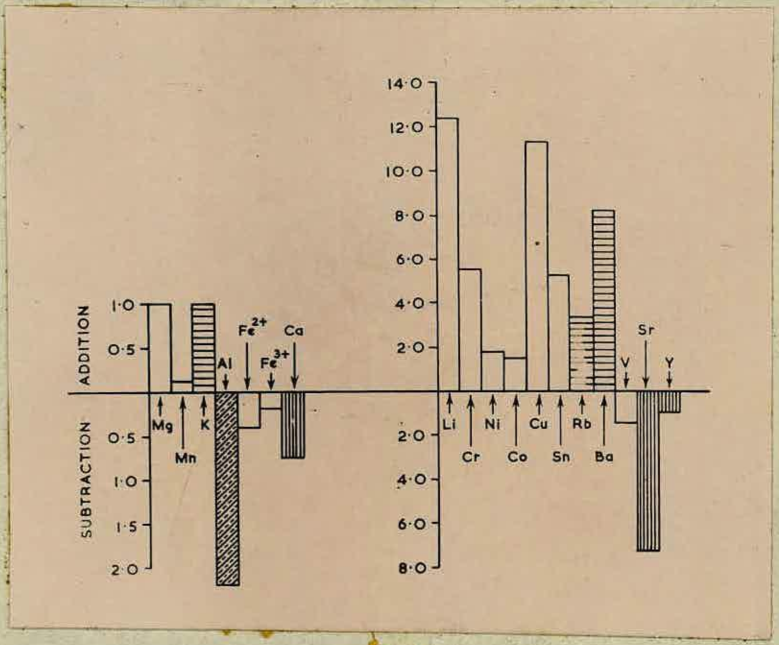

Fig. 1

Addition and subtraction (per rock "unit cell") of major and trace elements during the transformation of epidiorite (A) to biotite-epidiorite (B). The amounts in the case of the trace elements are multiplied by 1000.

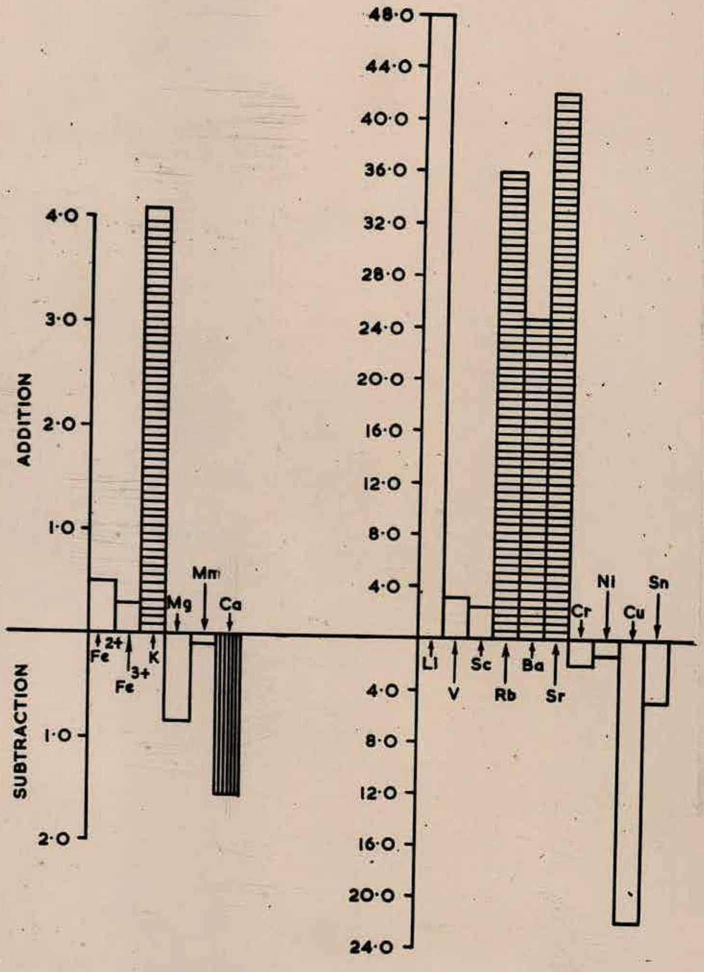

Fig. 2

Addition and subtraction (per rock "unit cell") of major and trace elements during the transformation of biotite-epidiorite (B) to biotite-skarn (C). The amounts in the case of the trace elements are multiplied by 1000.

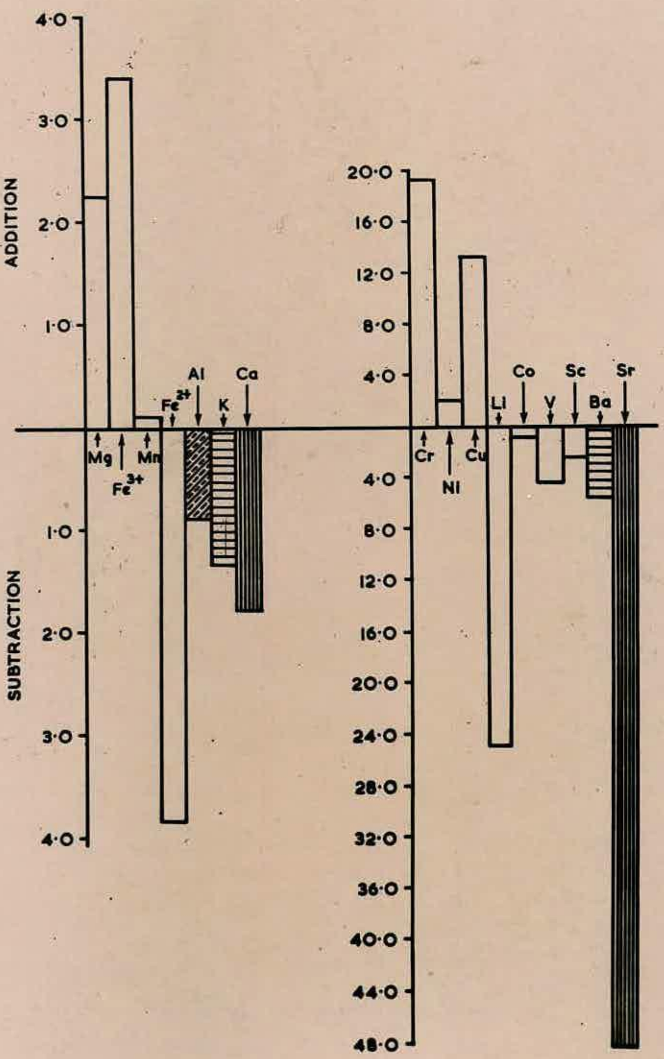

Fig. 3

Addition and subtraction (per rock "unit cell") of major and trace elements during the transformation of biotite-skarn (C) to lepidomelane-skarn (D). The amounts in the case of the trace elements are multiplied by 1000.

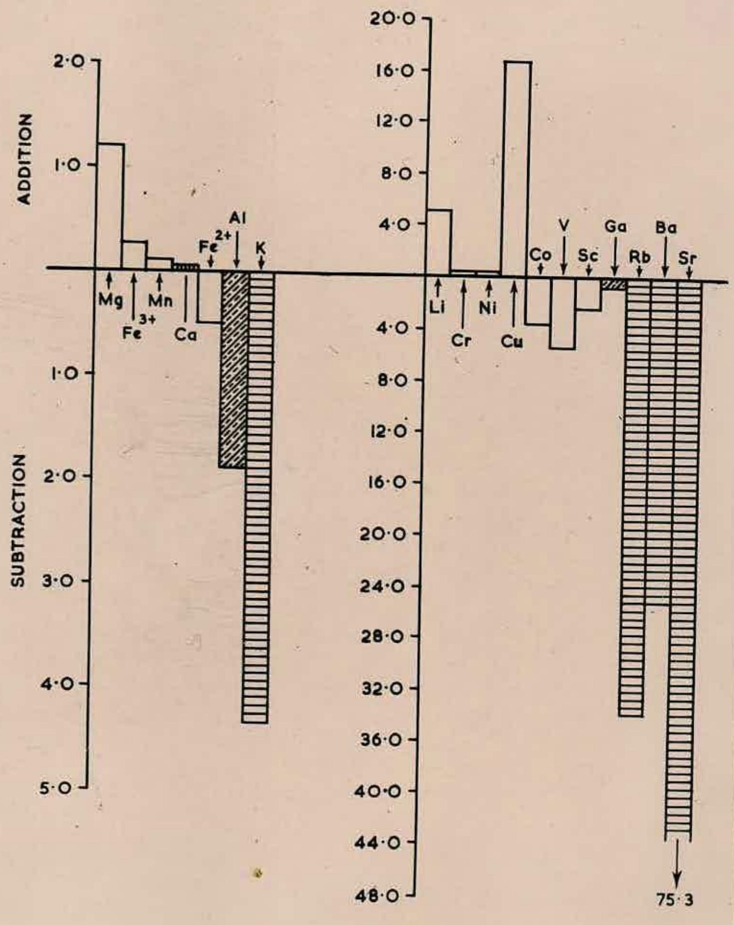

Fig. 4

Addition and subtraction (per rock "unit cell") of major and trace elements during the transformation of biotite-skarn (C) to chlorite-skarn (E). The amounts in the case of the trace elements are multiplied by 1000.

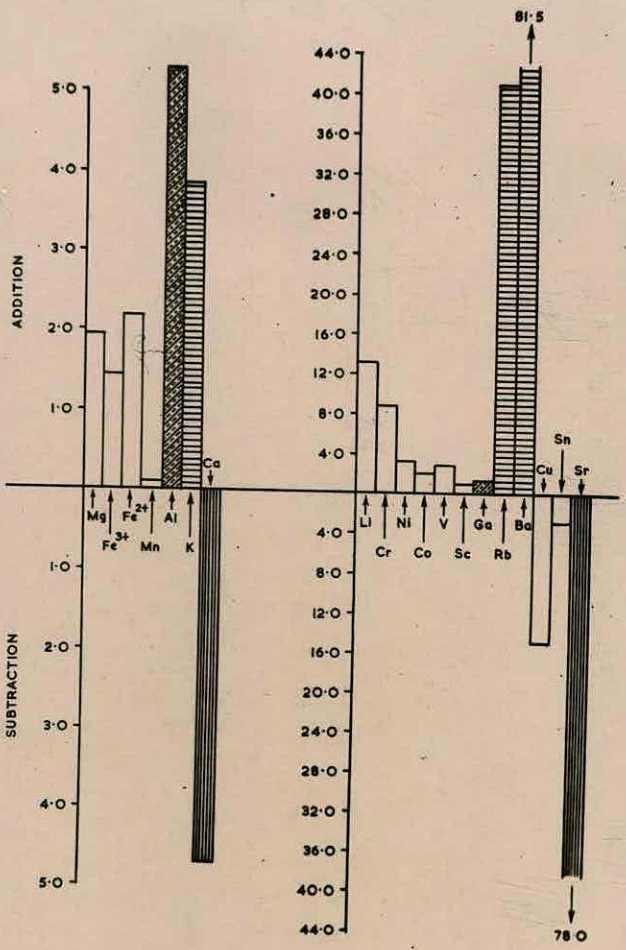

Fig. 5

Addition and subtraction (per rock "unit cell") of major and trace elements during the transformation of quartzite (F) to mica-schist (G). The amounts in the case of the trace elements are multiplied by 1000.

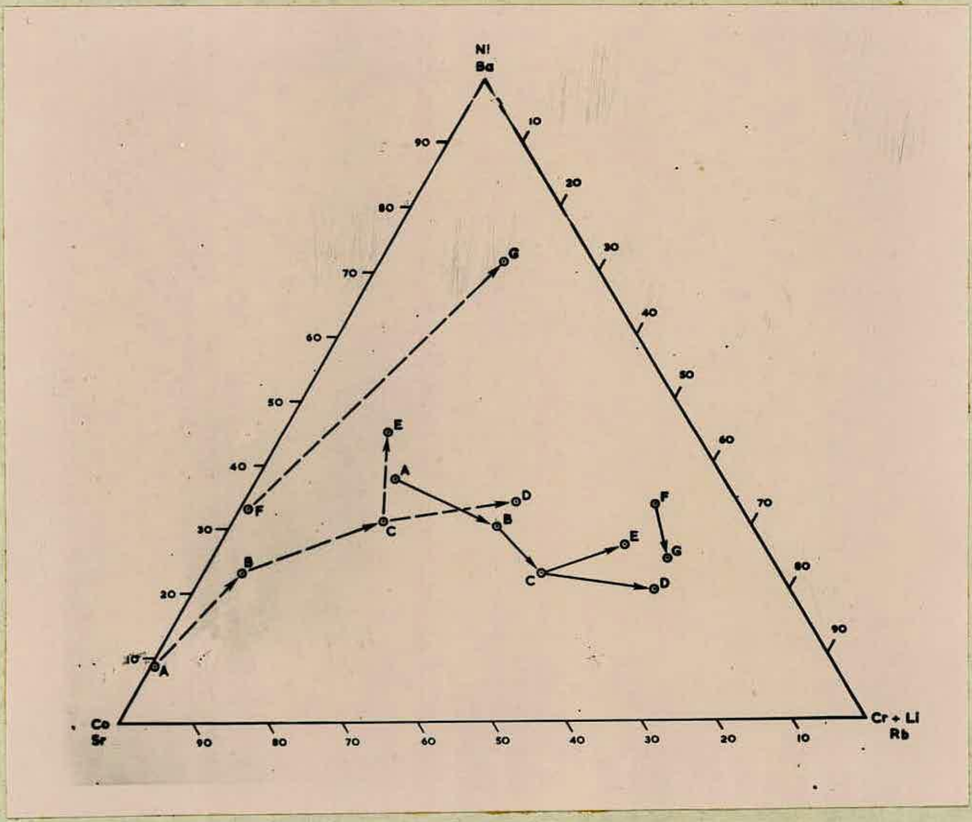

Fig. 6

Relative proportions of Ni, Co and Cr + Li (full line); and Ba, Sr and Rb (dotted line) in the analysed rocks. Notice that the trends in the transformation epidiorite to skarn-rocks with respect to change in the proportions of Ni, Co and Cr + Li; and Ba, Sr and Rb are respectively similar to those in the transformation quartzite to mica-schist. A epidiorite, B biotite-epidiorite, C biotite-skarn, D lepidomelane-skarn, E chlorite-skarn, F quartzite and G mica-schist.

TABLE 1

Element*	Wave Length in Å	Sensitivity in ppm.
Rb	7800.2	1
Li	6707.8	1
Ba	4934.1	5
Sr	4607.3	5
La	4333.7	30
Cr	4254.3	1
Sc	3911.9	10
Co	3483.5	2
Ni	3414.8	2
Zr	3391.9	10
Y	3327.9	30
Ag	3280.7	1
Cu	3247.6	3
V	3185.4	5
Mo	3170.3	1
Be	3131.7	5
In	3039.4	10
Ga	2943.6	1
Sn	2840.0	5
Pb	2833.1	10
Tl	2767.9	30
Ge	2651.6	10

*For ionic radii see Table 4.

TABLE 2

Chemical and spectrographic composition in weight per cent.

Oxide	A	B	C	D	E	F	G
SiO_2	47.32	48.34	45.65	48.13	44.98	72.06	65.36
Al_2O_3	17.39	15.49	15.56	14.76	14.44	10.92	15.68
Fe_2O_3	2.36	2.14	2.55	7.34	3.02	0.04	1.49
FeO	10.91	10.60	11.21	6.38	10.98	1.40	4.32
MgO	4.78	5.56	5.01	6.61	6.08	0.31	1.79
CaO	10.08	9.42	7.94	6.18	8.24	6.02	0.83
Na_2O	2.73	1.98	0.01	0.43	0.16	2.93	2.16
K_2O	0.54	1.36	4.77	3.59	1.23	1.16	4.54
H_2O+	0.96	1.54	2.35	2.82	5.19	0.84	2.32
CO_2	tr.	none	2.02	none	1.74	3.98	none
TiO_2	2.68	2.48	2.30	2.58	2.92	0.08	0.86
P_2O_5	tr.	0.32	0.30	0.22	0.29	none	0.18
MnO	0.20	0.34	0.23	0.32	0.35	0.07	0.21
Rb_2O	0.0005	0.006	0.066	0.08	0.009	0.004	0.076
Li_2O	0.002	0.005	0.017	0.01	0.02	0.0006	0.004
BaO	0.01	0.03	0.1	0.08	0.03	0.1	0.33
SrO	0.12	0.11	0.165	0.077	0.03	0.21	0.06
La_2O_3	*	*	*	*	*	0.005	0.006
Cr_2O_3	0.003	0.01	0.007	0.033	0.009	0.0003	0.01
Sc_2O_3	*	*	0.003?	*	*	*	0.001
CoO	0.009	0.01	0.01	0.01	0.006	0.0001	0.003
NiO	0.008	0.01	0.008	0.01	0.01	0.0004	0.006
ZrO_2	0.027	0.027	0.022	0.014	0.014	0.032	0.135
Y_2O_3	0.009	0.008	0.01	0.01	0.009	0.006	0.01
Ag_2O	<0.0001	0.0001	0.0004	<0.0001	*?	0.0007	0.0002
CuO	0.03	0.04	0.01	0.03	0.04	0.08	0.06
V_2O_3	0.05	0.047	0.05	0.045	0.045	0.01	0.015
MoO_2	<0.0001	0.0003	*	*	<0.0001	*	*
BeO	*	*	*	*	*	<0.001	0.002
In_2O_3	*	*	*	*	*	*	*
Ga_2O_3	0.005	0.005	0.005	0.005	0.003	0.003	0.005
SnO_2		0.01		0.0006	0.001	0.01?	0.004
PbO	<0.001	0.005	<0.001	0.002	0.001	0.01	0.004
Tl_2O	*	*	*	*	*	*	*
GeO_2	*	*	*	*	*	*	*

A = Epidiorite (No. 94), B = Biotite-epidiorite (No. 350), C = Biotite-skarn (No. 92), D = Lepidomelane-skarn (No. 381), E = Chlorite-skarn (No. 353), F = Quartzite (No. 394) and G = Mica-schist (No. 395).

Chemical analyses in Holmes and Reynolds (7), include:-

	H_2O-	BaO	NiO	Total	Analyst
A	0.05	0.01	-	100.01	Agnes Gibbs
B	0.16	-	-	99.73	W.H. Herdsman
C	0.10	0.02	tr.	100.02	Agnes Gibbs
D	0.39	-	-	99.75	W.H. Herdsman
E	0.18	-	-	99.80	"
F	0.26	-	-	100.07	"
G	0.34	-	-	100.08	"

Spectrographic analyst: R.A. Higazy

*= Element if present is in amount below the corresponding limit of sensitivity given in Table 1.

Error is of the order of 25-30 per cent over the range of approximately 10 to 300 ppm. If the element is over 1000 ppm. errors of 50 per cent are possible.

TABLE 3

Rock formulae of the analysed rocks

Element	A	B	C	D	E	F	G
Si	45.96	46.45	43.50	45.75	41.20	61.00	57.50
Al_3	19.80	17.40	17.40	16.50	15.50	10.90	16.22
Fe_2	1.72	1.54	1.82	5.25	2.08	0.03	1.47
Fe	8.87	8.44	8.92	5.06	8.42	0.99	3.17
Mg	6.90	7.96	7.10	9.36	8.32	0.40	2.35
Ca	10.40	9.66	8.10	6.30	8.12	5.47	0.78
Na	5.14	3.66	0.02	0.78	0.28	4.82	3.66
K	0.67	1.66	5.80	4.36	1.44	1.24	5.10
H	6.20	9.82	14.90	17.90	31.60	4.72	13.60
C	tr.	none	2.62	none	2.16	4.61	none
Ti	1.95	1.78	1.64	1.83	2.02	0.05	0.56
P	tr.	0.26	0.24	0.18	0.22	none	0.14
Mn	0.16	0.27	0.18	0.26	0.27	0.05	0.16
Rb	0.0003	0.004	0.04	0.048	0.005	0.002	0.04
Li	0.008	0.02	0.06	0.04	0.07	0.002	0.016
Ba	0.004	0.012	0.037	0.03	0.01	0.03	0.1
Sr	0.066	0.06	0.09	0.04	0.015	0.1	0.03
La	*	*	*	*	*	0.0015	0.002
Cr	0.002	0.008	0.005	0.024	0.006	0.0002	0.009
Sc	*	*	0.002?	*	*	*	0.001
Co	0.007	0.0087	0.0086	0.008	0.005	0.00007	0.002
Ni	0.006	0.008	0.006	0.009	0.007	0.0002	0.004
Zr	0.01	0.01	0.01	0.006	0.007	0.01	0.06
Y	0.005	0.004	0.0054	0.0058	0.0046	0.003	0.006
Ag	0.00004	0.00002	0.0002	0.00004	*	0.0003	0.00004
Cu	0.02	0.03	0.009	0.02	0.03	0.05	0.04
V	0.037	0.036	0.039	0.035	0.033	0.007	0.01
Mo	0.00004	0.0001	*	*	0.00005	*	*
Be	*	*	*	*	*	0.003	0.004
In	*	*	*	*	*	*	*
Ga	0.0029	0.0028	0.0028	0.003	0.002	0.002	0.003
Sn	*	0.005	*	0.0002	0.0005	0.004	0.001
Pb	0.0003	0.001	0.0003	0.0004	0.0003	0.003	0.001
Tl	*	*	*	*	*	*	*
Ge	*	*	*	*	*	*	*

A - G as in Table 2.

TABLE 4

Possible substitutions for the common rock-forming elements*

Major element	Mg^{2+}	Na^{+}	Fe^{2+}	Fe^{3+}	K^{+}	Ca^{2+}	Al^{3+}	Si^{4+}
Substituting Elements	Fe^{3+}	Mg	Mg	Al	Ag^{+}	Na	Fe^{3+}	Al
	Cr^{3+}	Fe^{2+}	Co^{2+}	Cr^{3+}	La^{3+}	In^{3+}	Cr^{3+}	Be^{2+}
	Mo^{4+}	Co^{2+}	Ca	Ga^{3+}	Pb^{2+}	Mn^{2+}	Ga^{3+}	P^{5+}
	Li^{+}	Cu^{2+}	Li^{+}	V^{3+}	Sr^{2+}	Ag^{+}	V^{3+}	Ge^{4+}
	Ni^{2+}	Zr^{4+}	Sc^{3+}	Ti^{4+}	Ba^{2+}	La^{3+}	Ti^{4+}	
	Ti^{4+}	In^{3+}	Ni^{2+}	Mg	Rb^{+}	Sr^{2+}	Mo^{4+}	
	V^{3+}	Li^{+}	Mo^{4+}	Li^{+}	Tl^{+}			
	Sn^{4+}	Ni^{2+}	Sn^{4+}	Ni^{2+}				
	Fe^{2+}	Mn^{2+}	Na	Mo^{4+}				
	Co^{2+}	Sc^{3+}	Zr^{4+}	Sn^{4+}				
	Cu^{2+}	Sn^{4+}	In^{3+}					
	Zr^{4+}	Ca	Mn^{2+}					
	In^{3+}	Ag^{+}						
	Mn^{2+}	Y^{3+}						
	Sc^{3+}							

*Ionic radii in KX for 6-fold-coordination taken from Rankama K. and Sahama, Th. G. "Geochemistry", Univ. Chicago Press (1950), appendix 3, pp. 794-5, are:

Mg^{2+} 0.78, Na^{+} 0.98, Fe^{2+} 0.83, Fe^{2+} 0.67, K^{+} 1.33, Ca^{2+} 1.06, Al^{3+} 0.57, Si^{4+} 0.39, Ag^{+} 1.13, Ba^{2+} 1.43, Be^{2+} 0.34, Co^{2+} 0.82, Cr^{3+} 0.64, Cu^{2+} 0.83, Ga^{3+} 0.62, Ge^{4+} 0.44, In^{3+} 0.92, La^{3+} 1.22, Li^{+} 0.78, Mn^{2+} 0.91, Mo^{4+} 0.68, Ni^{2+} 0.78, P^{5+} 0.35, Pb^{2+} 1.32, Rb^{+} 1.49, Sc^{3+} 0.83 Sn^{4+} 0.74, Sr^{2+} 1.27, Ti^{4+} 0.64, Tl^{+} 1,49, V^{3+} 0.65 Y^{3+} 1.06, and Zr^{4+} 0.87.

TABLE 5

Ratios of trace to major elements in the analysed rocks

Ratio*	A	B	C	D	E	F	G
Ga/Al	0.39	0.42	0.42	0.51	0.33	0.43	0.48
Ni/Mg	2.08	2.39	2.03	2.26	2.04	1.60	4.12
Co/Mg	2.43	2.69	2.81	2.01	1.37	0.53	2.32
Li/Mg	0.35	0.75	2.50	1.25	2.45	1.60	1.85
Co/Fe^{2+}	0.83	1.09	1.03	1.61	0.59	0.09	0.74
Cr/Fe^{3+}	1.21	4.68	2.80	4.38	2.85	7.15	8.62
Sr/Ca	14.00	13.40	24.62	14.75	4.25	41.70	84.50
Sr/(Ca+K)	13.15	11.41	14.50	8.80	3.62	34.20	10.90
Ba/K	22.20	26.60	22.70	25.20	27.40	93.50	79.80
Ba/(K+Ca)	1.32	3.81	9.39	10.12	4.05	17.10	67.00
Rb/K	1.11	4.87	15.15	26.80	8.30	4.14	18.50
Sr/K	222.00	79.60	35.40	21.80	24.40	187.00	13.25
(Rb+Ba)/K	23.31	31.47	37.85	52.00	35.70	97.64	98.30
(Sr+Rb+Ba)/K	245.31	111.07	73.25	73.80	60.10	284.64	111.55

A-G as in Tables 2 and 4.

*Ratios are expressed as multiplied by 1000 in each case.

TABLE 6

Gains and losses in biotite-skarn to give rise to both lepidomelane- and chlorite-skarns

Addition	Subtraction
1.89 Fe^{3}, 1.70 Mg, 0.51 Na, 9.58 H, 0.28 Ti, 0.06 P, 0.09 Mn, 0.01 Cr, 0.002 Ni, 0.01 Cu, 0.0003 Sn, 0.00002 Mo, 0.00005 Pb	0.03 Si, 1.40 Al, 2.18 Fe^{2}, 0.89 Ca, 2.90 K, 1.54 C, 0.0003 Ga, 0.005 Li, 0.002 Co, 0.005 V, 0.002 Sc, 0.06 Sr, 0.0002 Y, 0.01 Rb, 0.017 Ba, 0.0002 Ag, 0.003 Zr

TABLE 7

Cumulative gains and losses in epidiorite to give rise to the skarn rocks

Addition	Subtraction
1.90 Mg, 1.99 Fe^{3}, 2.23 K, 18.55 H, 1.08 C 0.05 Li, 0.01 Cr, 0.002 Ni, 0.0003 Sn, 0.11 Mn, 0.30 P, 0.03 Rb, 0.017 Ba, 0.00005 Pb	2.13 Fe^{2}, 3.80 Al, 4.55 Na, 3.19 Ca, 2.49 Si, 0.001 Co, 0.003 V, 0.03 Ti, 0.00002 Mo, 0.0004 Ga, 0.03 Sr, 0.0002 Y

TABLE 8

Cumulative gains and losses in epidiorite plus quartzite to give rise to skarn rocks plus mica-schist

Addition	Subtraction
1.52 Al, 3.43 Fe^{3}, 0.15 Fe^{2}, 3.85 Mg, 6.09 K, 27.43 H, 0.0006 Ga, 0.48 Ti, 0.44 P, 0.22 Mn, 0.06 Li, 0.02 Cr, 0.001 Co, 0.005 Ni, 0.0005 V, 0.06 Rb, 0.09 Ba, 0.002 Y	5.99 Si, 7.88 Ca, 5.71 Na, 3.53 C, 0.1 Sr, 0.0003 Ag, 0.001 Pb, 0.005 Cu, 0.002 Sn

PART II

THE DISTRIBUTION AND SIGNIFICANCE OF THE TRACE ELEMENTS IN THE BRAEFOOT OUTER SILL, FIFE.

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ABSTRACT

The Braefoot sill magma has been shown by Campbell, Day and Stenhouse (1933 & 1934) to have differentiated into picroteschenite, teschenite, dolerite pegmatite, dolerite, basalt and microsyenite. The trace element contents of these rocks have now been determined by semi-quantitative methods in order to study the behaviour of the trace elements during the progress of differentiation. It is found that Cr and Ni concentrate in the early stage of crystallisation; Co, V, Cu and Sr in the intermediate stage; and Li, Rb, Ba, Ga, La, Y and Be in the late stage. Sc is enriched in the early and intermediate stages. Zr remains uniform in the early and intermediate stages but increases later. Ag is enriched in the early stage and Mo in both the early and late stages. The variations of Sn, Tl, Ge and In cannot be recognised, since, if present, these elements occur only in amounts below their limits of sensitivity. The inter-relationships between certain trace elements are discussed. It is found that the rocks of the early and intermediate stages are characterised by the distribution $Cr > Ni > Co$ and $Sr > Ba$, whereas the rocks of the late stage have $Ni > Co > Cr$ and $Ba > Sr$. Certain ratios seem to furnish a guide for the degree of differentiation represented by a given rock. $(Mg+Fe^2+Fe^3)/(Na+K+Ca)$ and $(Cr+Co+Ni+V+Cu)/(Rb+Ba+Sr)$ decrease during the progress of the differentiation, while Li/Mg, Rb/Sr, Rb/Ba, Rb/K and Ga/Al increase. Fe^2/Mg and $(V+Co)/(Cr+Ni)$ reach their highest values in the intermediate stage.

INTRODUCTION

The Braefoot outer sill, which is probably of Carboniferous age, has been described in detail by Campbell, Day and Stenhouse (1933 and 1934). Their investigation has shown that the sill is variable in character, both vertically and along the strike. It attains its maximum thickness of 310 feet at the Braefoot Promontory (1933, map, Fig. 1, p. 344). There, from below upwards, it consists of the following members: (a) Basalt, with tachylitic margin; (b) picroteschenite; (c) teschenite, becoming coarser in texture upwards; (d) dolerite pegmatite; (e) dolerite and basalt. Narrow dykes of microsyenite are of widespread occurrence in the upper part of the sill. There is also a thin sill of hornblende-teschenite underlying the main sill and differing from the teschenitic members of the latter in being richer in alkalies. A complete petrographic description (with chemical analysis) of each of these rock types is given. The various members of the sill are thought to have resulted from the differentiation of an olivine-basalt magma, the original composition of which is most closely represented by the basal basalt. By gravitative separation, probably aided by magmatic movement, olivines of early crystallisation were added to the basal liquor to form the /

the picroteschenite. The alkali feldspar-rich residual liquor gave rise to the microsyenite dykes. Hydrothermal and pneumatolytic changes took place during and immediately following the consolidation. These changes comprise analcitisation, zeolitisation, albitisation, chloritisation and calcification of certain constituent minerals of the different rock types.

The purpose of the present paper is to record the results of an investigation of the distribution of the trace elements in representative analysed rocks of the sill in order to elucidate the role played by each element during the consolidation process.

It is a great pleasure to dedicate to Dr Robert Campbell this work.

SPECTROGRAPHIC ANALYSIS

Portions of the powders used for the chemical analyses were kindly provided by Dr R. Campbell. The spectrographic analyses were made by the writer at the Macaulay Institute for Soil Research, Aberdeen.

The semi-quantitative analytical method adopted in this /

this study has already been described in detail by Mitchell (1948). The same method has been used by him in analysing a series of rocks from the Skaergaard Complex of East Greenland (Wager and Mitchell, 1943) and a series of Caledonian rocks mainly of granodioritic composition (Nockolds and Mitchell, 1948). The possible errors in this method are of the order ± 25-30 per cent over the range of approximately 10 to 300 ppm. Errors of ± 50 per cent are possible if the abundance is over 1000 ppm.

For further details of the geochemistry of the determined elements, the respective wave lengths of their diagnostic lines and the sensitivity of each element see Higazy, 1952.

RESULTS

The major and trace element contents in parts per million are given in Table I. The major element contents are calculated from the percentages of their respective oxides given by Campbell, Day and Stenhouse (1933 and 1934).

DISCUSSION

Stages in the differentiation of the sill

The main process responsible for the variation within the Braefoot sill appears to have been crystallisation differentiation. There was some contamination by quartzose xenoliths during the formation of the upper dolerite, but this was purely local and subsidiary. The main consolidation process can be conveniently divided into three distinct stages: (1) an accumulative stage represented by the picroteschenite; (2) an intermediate stage represented by (i) teschenites, (ii) dolerite pegmatites and (iii) dolerite and upper basalts (the average composition of these rock types is taken to represent this stage); and (3) a late stage represented by the microsyenite dykes.

There are certain features which characterise each of these three stages with regard to (a) the normative compositions and (b) the relative proportions of certain major oxides.

(a) The normative compositions of the rocks of each of the three stages outlined above given by Campbell, Day and Stenhouse (1933 and 1934) are graphically shown in Fig. 1. Similar tendencies in the distribution of the normative compounds are found in the "Big" Trap differentiated ophitic basalts /

basalts of the Keweenawan series of the Michigan copper district studied by Cornwall (1951a, Fig. 9, p. 187).

(b) The values of the ratio 100($FeO+Fe_2O_3$)/($MgO+FeO+Fe_2O_3$) for each of the three stages of crystallisation are: 42.0 in the accumulative, 65.5 in the intermediate and 70.5 in the late, 53.5 being the value for the undifferentiated lower olivine-basalt. These figures agree very closely with those given by Walker and Poldervaart (1949, pp. 652-4) for the three corresponding stages of crystallisation of the Karroo dolerites; 25-50 (early stage); 50-70 (middle stage) and 70-80 (late stage).

The trend in the relative proportions of total iron oxides (as FeO), MgO and K_2O+Na_2O is clearly significant and effectively serves to distinguish the different stages of the crystallisation of the magma, since it includes MgO and iron oxides which are critical constituents of the ferromagnesian minerals (the discontinuous portion of the reaction series), and Na_2O and K_2O which are the critical constituents of the feldspars (the continuous portion of the reaction series). Fig. 2 illustrates that there is a relative enrichment in MgO in the picroteschenite (accumulative stage) in comparison to the undifferentiated olivine-basalt. The intermediate stage is characterised by enrichment in both FeO and alkalies and impoverishment in MgO /

MgO compared to the accumulative stage. The difference between the undifferentiated olivine-basalt and the average composition of the intermediate stage is not noticeable with respect to MgO and FeO, yet there is a slight increase in the alkalies in the latter. The late stage is much enriched in the alkalies and has lower proportions of both MgO and FeO than in each of the accumulative stage, the intermediate stage and the undifferentiated basalt. This trend is essentially similar to that followed during the differentiation of the Karroo dolerites (Walker and Poldervaart, 1949) as well as to the trends of various other differentiated sills and magmatic rocks represented graphically by these authors: namely, Tasmanian dolerites, Palisade sill, Siberian traps, the late Palaeozoic quartz-dolerites and tholeiites of Scotland and northern England, and the Hawaiian lavas (Walker and Poldervaart, 1949, Figs. 29-33, pp. 658-660). The trend of the differentiation of some Keweenawan lavas (Cornwall, 1951b, Fig. 10) is also identical with the above mentioned examples.

From these differentiation trends, representing similar petrographic provinces widely separated in space and time, it can therefore be considered as established that (1) the rocks produced at the early accumulative stage are generally richer in /

in Mgo than the undifferentiated original magma; (2) those formed during the intermediate stage are relatively enriched in FeO and (3) those formed in the late stage are enriched in the alkalies.

DISTRIBUTION OF Cr

Chromite and spinels in general -- the most important chromium bearing minerals -- are not uncommon constituents of igneous rocks, especially in the ultrabasic and basic types. Cr can enter into the structure of certain ferromagnesian silicate minerals. It is similar to Fe^3 in , ionic radius (Cr 0.64 A° and Fe 0.67), co-ordination, valency and E-Value (activation energy of migration).

The data given by Wager and Mitchell (1950, p. 144) show very clearly that Cr enters into the structure of pyroxene more readily than into that of olivine. The olivines of the eucrite and the olivine-gabbro of the Skaergaard intrusion of east Greenland have 20 and <1 ppm. of Cr respectively; whereas the pyroxenes of these rocks have 3000 and 350 ppm. of this element. This can be understood if we consider the paucity of trivalent iron in the olivine structure. When Cr replaces Mg /

Mg and/or Fe^2, it is essential to have univalent ions which should possess ionic radii similar to that of Cr and should be 6-fold in co-ordination in order that electrostatic equilibrium is maintained. Lithium satisfies these requirements, but its low E-Value makes it unlikely that it can enter into the olivine lattice. On the other hand pyroxenes, amphiboles and biotites generally contain Fe^3 and/or Al, and chromium can readily replace either of these trivalent elements. Amongst these ferromagnesian groups, pyroxenes seem to be the richest in Cr. The range in Cr content of the augites of the Caledonian granodioritic rocks studied by Nockolds and Mitchell (1948) is 1500-2500 ppm., while the range in the hornblendes of these rocks is 150-800 ppm. and that in the biotites is 25-800 ppm. The Cr content of some biotites of the granodioritic rocks of Jamestown, Colorado, examined by Bray (1942b, p. 801) ranges from 40-1090 ppm.

Generally the Cr content of the minerals of the continuous portion of the reaction series is relatively poor. The range in Cr content of the plagioclases of the rocks of the Skaergaard intrusion is 1-10 ppm. (Wager and Mitchell, 1950, p. 144). The Cr concentration varies from <2 to 15 ppm. in the plagioclases of the Caledonian rocks. A plagioclase Ab_{58} An_{42} separated from hornblende monzonite of the Front Range, Colorado /

Colorado, has 2 ppm. Cr (Bray, 1942a, p. 436) and a plagioclase of the Overland Mtn. granite, Jamestown, Colorado, has <1 ppm. (Bray, 1942b, p. 798). The Cr content of potash feldspar is also relatively low. The average for the potash feldspars of the Caledonian rocks is < 2 ppm. The range for the potash feldspars of the granodioritic rocks of Jamestown, Colorado, is <1-14 ppm. (Bray, 1942b, p. 796). If not due to contamination by ferromagnesian inclusions, such relatively small amounts of Cr as are found in the feldspars may be replacing Al in the crystal lattice.

It appears, therefore, that the Cr content of igneous rocks depends on the type and amount of the minerals of the discontinuous reaction series present, since the members of the continuous reaction series carry only negligible amounts of this element. It is known that during the fractional crystallisation of basic magma, chromite and/or spinels in general and/or olivine separate at the early stage. The resulting accumulative rocks would therefore be expected to be relatively rich in Cr. The Cr content of rocks which crystallise during the early intermediate stage is likely to be relatively high since pyroxenes are their predominant ferromagnesian minerals. The amphiboles commonly predominate in the late intermediate stages of magmatic crystallisation. The rocks of this stage would /

would therefore be expected to have less Cr than those of the early intermediate stage. The Cr content at the late stage when rocks relatively rich in biotite form, would again be less than that of rocks of the late intermediate stage. The Cr content of such felsic rocks as may form at the end of the crystallisation process would be negligible.

Table I shows that the picroteschenite -- the accumulative rock -- has the highest Cr content among the rocks of the Braefoot outer sill (950 ppm.). The lower undifferentiated olivine-basalt has 750 ppm. The sum of the modal pyroxene and iron-ore in the picroteschenite and the lower olivine-basalt are very similar being 30 and 29.5 respectively (Campbell et al, 1933). The difference in the modal olivine of these two rocks is rather noticeable. The picroteschenite has 35 olivine while the lower basalt has only 18.5. It was mentioned above that the Cr content of olivines is relatively poor. The richness of the picroteschenite in Cr may, therefore, be attributed to either or both of two possibilities: (a) the presence of minute crystals of chromite which separated with the olivine at an early stage; (b) the relative enrichment of the augite of the picro-teschenite in Cr as compared with that of the olivine-basalt. Cr has a smaller ionic radius than that of Fe^3 and, therefore, would show relative concentration in the earlier minerals according to Goldschmidt's rules (1934).

The /

The Cr contents of rocks of the intermediate stage are much lower than the content of the accumulative rock and are also lower than that of the undifferentiated basalt. The content of Cr in the dolerite pegmatite is <1 ppm., whereas it ranges from 40-180 ppm. in the teschenites, and from 400-550 ppm. in the dolerite and upper basalts.

The extreme deficiency of the dolerite pegmatite in Cr is very striking. The rock consists of large crystals of plagioclase (1.2 cm. in length), augite (up to 8 mm. in diameter), and iron oxides set in a vesicular crystalline mesostasis composed of feldspar and chlorite, or, rarely, chlorophaeite. The augites contain bands of fluid inclusions and in some cases, they are almost completely replaced by chlorite and carbonates (Campbell et al, 1933, p. 354). That the dolerite pegmatite stage was greatly enriched in volatiles is evidenced by the vesicular character of its mesostasis and of the presence of fluid inclusions in the augites. The volatiles decreased the viscosity and thus pegmatitic crystals were developed. The gases might also have been responsible of decreasing the temperature of crystallisation to such an extent as Cr could no longer enter into the augite structure. Moreover, the hydrothermal replacement of augite by chlorite and carbonates /

carbonates might have been a factor responsible for the deficiency of the dolerite pegmatite in Cr. The dolerite pegmatite of the Karroo rocks given by Walker and Poldervaart (1949, p. 662) has much less Cr (45 ppm.) than the other doleritic rocks of the Karroo (e.g. 260 ppm.). The difference in Cr content of the dolerite pegmatite of the Braefoot outer sill and that of its dolerite is far more than that found in case of the Karroo rocks.

The dolerite pegmatite of the Whin sill has been considered by Tomkeieff (1929) to be formed from the segregation of a wet magmatic fraction. Walker and Poldervaart (1949, p. 662) accept Tomkeieff's point of view regarding the origin of the Karroo dolerite pegmatite. They, however, consider it as an advanced phase during the crystallisation of the parent source and not as a heteromorphic variety of the normal rock as Tomkeieff suggested in connection with the dolerite pegmatite of the Whin sill. The relative proportions of FeO, MgO, and Na_2O+K_2O of the normal rock from which the dolerite pegmatite of the Karroo was derived as well as the dolerite pegmatite itself indicate that the latter is further along the path of crystallisation than the former. This is also the case in the dolerite pegmatite of the Braefoot sill. The plot of the relative proportions of FeO, MgO, and Na_2O+K_2O of the undifferentiated olivine-basalt and the dolerite /

dolerite pegmatite given in Fig. 2 shows that the dolerite pegmatite composition relative to that of the olivine-basalt is upward away from the MgO corner toward the FeO apex indicating a more advanced stage of crystallisation.

On the whole, the average Cr content of the three types of rocks of the intermediate stage, that is, teschenites, dolerite pegmatite and dolerite and upper basalts is 224 ppm. compared to 950 ppm. in the accumulative rock and 750 ppm. in the undifferentiated rock. This shows the decrease in Cr content as crystallisation proceeds towards the intermediate stage.

The decline in Cr content continued, since the content of the microsyenite which marked the late stage of the differentiation of the Braefoot sill magma is negligible being less than the sensitivity of the method used, that is, less than 1 ppm. The microsyenite is a felsic rock very poor in pyroxenes. The deficiency in Cr in this microsyenite is, therefore, understandable.

The concentration of Cr in the three stages of the crystallisation of the Braefoot magma agrees very closely with what would be expected during the normal course of the differentiation of the basic magma.

DISTRIBUTION OF Ni

The sulphides of Ni are not common constituents of igneous rocks. It can be present in iron-ores. Magnetite of olivine-gabbro of the Skaergaard intrusion has 300 ppm. (Wager and Mitchell, 1950). Ni can enter very readily into the ferro-magnesian mineral structure mainly replacing Mg. Ni and Mg have exactly the same ionic radii 0.78 Å, they are both divalent, 6-coordinated and have large E-values. Ni can also replace Fe^2 since the difference in their radii is not big (Fe^2 0.83 A°).

The Ni contents of the olivines and pyroxenes of the Skaergaard intrusion (Wager and Mitchell, 1945) show (1) Ni is more concentrated in the olivines than in the pyroxenes since the olivines of the gabbro picrite, olivine-gabbro and hortonolite ferro-gabbro have 1000, 400 and 10 ppm. respectively while the pyroxenes of the same rocks have 80, 50 and $<$ 2 ppm. (2) the Ni contents of the olivines and pyroxenes found in rocks formed at earlier stages are relatively higher than those of the late stages. The supposed order of crystallisation of these three types of the Skaergaard rocks is gabbro picrite, olivine-gabbro and hortonolite ferro-gabbro. The two olivines analysed by Goldich and given by Sandell and Goldich (1943, p. 177) contain 2350 and 3060 ppm. Ni. The latter which is richer in Ni has /

has higher MgO content, being 51.43 per cent while the former has 49.78 per cent.

The amphiboles seem to have lower Ni content than the olivines and/or the pyroxenes. The biotites appear to possess approximately similar Ni concentration like that of the amphiboles if not a little lower. The ranges of the Ni content of the pyroxenes, hornblendes and biotites of the Scottish Caledonian rocks found by Nockolds and Mitchell (1948) are: augites 90-200 ppm., hypersthene 300 ppm., hornblendes 80-150 ppm. and biotites 30-150 ppm. The range of Ni content in the biotites of the granodioritic rocks of Jamestown, Colorado given by Bray (1942b, p. 808) is 25-170 ppm. The Ni contents of the members of the discontinuous series decrease regularly from olivine to biotites.

The plagioclase feldspars contain negligible amounts of Ni. The plagioclase of the eucrite of the Skaergaard intrusion has 10 ppm. Ni while each of the plagioclases of the olivine-gabbro, middle gabbro, hortonolite ferro-gabbro and fayalite ferro-gabbro has <2 ppm. Ni (Wager and Mitchell, 1950, p. 144). Moreover the range of Ni content in the plagioclases of the Scottish Caledonian rocks in <2-20 ppm. (Nockolds and Mitchell, 1948). The potash feldspars are similar to the plagioclases /

plagioclases in being poor in Ni. The potash feldspars ofthe Caledonian rocks have $<$ 2-5 ppm.

Evidently, the concentration of Ni in rocks depend on the amount and type of the minerals belonging to the discontinuous reaction series present in the rock. Those rich in olivine and/or pyroxenes such as the accumulative and the ultrabasic and basic types in general are relatively the richest in Ni. The intermediate rocks which usually contain pyroxenes and/or amphiboles are richer in Ni than the acidic types which contain amphiboles and/or biotites. The felsic rocks which are generally very poor in the ferromagnesians would have very negligible amounts of Ni. The trend in the concentration of Ni during the normal fractionation of the magma is, therefore, towards a regular decrease in the amount of Ni.

The picroteschenite of the Braefoot outer sill is the richest type in Ni among the rocks of this sill. The accumulative rocks are also the richest in Ni in case of the Skaergaard intrusion and the Karroo dolerites. The difference in Ni content between the picroteschenite (430 ppm.) and the undifferentiated olivine-basalt (340 ppm.) is not as big as that between the gabbro picrite of the Skaergaard intrusion (600 ppm.) and its marginal olivine-gabbro (100 ppm.) which is supposed /

supposed to represent the Skaergaard magma (Wager and Mitchell, 1943); or that between the olivine-basalt of the Karroo (Portje type) which has 200 ppm., while the undifferentiated dolerite (Kokstad type) has 80 ppm. (Walker and Poldervaart, 1949, p. 644). The ratios of the Ni content of the accumulative types to that of the undifferentiated rocks in the Braefoot sill, Skaergaard intrusion and the Karroo dolerites are 1.3, 6.0 and 2.5 respectively. The undifferentiated rock of the Braefoot sill is the richest in Ni (340 ppm.), the corresponding Skaergaard and Karroo rocks each having 100 ppm. The accumulative rock of the Braefoot, however, having 430 ppm. is poorer than that of the Skaergaard intrusion on one hand, and richer than that of the Karroo dolerites on the other. The ratio Fo:Fa in the olivines separating gravitationally to form each of these accumulative rocks is quite likely different. The olivine of the Skaergaard's gabbro picrite seems to be the richest in Fo; and that of the Karroo (olivine-basalt, Portje type) may be the poorest in this molecule. This seems to be true since the Mgo contents of the gabbro picrite and that of the olivine-basalt of the Karroo are 27.09 and 12.91 per cent respectively. The MgO content of the picroteschenite of the Braefoot is 14.96 per cent. The Ni contents of these rocks increase with increase in the Mg content.

The /

The Ni contents of the rocks of the intermediate stage are less than those of both the picroteschenite and the undifferentiated basalt. The dolerite pegmatite, which may have been formed from segregation of fractions rich in the volatiles, has lower Ni (48 ppm.) than the teschenites (80 ppm.), and dolerite and upper basalts (100 ppm.). On the whole, the average Ni content of all the types of the intermediate stage is 84 ppm. The microsyenite which forms at the late stage of the crystallisation of the Braefoot magma has 40 ppm., that is, the lowest Ni content among the Braefoot rocks. The trend in Ni during the fractionation of the Braefoot magma, has been, therefore, towards a regular marked decrease.

DISTRIBUTION OF Co

The sulphides of Co are not common in igneous rocks. It can be present in the iron-ores ubiquitously found as minor accessories in rocks. Ilmenite of the middle gabbro of the Skaergaard intrusion has 100 ppm. (Wager and Mitchell, 1950, p. 144). Co can enter the ferromagnesian mineral structures mainly replacing Fe^2. Available data concerning the concentration /

concentration of Co in the ferromagnesian minerals indicate only a small change in the different groups. The olivines have slightly higher Co content than the pyroxenes. The olivines of the eucrite and olivine-gabbro of the Skaergaard intrusion have 150 and 125 ppm. respectively, while the pyroxenes of the same rocks have 60 and 50 ppm. (Wager and Mitchell, 1950). The similarity in Co content between olivine and pyroxene of the fayalite ferro-gabbro of the same intrusion is more pronounced. The olivine has 20 and the pyroxene has 15 ppm. The amphiboles and the biotites seem to have approximately identical Co content which is a little lower than that of the pyroxenes. The Co content of the Caledonian minerals are: augites 30-70, hypersthene 100, hornblendes 20-40 and biotites 15-40 ppm.

The feldspars contain negligible amounts of Co since they lack Fe and Mg in their composition and their major elements, that is, Ca, Na and K have generally higher coordination numbers than that of Co. The ionic radius of Co^2 is 0.82 A° closer to that of Na 0.98 A° than to that of Ca or K. The small proportions of Co generally found in the feldspars might replace Na in their structure provided that other replacements take place to satisfy the electrostatic equilibrium.

From the brief outline mentioned above, it seems that the Co content of a rock depends rather on the amount of the ferromagnesian /

ferromagnesian minerals present. The type of the ferromagnesian mineral does not have great significance on the Co content. The ultrabasic types would be expected to have relatively high Co content since they are composed almost exclusively of ferromagnesian minerals. The basic and other rocks which form at the early intermediate stage of the crystallisation of the magma could also be considered as relatively rich in this element. Rocks of the late intermediate stage and the felsic types of the late stage would be impoverished in Co compared to the others which crystallise at earlier stages.

The distribution of Co in the Braefoot sill corresponds to expectation. The Co content of the picroteschenite is 85 ppm. very close to that of the undifferentiated basalt (90). The derivatives of the intermediate stage are not much lower in Co than the accumulative picroteschenite, the averages being: teschenites 70, dolerite pegmatite 55 and dolerite and upper basalts 58 ppm. The Co content of the dolerite pegmatite compared to that of the dolerite is very interesting. It may be recalled that both Cr and Ni are lower in the pegmatitic phase. Co, however, is almost the same in the pegmatite (55 ppm.) and the dolerite (50). The dolerite pegmatite of the Karroo and the dolerite of the same locality (Walker and Poldervaart /

Poldervaart, 1949, Analyses 66 and 5, Table 14, p. 644) have 31 and 28 ppm. of Co respectively. Cr and Ni of these two Karroo rocks, however, are much higher in the dolerite than in the pegmatite, as in the Braefoot sill. It seems reasonable to infer, therefore, that the lowering of the temperature, due to the volatiles, does not appear to decrease the tendency of Co to enter into the ferromagnesian mineral structures, contrary to what happens with Cr and Ni.

The average Co content of all the rocks of the intermediate stage is 61 ppm., again not much lower than that of the picroteschenite (85 ppm.). The Co content of the late stage microsyenite is, however, noticeably lower (10 ppm.). This is consistent with what would be expected had these rocks been fractionated from a basic magma.

Cr : Ni : Co

Lundegårdh (1949) investigating the geochemistry of Cr, Ni and Co has ascertained that, according to Goldschmidt's rules, the ultrabasic rocks and those of the early stages of the crystallisation of the magma as a whole, should be characterised by the following order of distribution

$$\mathrm{Cr} > \mathrm{Ni} > \mathrm{Co},$$

whereas /

whereas the latest differentiates should have

$$Co > Ni > Cr.$$

The undifferentiated lower olivine-basalt of the Braefoot sill as illustrated in Table I has $Cr > Ni > Co$. The picroteschenite which is considered to be the accumulative derivative shows also the same relationship.

The distribution in the teschenites as well as in the dolerite and upper basalts of the intermediate stage is $Cr > Ni > Co$. The averages for the two teschenites are Cr 110, Ni 80 and Co 70 ppm., while those of the dolerite and upper basalts are Cr 450, Ni 110, and Co 58 ppm. The dolerite pegmatite, however, has a distribution which, according to Lundegårdh, typifies rocks of the late magmatic stage, that is $Co > Ni > Cr$.

The averages for the rocks of the intermediate stage as a whole given in Table II are Cr 224, Ni 84 and Co 61 ppm., i.e., $Cr > Ni > Co$. The intermediate stage has, therefore, the distribution characteristic of basic rocks.

Lundegårdh (1949, p. 21) has suggested that the distribution normally prevailing in late stage magmatic rocks is $Co > Ni > Cr$. However, the Braefoot microsyenite has $Cr < 2$, Ni 40 and Co 10 ppm., i.e., $Ni > Co > Cr$, and, moreover, there are other late magmatic rocks which are similarly at variance with Lundegårdh's /

Lundegårdh's suggestion. The acid granophyre which marks the latest stage in the fractionation of Skaergaard intrusion has Cr 3, Ni 5 and Co 3 ppm., i.e. Ni > Co = Cr (Wager and Mitchell, 1943, p. 287). This granophyre has 75.03 per cent SiO_2 and Lundegårdh accepts its magmatic derivation (1949, p. 14). The porphyries and rhyolite analysed by Lundegårdh (1949, Table 4, p. 41) show also deviation from the distribution Co Ni Cr. The Tertiary rhyolite of Ramsö, Lake Mien, Kronbergs Iän, for instance, has Cr 6, Ni 50 and Co $\leq$ 2 ppm., that is, Ni > Cr > Co. Moreover, the average of 29 samples of silicic rocks (SiO_2 63 per cent) studied by Sandell and Goldich (1943, p. 182) is Ni 6 and Ci 3 ppm., that is, Ni > Co. Cr unfortunately was not determined in these rocks. The average of coarse granite and other monzonitic rocks of Oliverian magma series of New Hampshire studied by Billings and Rabbitt (1947, Table 4, (1), p. 581) is Cr 14, Ni 16 and Co 7 ppm., that is, Ni > Cr > Co.

It can be said that the ultrabasic and the basic rocks appear to have the distribution Cr > Ni > Co. During the fractionation of the magma Cr and Ni decrease, the decrease of the latter is slower, whereas the Co content remains relatively more uniform. This behaviour gives rise to the extreme impoverishment of the latest differentiates in Cr whereas Ni and Co would be higher in content compared to that of Cr. If the decrease /

decrease in Ni is very sluggish owing to a very slow decrease in temperature during the crystallisation of the magma, the content of this element is liable to be higher than that of Co in the latest differentiates.

DISTRIBUTION OF V

Vanadium may be tri-, tetra- or quinquevalent. The ionic radii are V^3 0.65, V^4 0.61 and V^5 0.4 A°. The ionic radius of V^3 is very close to that of Fe^3 0.67 A° and therefore, can substitute for it in suitable mineral structures. The olivines which generally lack Fe^3 in their composition are very poor in V^3. Each of the olivines of the eucrite, olivine-gabbro and hortonolite ferro-gabbro of the Skaergaard intrusion (Wager and Mitchell, 1950, p. 144) has 5 ppm. V. The pyroxenes of the same rocks, however, have 300, 250 and 30 ppm. respectively. The augite of augite-peridotite of the Garabal Hill-Glen Fyne Complex (Nockolds and Mitchell, 1948, p. 561) has 250 ppm. Hypersthene and augite of pyroxene mica-diorite of the same complex have 100 and 200 ppm. respectively. The range of V in the hornblendes of the Garabal Hill rocks as well as other /

other Scottish Caledonian granodioritic rocks is 100-300 ppm. The distribution of V in the few analysed pyroxenes and hornblendes of the Caledonian rocks indicates that V is slightly enriched in the hornblendes compared to the pyroxenes. The range of V in the biotites of the same rocks is 100-1000 ppm. showing a tendency of V to be more enriched in the biotites than any of the other ferromagnesian minerals.

The feldspars are generally poor in V. The plagioclases of the rocks of the Skaergaard intrusion have 5-10 ppm. Those of the Caledonian Scottish rocks have 10-30 ppm. The potash feldspars are poorer in V than the plagioclases. Most of the potash feldspars of the Caledonian rocks have $<$ 5 ppm. of V.

V^3 appears, therefore, to be enriched in rocks relatively rich in the amphiboles and/or the biotites, that is, those rocks which usually form at the late intermediate stages of the magmatic crystallisation.

V^4 has an ionic radius 0.61 Å very close to that of Ti^4 0.64 Å. The presence of appreciable amounts of V in sphene and ilmenite is, therefore, understandable. Sahama (1946) reports 615 ppm. in a sphene from Ilöjärvi. The V content of each of the four sphenes of the granodioritic rocks of the /

the Garabal Hill is 300 ppm. Ilmenite of the olivine-gabbro of the Skaergaard intrusion has 600 ppm. The magnetite of the same rock, however, has 2000 ppm. much higher than the ilmenite. Moreover, magnetites of the middle gabbro and the hortonolite ferro-gabbro have 800 and 300 ppm. respectively whereas ilmenites of the same rocks have only 300 and 20 ppm. The V content of magnetite seems to be higher than that of ilmenite and apparently most of the vanadium of the magnetites is in the trivalent state of ionisation. In fact, the ionic radii of Fe^3, Ti^4, and V in its tri- and tetravalencies are not very different from each other. This makes it likely that vanadium in entering into the magnetite and ilmenite structures is distributed between both Fe^3 and Ti^4, with more preference to Fe^3.

Pentavalent vanadium with an ionic radius of ~ 0.4 A° can replace P^5 in minerals especially those rich in the latter such as apatite.

The V content of the Braefoot sill rocks is in harmony with the general distribution of this element in the different members of the discontinuous reaction series. The average content of the rocks of the intermediate stage (340 ppm.) is higher than that of the accumulative rock (220), while that of the late stage is very low (8). The content of the undifferentiated basalt /

basalt is 330 ppm. slightly lower than the average of the rocks of the intermediate stage. V is enriched in the intermediate stage of the crystallisation of the Braefoot magma and becomes greatly impoverished during the latest stage.

Vanadium is more related in its distribution to Co than to either Cr or Ni. Both V and Co are relatively enriched in the intermediate stage. They mainly replace Fe in the structures of the ferro-magnesian minerals, yet Co is more enriched in the pyroxenes (early intermediate stage), whereas V appears to be relatively more concentrated in the biotites (late intermediate stage).

DISTRIBUTION OF Li

The lithium minerals such as spodumene and amblygonite are commonly found in granitic pegmatites indicating the enrichment of this element in the very latest residual magmatic liquors. The mechanism of separation of lithium-rich liquors to form lithium-rich pegmatites from the bulk of the alkaline-rich residual liquor is still an unsolved problem (Higazy, 1949, p. 565).

Li /

Li with an ionic radius of 0.78 A° usually replaces Mg which has exactly the same radius. Available data concerning the content of Li in the ferromagnesian minerals of the Scottish Caledonian rocks indicate very clearly that Li is more enriched in biotites than in pyroxenes or hornblendes. The ranges of Li content are 2-5 ppm. in the pyroxenes, 5-30 in the hornblendes and 80-800 in the biotites. The olivines are generally very rich in Mg yet their Li content is negligible. The dunite of the Garabal Hill (Nockolds and Mitchell, 1948) for instance, has <1 ppm. Li. According to Wickman (1943), Li has a low E-value and therefore, can only be incorporated to a very limited extent in minerals formed at relatively high temperatures such as the olivines.

The feldspars in general are poor in Li perhaps because of (1) the lack of Mg and (2) the low coordination and small ionic radius of Li. However, Lundegårdh (1947, p. 108) suggests that Li may replace Al in the feldspar structure. According to Ahrens (1945a, p. 82), a content greater than 2-5 ppm. is exceptional in the feldspars. The plagioclases of the Scottish Caledonian rocks have 1-15 ppm. and the average for the potash feldspars in these rocks is 1 ppm. In some pegmatites, however, the Li content of feldspars is enormously greater /

greater. Hess (1940) finds as much as 1.2 per cent Li in pegmatitic microcline. Moreover, the perthites of the Black Hills pegmatites, South Dakota, recently analysed by the writer, have up to 300 ppm.

The distribution of Li in the members of both the discontinuous and continuous reaction series suggests that Li would be relatively enriched in the mica-rich rocks, that is, those which form at the late stage of the magmatic crystallisation. This is the case in the Braefoot sill rocks. The microsyenite has 50 ppm. Li, whereas the undifferentiated basalt has 12 ppm. and the accumulative rock 20 ppm. The average Li content for the intermediate stage is 24 ppm., very close to that of the picroteschenite (accumulative stage). The lithium distribution in the Braefoot sill indicates little difference between the accumulative and intermediate stages, but notable enrichment in the late stage.

DISTRIBUTION OF Rb

Rubidium minerals are unknown in igneous rocks. Rb enters into the mineral structures replacing K since (a) these elements /

elements are closely similar in ionic radius: Rb 1.49 and K 1.33 A°, and (b) their coordination numbers are usually 9-10. Absence of Rb from olivines and pyroxenes is therefore to be expected. The amphiboles, which usually contain but little K, are relatively poor in Rb. The range of the Rb content in the hornblendes of the Scottish Caledonian rocks is 20-30 ppm. The biotites and the micas in general are relatively very rich in this element. The range in the biotite micas of the Scottish rocks is 400-2500 ppm. The muscovite of the pegmatites of Uranoop River area, Namaqualand, S. Africa have 100-1280 ppm. (Ahrens, 1945b, p. 223). The micas are, therefore, the only member of the discontinuous reaction series which can be considered as having appreciable amounts of Rb.

The plagioclase feldspars have generally only a small proportions of K. Consequently, their Rb contents are not very high. The range in the plagioclases (chiefly albitic) of certain South African rocks is nil-110 ppm. (Ahrens, 1945 b, p. 219). Ahrens also reports 11,880 ppm. Rb in the green microcline of Pike's Head, Colorado. The perthites of the Black Hills, S. Dakota analysed by the writer have up to 9500 ppm.

The survey of the distribution of Rb in the members of the reaction series indicates that the mica- and potash feldspar-rich rocks should be enriched in this element. These are /

are generally felsic rocks which form at the latest stages of the crystallisation of the magma.

The distribution of Rb in the rocks of the Braefoot sill is in harmony with this general concept. The microsyenite has 100 ppm., twenty times as much as the content of the undifferentiated basalt. The picroteschenite has only 3 ppm. and the average Rb content of the rocks of the intermediate stage is 16 ppm., indicating a regular increase in Rb during the progress of the differentiation of the Braefoot magma.

DISTRIBUTION OF Ba

Ba minerals are not common constituents of igneous rocks. The ionic radius of Ba is 1.43 Å , close to that of K 1.33 A° . The substitution of K by Ba in crystal structures has been mentioned by several investigators. The ionic radius of Ca is 1.06 A° and inter-replacement between Ba and Ca is possible. Neither Ca nor K is found in the composition of the olivines. Accordingly the Ba content of this group should be negligible. The pyroxenes usually have Ca but, according to

Wickman /

Wickman (1943), the transition of Ca from 8- to 6- coordination may cause shrinkage in the structure of the pyroxene and, consequently Ca should be replaced by Fe^2 and/or Mg but not by Ba. This may account for the rather insignificant Ba content in the pyroxenes. Augite and hypersthene from the Garabal Hill-Glen Fyne Complex, for example, have 5-20 ppm. The amphiboles seem to be richer in this element than the pyroxenes. The range in the hornblendes of the Scottish Caledonian rocks is 20-100 ppm. Biotites, which have K as one of their most significant elements usually contain appreciable amounts of Ba. The biotites of the Caledonian rocks have 1500-4000 ppm. Those of the igneous rocks of Jamestown, Colorado, (Bray, 1942b, p. 808) have 90-450 ppm.

The plagioclases are relatively rich in Ba. Ca in their structure is in 8-coordination and can be substituted by Ba. Plagioclases from the Caledonian rocks have 200-1500 ppm. and those of the rocks studied by Bray (1942b) have 40-1030 ppm. The potash feldspars are known to be highly enriched in Ba and figures need not be mentioned. There is a continuous isomorphous series between orthoclase and celsian which ranges from Cr_{85} Ce_{15} to Cr_{67} Ce_{33}.

Ba is evidently enriched in the mica-rich and felsic rocks. These rocks generally form at the late stage of the magmatic /

magmatic crystallisation, though it has been pointed out by Engelhardt (1936) that Ba is relatively enriched in potash feldspars which have formed at earlier stages of crystallisation compared with those formed later. The bulk of the Ba, however, seems to remain in the residual melt until the late stage of crystallisation is reached. At this stage the feldspars, especially the potash types, are the dominant minerals. The earlier products of the late stage should have potash feldspars with a higher Ba content than those formed still later.

The microsyenite of the Braefoot sill contains 1200 ppm. This is higher than the contents of the undifferentiated basalt (950 ppm.), the picroteschenite (650 ppm.) and the average of the rocks of the intermediate stage (936 ppm.). Although the picroteschenite has the lowest content, it should be mentioned that the amount is higher than would be expected in an accumulative rock. Its modal plagioclase percentage is 23, and it has 5 per cent of modal chlorite, analcite and zeolites. Perhaps the plagioclase and zeolites are responsible for the relatively high proportion of Ba, since it is not likely that the other constituents would have an appreciable amount of Ba.

(Cr+Ni+Li) : (Co+V) : (Rb+Ba)

The behavious of Cr, Ni and Li, Co and V, and Rb and Ba have been already discussed. The trend in the relative proportions of (Cr+Ni+Li):(Co+V):(Rb+Ba) during the stages of the magmatic crystallisation seems to be of significance. The trend in the relative proportions of MgO:FeO:(Na_2O+K_2O) of the rocks developing at the three main stages of the magmatic crystallisation has been shown by Walker and Poldervaart (1949) to be essentially the same in many magmatic rocks of different provinces. The trend in the relative proportions of these oxides in the Braefoot rocks shown in Fig. 2 does not deviate from that given by Walker and Poldervaart as was discussed previously (p. 7). It may be recalled that Cr, Ni and Li are very much related to Mg, and that Co and V, on the other hand are more related to Fe than to Mg. Rb and Ba however, are elements mainly present in the feldspars and their geochemical relationship with K is seemingly fully established.

Fig. 2 shows that the trend in the relative proportions of (Cr+Ni+Li):(Co+V):(Rb+Ba) is similar to that of MgO:FeO:(Na_2O+K_2O). There has been a relative enrichment in (Cr+Ni+Li) in the early accumulative stage corresponding to that of MgO. As crystallisation proceeded to form rocks of the intermediate stage, there were enrichments in the relative proportions both of /

of (Co+V) and of(Rb+Ba). In the late stage there was a marked increase in the relative proportions of (Rb+Ba) accompanied by impoverishment in the proportions of both (Cr+Ni+Li) and (Co+V).

DISTRIBUTION OF Sr

The Sr minerals are not common constituents of igneous rocks. The ionic radius of Sr is 1.27 A°, between the radii for Ca (1.06 A°) and K (1.33 A°). Sr can replace both these elements in crystal lattices at favourable temperatures. The inter-replacement between Sr and Ca seems to be more conspicuous than that between Sr and K. Both Sr and Ba can replace Ca and/or K, but as the ionic radius of Ca is closer to that of Sr than Ba (1.43 A°), Ca is preferably replaced by Sr. Actually, the ionic radius of Sr is very close to that of K, but the ionic radius of Ba is also very suitable for replacing K. The inter-replacement between Ba and K seems tobe stronger than that between Ba and Ca.

Olivines should have very negligible amounts of Sr since Ca and K are usually lacking. Amphiboles are apparently richer in Sr than both pyroxenes and biotites. The range of

Sr /

Sr content in the Caledonian minerals are: pyroxenes, 10-30 ppm., hornblendes, 30-300 ppm. and biotites, 30-200 ppm.

The content of Sr in feldspars is relatively higher than that in ferromagnesian minerals. The feldspar structure seems to be more favourable for Sr. Plagioclases which usually contain appreciable amounts of Ca have greater amounts of Sr than potash feldspars. The range in the Caledonian plagioclases is 1500-3000 ppm. and in the potash feldspars 50-2000 ppm.

Sr, therefore, should be enriched in rocks with predominant plagioclase. Such rocks crystallise mainly in the intermediate stages of magmatic history.

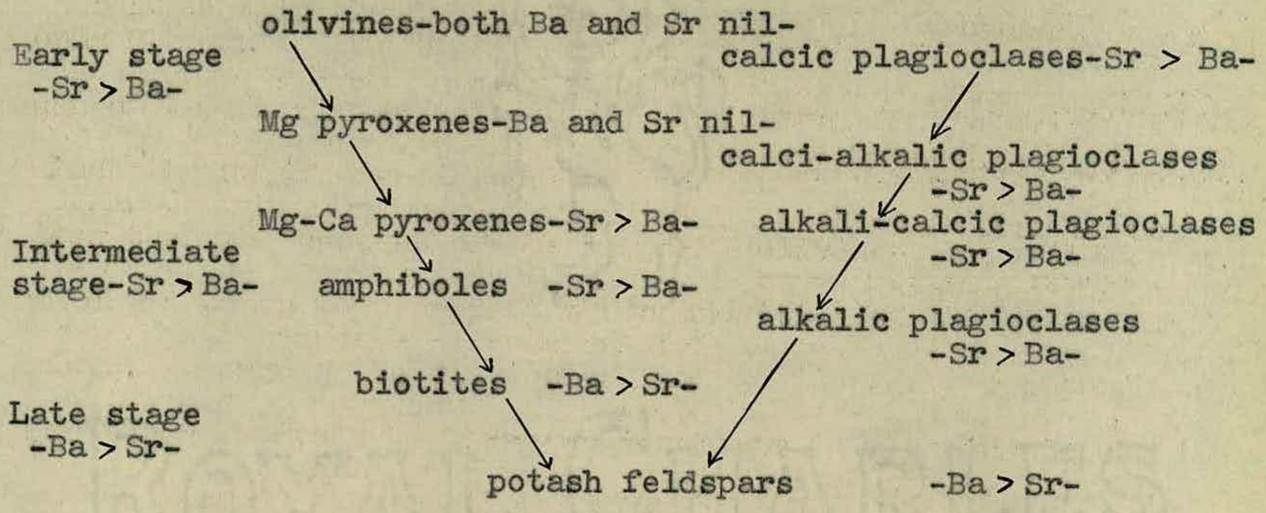
The distribution of Sr in the Braefoot sill indicates that there was impoverishment in both the accumulative and the late stages in comparison to the undifferentiated basalt. The picroteschenite and the microsyenite have 300 and 450 ppm. respectively, whereas the undifferentiated basalt has 900 ppm. The average Sr content in the rocks of the intermediate stage is 864 ppm. approximately the same as the undifferentiated basalt, indicating that the relative enrichment of Sr took place in the intermediate stage. Actually, the Sr content of the picroteschenite is high relative to that of other accumulative rocks; e.g. the gabbro picrite of the Skaergaard intrusion has only /

only 85 ppm. This high amount of Sr in the picroteschenite cannot be attributed to relative enrichment in the original magma, since the undifferentiated Braefoot basalt has 900 ppm., that is, less than the content of the marginal olivine-gabbro (1690 ppm.) which is taken to represent the composition of the Skaergaard magma. Perhaps the plagioclase and zeolites are responsible for the relatively high proportion of Sr in the picroteschenite as has already been mentioned with respect of Ba.

Ba : Sr

The relationship between Ba and Sr seems to be of some significance in distinguishing rocks formed at the different stages of magmatic crystallisation. The known relations between Ba and Sr in the different groups of minerals of the discontinuous and continuous reaction series are indicated below. These relations are based mainly on the Caledonian minerals (Nockolds and Mitchell, 1948), but since the number of the analysed minerals may not be sufficient to justify so definite a statement this scheme should be considered as only tentative until more data are available.

Early /



It appears that the Ba content should be less than that of Sr in the rocks of both early and intermediate stages, since the minerals of the reaction series which prevail in these stages are characterised by such a distribution. On the other hand, rocks of the late stage should have Ba > Sr since they are essentially composed of potash feldspars and biotites.

The distribution in the Braefoot sill, however, shows slight deviation from expectation. The picroteschenite has Ba Sr with Ba:Sr = 2.1. The ultrabasics of Southern Lappland (Sahama, 1945) also show this character with Ba:Sr = 2.0. It may be that the late hydrothermal action had a significant influence in changing the Ba and Sr distribution in the picroteschenite. But, if so, why did these hydrothermal activities change the distribution of Ba and Sr in the picroteschenite and not /

not in the rocks of the intermediate stage, which still have Sr > Ba? Possibly the amount of Sr in the intermediate rocks may have been originally so high that the hydrothermal addition of Ba did not reverse the relation Sr > Ba. The microsyenite (late stage) has 1200 ppm. Ba and 450 ppm. Sr, that is, Ba > Sr as seems to be characteristic of late-stage magmatic rocks.

DISTRIBUTION OF Ga

The most important occurrence of Ga in igneous rocks is known to be replacing Al in silicate structures. Ga feldspars $K\ Ga\ Si_3O_8$ and $Na\ Ga\ Si_3O_8$ where Ga completely replaces Al have been synthesized by Goldsmith (1950). Olivines thus have very negligible amounts of Ga. The ranges of Ga in the augites, hornblendes and biotites of the Caledonian rocks are 6-8, 15-30 and 10-30 ppm. respectively. The Ga content of the Caledonian plagioclases ranges from 20 to 50 ppm. and that of the potash feldspars from 15 to 30 ppm., indicating a slight enrichment in the plagioclases.

On the whole, there seems to be no appreciable difference /

difference in the Ga content of the various aluminous minerals, but because of the relative deficiency in olivine and augite Ga should be relatively impoverished in the early accumulative rocks. In the rocks of the intermediate and late stages of the magmatic crystallisation Ga should be more or less uniform. The felsic rocks of the latest stages should show a slight enrichment in this element.

The picroteschenite of the Braefoot sill has 6 ppm., the lowest among the other types of its rocks. The average content of the rocks of the intermediate stage is 32 ppm., very close to that of the undifferentiated basalt (30 ppm.). The microsyenite has 40 ppm. indicating a slight increase in the Ga content at the late stage of crystallisation.

DISTRIBUTION OF La AND Y

According to Sahama and Vähátälo (1941), the rare earths are present in appreciable amounts in certain accessory minerals of igneous rocks. The most important of these minerals are: xenotime, fluorite, apatite, sphene, orthite and monazite. The /

The occurrence of both apatite and sphene in igneous rocks is known to be ubiquitous. Apatites of the Caledonian rocks contain 200-3000 ppm. La and 600-5000 ppm. Y, while sphenes of the same rocks contain 500-1000 ppm. La and 400-1000 ppm. Y (Nockolds and Mitchell 1948). In entering the apatite and sphene structures Y (ionic radius 1.06 A°) replaces Ca which has a similar ionic radius. Electrostatic neutrality can be maintained by the replacement of P^5 by Si^4 in case of apatite and of Ti^4 by Al^3 in sphene (Wickman, 1943, pp. 387-88).

The distribution of La and Y in common rock forming silicate minerals is not yet thoroughly investigated. It may be surmised that olivines contain undetectable amounts of La and/or Y since Ca is lacking. The Y contents of the pyroxenes, hornblendes and biotites of the Caledonian rocks are $<$ 30-100, $<$ 30-50 and $<$ 30-200 ppm. These data are not sufficient to determine the degree of relative enrichment of this element in these mineral groups. There are three reasons for this: (1) The number of the analysed samples in each of the groups is different. (2) The variation from one sample to another in the same group is rather wide. The Y content in one augite is 100 ppm. and in each of the other two samples is $<$ 30 ppm. There are 8 analysed hornblendes and only three contain 50 ppm. while the /

the others have 30 ppm. Moreover, two of the 13 analysed biotites have 200 and 100? ppm., while the others have < 30 ppm. (3) Minute inclusions of apatite and/or xenotime or monazite, which are significant sources for the rare earths, may be present - especially in the biotites as nuclei of the pleochroic haloes (Hutton, 1947). Nevertheless, if the bulk of La and/or Y is present mainly in the lattices of the ferromagnesian minerals, it may be in the Ca positions. It is probable that La with an ionic radius of 1.22 A° replaces K 1.35 A°. $K\,Fe^3 \longleftrightarrow La^3\,Li$ may be a possible mode of substitution.

The La content of the plagioclases of the Caledonian rocks ranges from <10-100 ppm. According to Wickman (1943) the rare earths cannot enter the feldspar lattice at high temperatures though they have high E-value. He mentions that the entrance of these elements into the feldspar structures depends to a great extent on Be which has a low E-value: accordingly, the rare earths should enter mineral structures formed at relatively lower temperatures. The type of substitution suggested by Wickman (1943), p. 387) in order that Y can enter into the feldspar lattice is $Ca\,Al_2\,Si_2O_8$ - $Y\,(Be\,Al)\,Si_2O_8$. Wickman's suggestion makes it appear that both La and Y should be relatively enriched in the late differentiates but the distribution of these elements given by Rankama and Sahama (1950, pp. 527-8) shows /

shows that Y is enriched in basic rocks, compared with La. Their explanation is that substitution of Ca by Y is easier than by La.

La is present in amounts below its limit of sensitivity (30 ppm.) in all the rocks of the Braefoot sill except the microsyenite (late stage) which contains 75 ppm. The idea of relative enrichment in the early or intermediate stages cannot, therefore, be justified in the case of the Braefoot sill. There is, on the other hand, an obvious enrichment in the late stage. Y is more abundant in the Braefoot rocks than La, the contents being 25 ppm. in the picroteschenite, 50 ppm. in the undifferentiated basalt, 56 ppm. in the average of the rocks of the intermediate stage and 200 ppm. in the microsyenite. These figures indicate (1) that there was a relative impoverishment in Y in the early accumulative stage; (2) that Y is very slightly enriched in the intermediate stage; and (3) that there was a notable enrichment in the late stage; the Y content of the microsyenite is four times as high as that of the undifferentiated basalt.

Be as mentioned elsewhere (p. 51) is also enriched in the late stage, in agreement with Wickman's suggestion concerning the type of substitution for Y to enter into the feldspar lattice.

DISTRIBUTION OF Zr

Zircon is a ubiquitous accessory in igneous rocks and is likely to be the main source of Zr in such rocks. The Zr contents of the pyroxenes, hornblendes and biotites of the Caledonian rocks reported by Nockolds and Mitchell (1948) range from 10-100 ppm. There is reason to believe that the presence of Zr in these species may be due to the presence of minute inclusions of zircon. According to Rankama and Sahama (1950, p. 564) the coordination of Zr (ionic radius 0.87 A°) should be near the border-line between 6- and 8-. Assuming that Zr is actually present in the crystal structures of the ferromagnesian minerals, it may replace Mg and/or Fe^2, both of which have 6-coordination and ionic radii fairly close to that of Zr. Electrostatic neutrality must, of course, be maintained by means of other suitable substitutions in the structures. The feldspars may contain small amounts of Zr which may be due to zircon inclusions or to substitution of Na (0.98 A°) in the structure.

There is no statistical information about the frequency of zircon in the different types of igneous rocks, but it is well known that zircon is more abundant in acidic than in ultrabasic or basic rocks. Zr should therefore be relatively enriched in the rocks of the late stage and data recorded by Rankama and Sahama (1950, p. 566) conforms with expectation:

Rock /

Rock	Zr (g/ton)
Peridotites, eclogites, dunites	60
Gabbros	140
Diorites	280
Granites	460

The distribution of Zr in the Braefoot sill (Tables I and II) shows that (1) there was slight impoverishment in the early accumulative stage, (2) little variation during the intermediate stage and (3) marked relative enrichment in the late stage.

DISTRIBUTION OF Sc

Sc has an ionic radius of 0.83 Å close to that of Fe^2 0.83 Å and Mg 0.78 Å. It can replace both elements in the ferromagnesian structures provided that other replacements take place in order to maintain electrostatic neutrality. The feldspars should have negligible amounts of this element, if any, since they lack Mg and/or Fe^2 and the inter-replacement between Sc and Al is likely to be weak.

According to the general distribution in igneous rocks recorded by Rankama and Sahama (1950, p. 516), Sc seems to be enriched in basic rocks and especially in pyroxenites. The distribution of Sc in the Braefoot sill indicates that it is relatively /

relatively enriched in the early accumulative stage. Actually, the upper ocellar basalt contains the highest Sc concentration amongst the Braefoot rocks (20 ppm.) but the average of all the rocks of the intermediate stage is only 3 ppm. The late stage is impoverished in this element since the content of the microsyenite is below the limit of sensitivity.

DISTRIBUTION OF Cu

Cu is far more common in sulphide minerals than in silicates. Examination of the textural features and the study of polished specimens of the fayalite ferro-gabbro of the Skaergaard intrusion led Wager and Mitchell (1950, p. 147) to the belief that, at an early stage of the magmatic history, an immiscible liquid sulphide phase formed as droplets in the silicate melt and that the available Cu was largely concentrated in the sulphide liquid. This suggestion seems to be sound, but it does not rule out the possibility that separation by immiscibility could take place during each of the successive stages of magmatic crystallisation -- earlier as well as later -- irrespective of the different temperatures concerned. This possibility appears to be borne out by the actual data for earlier and later rocks recorded in the paper referred to above. In particular there is a tendency for Cu to be relatively enriched in the rocks of the intermediate stage of the Skaergaard intrusion.

The /

The data given by Sandell and Goldich (1943, p. 175) shows that Cu occurs in largest amounts in basic rocks. Silicic rocks (average SiO_2, 72 per cent) have an average Cu content of 16 ppm., intermediate rocks (average SiO_2, 62 per cent) contain 38 ppm. and subsilicic rocks (average SiO_2, 48.5 per cent) 149 ppm. There is also a tendency for Cu to be relatively enriched in the rocks of the intermediate stage of the Skaergaard intrusion (Wager and Mitchell, 1950, p. 144). The ionic radius of Cu^2 is 0.83 A^o, very close to the radii of Fe^2 (0.83 A^o) and Mg (0.78 A^o). The relatively small proportions of Cu which enter into the silicate structures occur essentially in the ferromagnesian minerals, since Cu can replace both Fe^2 and Mg.

In the Braefoot sill (Table II) Cu is found to be more abundant in the rocks of the intermediate stage than in either the early or late stage. This distribution is very similar to that of V.

DISTRIBUTION OF Pb

The Pb sulphide, galena, does not commonly occur in igneous /

igneous rocks. Substitution if K by Pb can be considered as the most pronounced replacement of Pb in silicate structures, since the ionic radii are very nearly the same (Pb^2, 1.32 A° and K, 1.33 A°). Consequently, biotites and potash feldspars, which are usually abundant constituents of the late stage rocks, should be richer in this element than any of the other groups of minerals.

The low and uncertain contents of Pb in most of the rocks of the Braefoot sill justify no more than the statement that the distribution appears to be fairly uniform in the three main stages.

DISTRIBUTION OF Ag

Information about the distribution of Ag in minerals and rocks is exceedingly scarce. Ag seems to be more concentrated in the sulphide minerals than silicates. According to Rankama and Sahama (1950, p. 703) Ag readily becomes enriched in the sulphides that separate during the early stages of magmatic differentiation.

The content of Ag is highest in the early stage Braefoot /

Braefoot rocks. The exact manner of the relatively high amount of Ag in the picroteschenite (10 ppm.) cannot be established. The ionic radius of Ag (1.13 Å) is far too big for Ag to substitute for either Fe^2 or Mg but is fairly close to that of K. However, it may be surmised that Ag cannot be mainly present in the lattices of the picroteschenite feldspars which are principally plagioclases poor in K. Moreover, the microsyenite shows relative impoverishment in Ag. It is more appropriate to suppose that Ag is mainly present in combination with S in very minute granules of sulphide minerals. The contents of S calculated from the chemical analyses of the Braefoot rocks are recorded in Table II. The picroteschenite has higher S than either the average of the rocks of the intermediate stage or the microsyenite, but while Ag corresponds in this general way there is no close correlation between S and Ag amongst the individual rocks.

DISTRIBUTION OF Mo

The distribution of Mo in the silicate minerals is not well known. Affinity to S seems to be pronounced since the most /

most important occurrence of this element is in the sulphide form. Actually, however, the distribution of Mo in the rocks of the Braefoot sill is quite different from that of Ag. Mo is relatively enriched in both the early accumulative and the late stages compared to the undifferentiated basalt and the intermediate stages. The picroteschenite contains 3 ppm. and the microsyenite has 4 ppm. whereas the undifferentiated basalt contains 1 ppm. and the average of the rocks of the intermediate stage is only 0.3 ppm.

DISTRIBUTION OF Sn, Tl, Ge, In and Be

Sn, Tl, Ge and In, if present in the rocks of the Braefoot sill, occur in amounts below their limits of sensitivity and, therefore, their exact behaviour during the progress of differentiation cannot be discussed. It need only be mentioned that these elements are very scarce in igneous rocks in comparison with all the others so far discussed.

The content of Be is also below its limit of sensitivity except in the late stage. The microsyenite has < 5 ppm. Be. If this has any significance it implies relative enrichment of Be towards the end of the differentiation; such is generally /

generally considered to be the case.

TRENDS OF THE RATIOS OF THE VARIOUS ELEMENTS DURING THE PROGRESS OF DIFFERENTIATION

So far, we have mainly discussed the concentration of each of the different investigated elements during the progress of the differentiation of the Braefoot magma. The behaviour of most of the elements is in good agreement with the recent findings of Wager and Mitchell (1951) concerning the fractionation of the Skaergaard magma. It is also important to understand the relationship between the different elements in this process. Certain ratios in the three stages of the differentiation of the Braefoot magma are calculated and recorded in Table III. The graphical representations of these ratios are illustrated in Figs. 3-6. The total $Mg+Fe^2+Fe^3$ of each of the three stages which is taken as the abscissa in each of the figures decreases gradually from the early to the late stage.

Figs. 3-6 show that there are certain ratios which attain their highest values in each of the different stages.

Fig. 3 shows ratios which are greatest in the early accumulative stage: Cr/Co, $(Mg+Fe^2+Fe^3)/(Na+K+Ca)$, $(Cr+Co+Ni+V+Cu)/(Rb+Ba+Sr)$, Cr/Fe^3 and Co/Fe^3.

Fig. 4 shows ratios which are highest in the undifferentiated basalt: Co/Fe^2, Ba/K, Cr/Mg, Sr/(K+Ca), Sr/K and Ni/Mg.

Fig. 5 shows ratios which attain their maximum values in the intermediate stage: V/Fe^2, Cr/Ni, V/Fe^3, Fe^2/Mg, (Co+V)/(Cr+Ni) and Co/Ni.

Fig. 6 shows ratios which are highest in the late stage: Ba/Ca, Ba/(Ca+K), $(Fe^3+Fe^2)/Mg$, Sr/Ca, Rb/K, Rb/Ba, Li/Mg and Ga/Al. Ratios which behave similarly but not represented in Fig. 6 are: Li/Ni, Li/Cr, Ba/Sr, Fe^3/Fe^2, Rb/Sr and $(FeO+Fe_2O_3)/(MgO+FeO+Fe_2O_3)$.

There are a few points of interest which can be considered in the light of the general behaviour of these ratios.

(1) The ratio of the major elements $(Mg+Fe^2+Fe^3)/(Na+K+Ca)$ and that of their corresponding interchangeable trace elements (Cr+Ni+Co+V+Cu)/(Rb+Ba+Sr) behave similarly. They both attain their highest values in the early accumulative stage and decrease during the progress of the differentiation. Mg and Fe are common constituents of the ferromagnesian minerals whereas Na, K and Ca are much more abundant in the feldspars. It is usually the /

the case that the ratio ferromagnesian minerals/felsic minerals decrease as the magmatic crystallisation proceeds. Consequently the ratio of the trace elements which most commonly enter into the ferromagnesian mineral lattices to those which are generally present in the feldspar structures also decreases during the course of normal differentiation.

(2) The ratio Fe^2/Mg is highest in the intermediate stage. This confirms Wickman's view (1943) that the E-value for Fe^2 is less than that of Mg and, therefore, that the latter should be enriched in the earlier differentiates relative to the former. Moreover, it is known that Fe^2 is enriched in the later ferromagnesian-bearing rocks. It is interesting to find that the ratio (Co+V)/(Cr+Ni) in the rocks of the Braefoot sill behaves in essentially the same manner as the ratio Fe^2/Mg indicating that both V and Co are more related to Fe^2 than to Mg in their distribution during the fractionation of the magma.

(3) The ionic radii of Li, Ni and Mg are the same, 0.78 A°, but Li/Mg is highest in the late stage whereas Ni/Mg attains its greatest value in earlier rocks. This feature may be explained by the relationship between their E-values given by Wickman (1943, p. 385). He assumes that the E-value for Ni is higher than that for Li, and therefore, that Li should be concentrated /

concentrated in the later rocks, as compared to Ni, if both elements replace Mg in the different crystal structures. It has also been pointed out by Strock (1936) that Li_2O/MgO increases at the latest stages of magmatic differentiation. In the rocks of Central Roslagen, Sweden (Lundegardh, 1946, p. 112) Li/Mg shows a definite increase with progress of fractionation similar to that found in the Braefoot sill. It can be emphasised that Li/Mg provides a good index of the stage of differentiation reached by a given rock as first suggested by Strock (1936).

Ni/Mg, however, does not behave so uniformly in different differentiation suites and cannot be of the same significance as Li/Mg.

(4) Rb shows a definite increase during the progress of differentiation with respect to K, Ba and Sr, since the ratios Rb/K, Rb/Ba and Rb/Sr are highest in the late stage. This feature can be explained by Goldschmidt's rules (1934) according to which the element with bigger ionic radius is relatively enriched in the latest differentiates compared with its other interchangeable elements. These ratios seem to be indicative of the stage of differentiation attained.

(5) Sr/Ca and Ba/Ca are both highest in the late stage. This /

This is what would be expected, since the ionic radius of both Sr and Ba is bigger than that of Ca. But Sr/K and Ba/K is highest in earlier rocks. The behaviour of Sr/K is understandable because Sr has a small ionic radius than K but the ionic radius of Ba is bigger than that of K and accordingly Ba/K should be higher in the later rocks. This discrepancy may be due to the hydrothermal activity which took place at the end of the magmatic history. But the absence of the effect of these activities on Ba/Ca, Sr/Ca or Sr/K makes this explanation rather doubtful. Ba/(K+Ca) however, is highest in the late stage whereas Sr/(K+Ca) attains its maximum value in earlier rocks. Ba appears to be enriched with respect to the total of K and Ca at relatively lower temperatures. Sr on the other hand, seems to be concentrated with respect to the same total in rocks formed at relatively higher temperatures. This accords with the finding (p. 39) that Ba/Sr is highest in the late stage.

(6) Certain other ratios call for brief mention.

(a) Li/Ni and Li/Cr attain their greatest values at the late stage, indicating enrichment of Li with respect to both Ni and Cr at relatively low temperature.

(b) /

(b) Ga/Al increases during the progress of differentiation. This is in harmony with Goldschmidt's rules, since Ga has a bigger ionic radius than Al.

(c) The individual ratios of Cr, Ni and Co to Mg and Fe show relative increase in the earlier rocks, while those of V to Fe^2 and Fe^3 are highest in the intermediate stage.

CONCLUSIONS

The trace element contents of the differentiated rocks of the Braefoot sill indicate that certain elements concentrate at particular stages of magmatic crystallisation. The closest approach to the original magma of this sill is considered to be represented in composition by olivine-basalt outcropping at the lower levels of the sill. The stages of crystallisation are classified into early (accumulative), intermediate and late on the basis of the ratio $(FeO+Fe_2O_3)/(MgO+FeO+Fe_2O_3)$, which increases from early to late. The distribution of the trace elements is found to depend mainly on the amount and type of the minerals of the discontinuous and continuous reaction series predominating in the rock. Cr and Ni concentrate in the early accumulative /

accumulative types, rich in olivines and/or pyroxenes. Co, V, Cu and Sr are relatively enriched in the rocks of the intermediate stage rich in pyroxenes, amphiboles and calc-alkalic plagioclases. Li, Rb, Ba, Ga, La, Y and Be concentrate in the rocks of the late stage of magmatic crystallisation rich in biotites and potash feldspars.

The early and intermediate stages are characterised by having the inter-relationship $Cr > Ni > Co$ and $Sr > Ba$ whereas the late stage has $Ni > Co > Cr$ and $Ba > Sr$. The relative proportions of (Cr+Ni+Li) : (Co+V) : (Rb+Ba) in the different stages show a trend similar to that of $MgO:FeO:(Na_2O+K_2O)$.

There are certain ratios which attain their highest values at particular stages. The most important of these are $(Mg+Fe^2+Fe^3)/(Na+K+Ca)$ and (Cr+Co+Ni+V+Cu)/(Rb+Ba+Sr) in the early stage; Fe^2/Mg and (V+Co)/(Cr+Ni) in the intermediate stage and $(FeO+Fe_2O_3)/(MgO+FeO+Fe_2O_3)$, Li/Mg, Rb/Ba, Rb/K and Ga/Al in the late stage.

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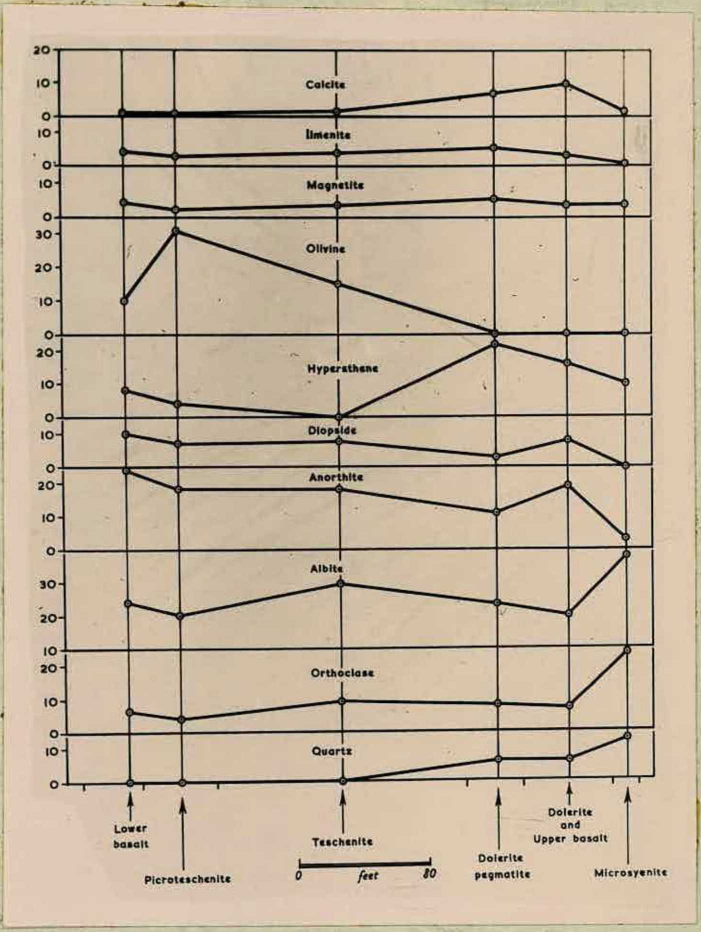

Fig. 1

Normative composition of the rocks of the Braefoot sill. Abscissa represents depth of rocks from the surface taken from the diagrammatic vertical section of the sill north of the Braefoot Bay fault (Campbell et al, 1933, Fig. 2, p. 345).

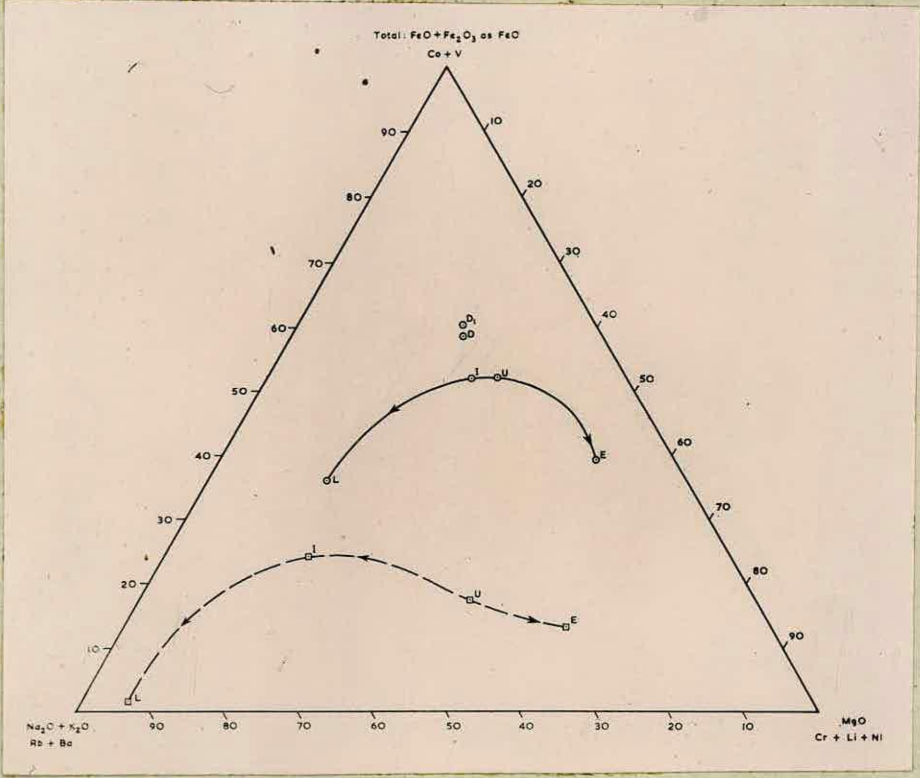

Fig. 2

Trend of major oxides and trace elements during the different stages of crystallisation of the Braefoot sill. Full line = trend of major oxides and dotted line = trend of trace elements. E = early accumulative stage, U = undifferentiated basalt, I = intermediate stage and L = late stage. D = chlorophaeite dolerite pegmatite and D$_1$ = chloritised dolerite pegmatite.

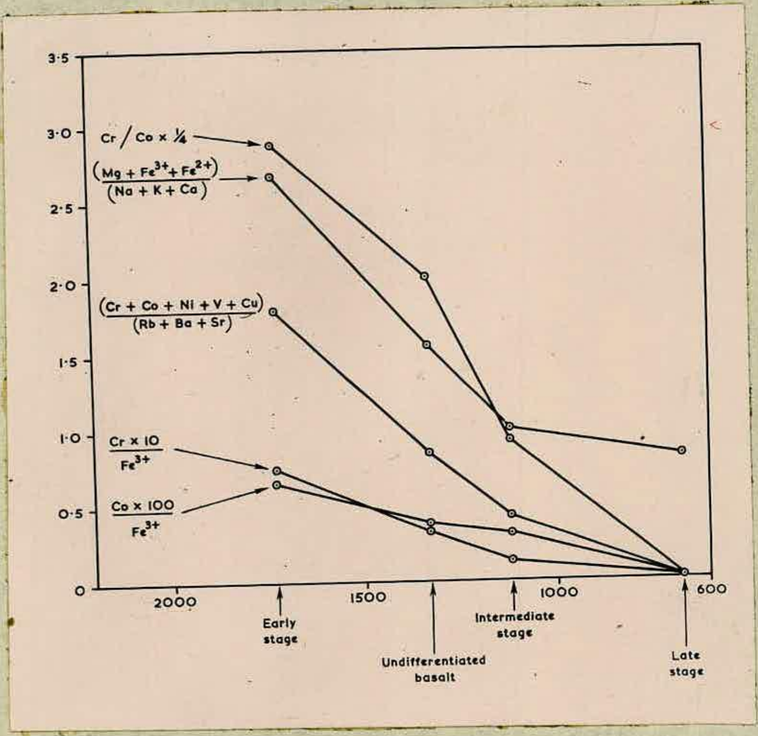

Fig. 3

Trend in ratios attaining their maxima in the early stage of crystallisation of the Braefoot magma. Abscissa represents total Mg + Fe^2 + Fe^3 in parts per ten thousand in the three main stages of crystallisation.

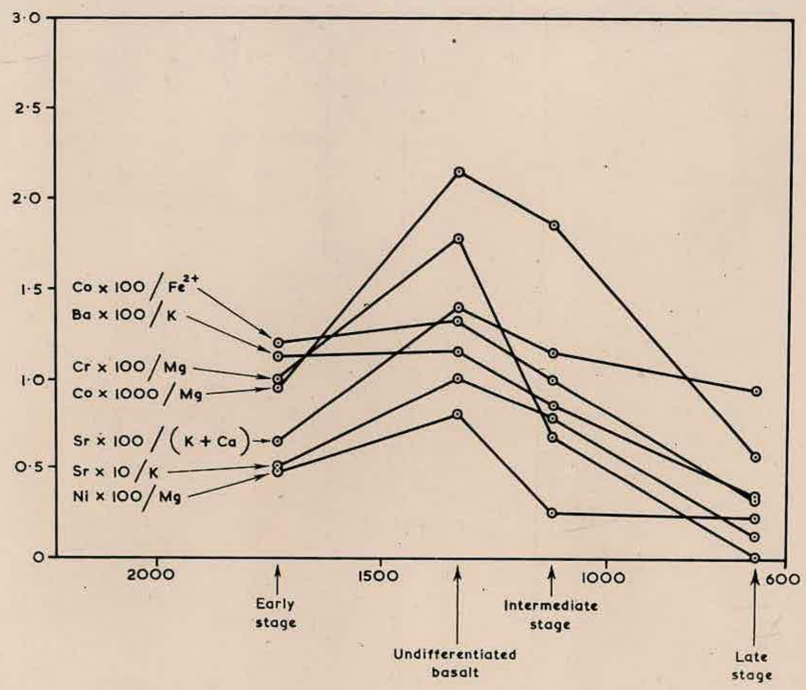

Fig. 4

Trend in ratios attaining their maxima in the undifferentiated basalt of the Braefoot sill. Abscissa is the same as in Fig. 3.

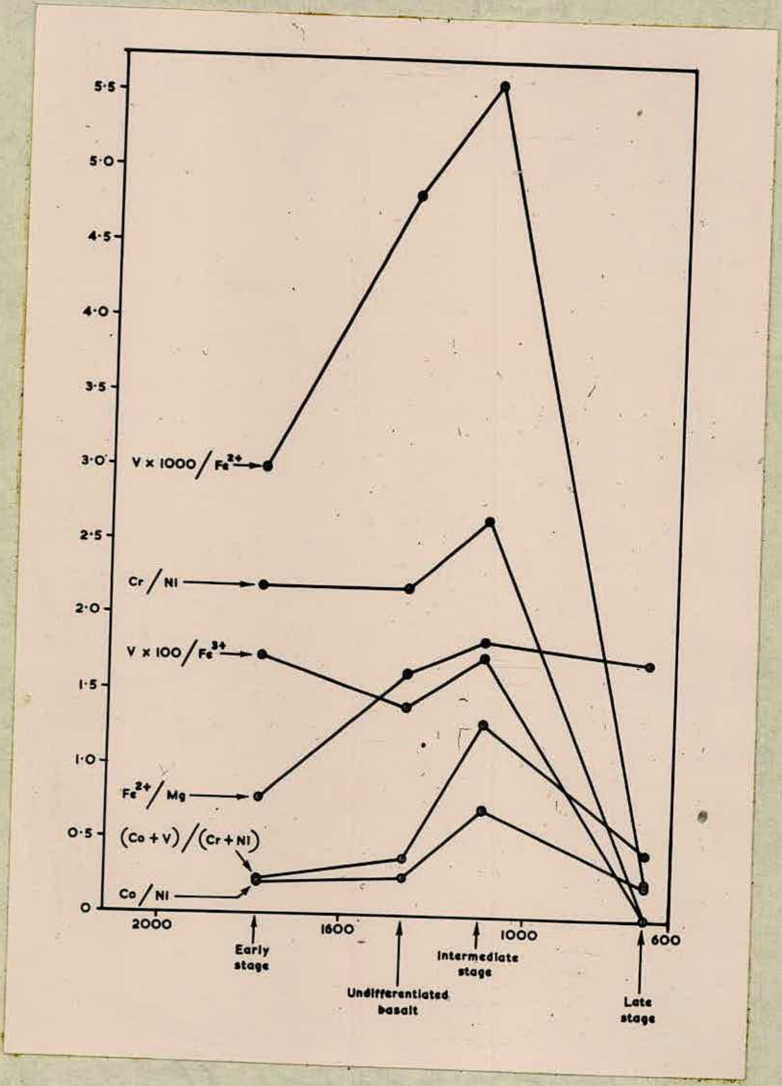

Fig. 5

Trend in ratios attaining their maxima in the intermediate stage of crystallisation of the Braefoot magma. Abscissa is the same as in Fig. 3.

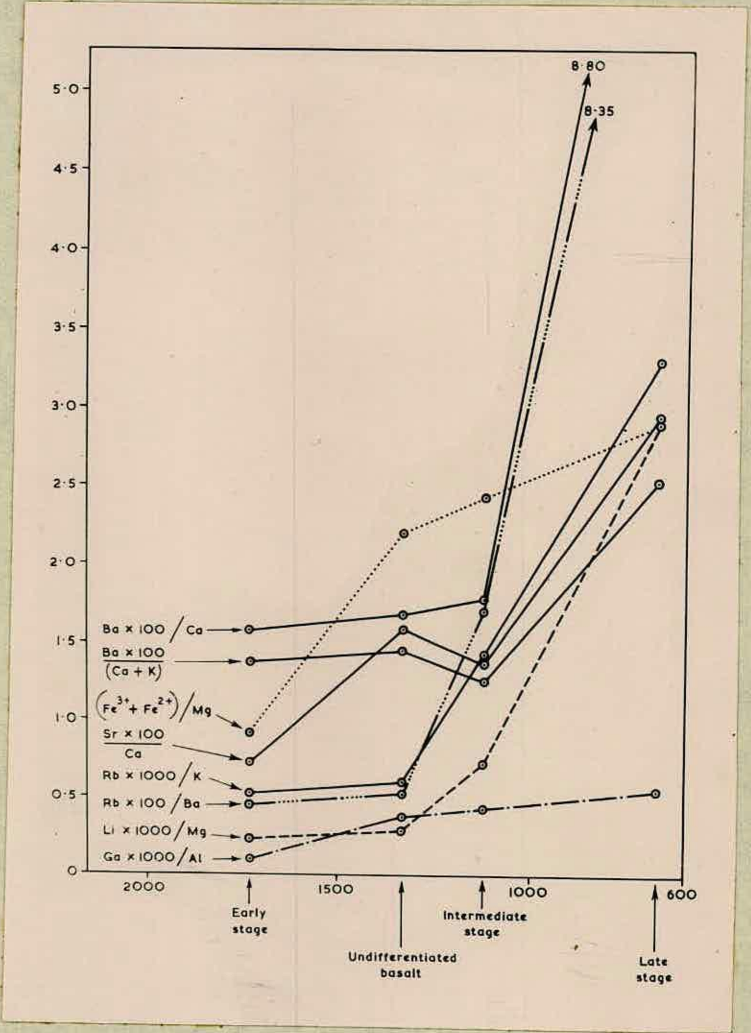

Fig. 6

Trend in ratios attaining their maxima in the late stage of crystallisation of the Braefoot magma. Abscissa is the same as in Fig. 3. Other ratios behaving essentially the same but not shown graphically are : Li/Ni, Li/Cr, Fe^3/Fe^2, Rb/Sr and (FeO + Fe_2O_3)/(MgO + FeO + Fe_2O_3).

TABLE II

Trace element content in the different stages of crystallisation of the Braefoot magma.

Element	Early	Undifferentiated basalt	Intermediate	Late
Rb	3	5	16	100
Li	20	12	24	50
Ba	650	950	936	1200
Sr	300	900	864	450
Cr	950	750	224	*
Co	85	90	61	10
Ni	430	340	84	40
Zr	220	290	230	1100
La	*	*	*	75
Y	25	50	56	200
Cu	25	40	53	10
V	220	330	340	8
Ga	6	30	32	40
Tl	*	*	*	*
Sn	*	*	*	*
Pb	<10	<10	<12	10
Sc	10	<10	3	*
Mo	3	1	0.3	4
Ge	*	*	*	*
Be	*	*	*	5
Ag	10	1	2.5	2
In	*	*	*	*
*S	2770	960	2297	1170

* Analysed for chemically

TABLE III

Ratios of the various elements in the different stages of crystallisation

	Early	Undifferentiated basalt	Intermediate	Late
$100(FeO+Fe_2O_3)/(MgO+FeO+Fe_2O_3)$	42.00	53.50	65.50	70.50
Fe^3/Fe^2	0.18	0.35	0.32	0.66
$(Fe^3+Fe^2)/Mg$	0.92	2.20	2.44	2.90
1000 Ga/Al	0.10	0.38	0.42	0.55
1000 Li/Mg	0;22	0.29	0.73	2.90
1000 Rb/K	0.52	0.60	1.43	2.94
1000 Rb/Ba	0.46	0.53	1.71	8.35
1000 Rb/Sr	1.00	0.56	1.85	22.20
Ba/Ca	1.57	1.68	1.77	8.80
100 Ba/(Ca+K)	1.37	1.46	1.25	2.52
100 Sr/Ca	0.72	1.59	1.35	3.31
Ba/Sr	2.16	1.05	1.08	2.66
Li/Ni	0.05	0.04	0.29	1.25
Li/Cr	0.02	0.02	0.11	>25.
Fe^2/Mg	0.78	1.63	1.85	1.75
(Co+V)/(Cr+Ni)	0.22	0.38	1.30	0.45
$100\ V/Fe^3$	1.72	1.40	1.74	0.04
$100\ V/Fe^2$	3.14	4.85	5.61	0.26
Co/Ni	0.20	0.26	0.72	0.25
Cr/Ni	2.20	2.20	2.67	*
100 Ni/Mg	0.48	0.81	0.25	0.23
100 Cr/Mg	1.06	1.78	0.68	*
1000 Co/Mg	0.95	2.15	1.87	0.58
$1000\ Co/Fe^2$	1.21	1.32	1.01	0.33
10 Ba/K	1.12	1.14	0.84	0.35
10 Sr/K	0.52	1.08	0.77	0.13
100 Sr/(Ca+K)	0.64	1.39	1.15	0.95
$(Mg+Fe^3+Fe^2)/(Na+K+Ca)$	2.68	1.54	1.14	0.82
(Cr+Co+Ni+V+Cu)/(Rb+Ba+Sr)	1.80	0.84	0.42	0.04
$\frac{1}{4}$ (Cr/Co)	2.87	2.08	0.92	*
$10\ Cr/Fe^3$	0.74	0.32	0.12	*
$100\ Co/Fe^3$	0.66	0.38	0.31	0.05

PART III

A GEOCHEMICAL STUDY OF THE REGIONAL METAMORPHIC ZONES OF THE SCOTTISH HIGHLANDS

To be presented at the International Geological Congress
XIX Session, Algiers, September 5-12, 1952.

ABSTRACT

A representative rock of each of the regional metamorphic zones of the Scottish Highlands has been chemically analysed and its trace elements determined spectrographically, using semi-quantitative methods, in order to elucidate the geochemical changes which take place during the development of the rocks of the different zones. The grades of regional metamorphism are conveniently divided into low, medium and high, comprising rocks of the chlorite zone (green schist facies), the biotite and garnet zones (epidote-amphibolite facies) and the staurolite and sillimanite zones (amphibolite facies) respectively. It is found that the ratios $(FeO+Fe_2O_3)/(MgO+FeO+Fe_2O_3)$ and K_2O/Al_2O_3 do not substantially differ in the three grades. Fe^3/Fe^2 and Fe_2O_3/MgO show a regular increase from low to high. The geochemical changes involved during the development of the rocks of the different grades seem to have been (a) decrease in Al and K, and a slight increase in the total of Mg, Fe^2 and Fe^3 in the low grade; (b) decrease in Al, Ca and $(Mg+Fe^2+Fe^3)$, and increase in K in the medium grade; and (c) very slight decrease in K, and increase in Al, Ca and $(Mg+Fe^2+Fe^3)$ in the high grade. K, therefore, behaves differently from Mg, Fe^2 and Fe^3 in all these changes.

The trace elements behave like the major elements which have approximately the same ionic radii. Ga follows Al; Ti, Mn, Li, Cr, Ni, Co and V follow Mg, Fe^2 and Fe^3; Sr, Y and La follow Ca; and Rb, Ba and Pb follow K. The distribution $Cr > Ni > Co$ and $Ba > Sr$ is similar in each of the three grades of regional metamorphism.

INTRODUCTION /

INTRODUCTION

In the study of progressive regional metamorphism in the Scottish Highlands the following successive zones have been recognised: chlorite, biotite, garnet, staurolite and sillimanite zones.

The P T conditions under which the rocks of these different zones recrystallised are considered to correspond to: (a) the green schist facies in the case of the chlorite and biotite zones; (b) the epidote-amphibolite facies in the case of the garnet and staurolite zones; and (c) the amphibolite facies in the case of the sillimanite zone.

Very little is known about the geochemistry of these zones, and the manner of the development of their index minerals is not fully understood. This paper deals mainly with the behaviour of the trace elements and their relation to the major elements in the different zones.

ANALYTICAL METHODS AND DATA OBTAINED

A representative rock of each of the chlorite, biotite, garnet, staurolite and sillimanite zones was selected by Dr R. Campbell /

Campbell and the writer after a careful petrographical examination of at least thirty rocks of each of these zones. The rocks were chemically analysed by Mr W.H. Herdsman. Their trace elements were determined spectrographically by the writer at the Macaulay Institute for Soil Research at Aberdeen, Scotland, using portions of the powders prepared for the chemical analysis.

The semi-quantitative method adopted in this study has been described in detail by Mitchell (1948). The error in this method is stated to be of the order of ± 25-30 per cent over the range of approximately 10 to 300 ppm. If the element is over 1000 ppm. errors of ± 50 per cent are said to be possible. The spectrographic determinations were carried out in duplicate and the diagnostic lines of the different trace elements were compared with the standard plate on the Judd Lewis comparator on two different occasions with very close correspondence. It is believed, therefore, that the actual errors are far less than ± 25-50 per cent; more probably they are about ± 10-25 per cent.

The chemical and spectrographic composition of the rocks investigated are given in Table I. The trace element contents in ppm. are given in Table II. Their modal compositions are given in Table III.

DISTRIBUTION OF THE ELEMENTS

Silicon

It is known that the ratio of psamitic to pelitic material in the original country rock commonly varies between wide limits. The SiO_2 content of the psammo-pelitic schists depends mainly on the amount of the detrital quartz and the other silica particles present in the original rock.

The reactions responsible for the production of the index minerals of the different zones are not exactly known. It may be that all the mineral constituents play some part in this respect. Quartz, however, is commonly found in the psammo-pelites in surplus and it appears that only a very small proportion of the amount present of this mineral is needed to complete the reactions. Moreover, quartz seems to carry only negligible amounts of the trace elements compared to the other silicate minerals. The relative abundance of quartz would be, therefore, of little significance in the distribution of the trace elements of the psammo-pelitic schists, affecting their abundances but not their relative proportions.

The SiO_2 percentage in the analysed rocks ranges between 50.63 and 68.05. Its average in these rocks is 57.05, close to the SiO_2 of the average shale (58.10) quoted by Pettijohn (1949).

There /

There seems to be no regular relationship between the content of silicon of the analysed rocks and the other major elements, namely, Fe^2, Fe^3, Mg, Ca, K and Na. The trace elements resemble the major elements in this respect. They, too, show no regular relationship with Si. The Rb_2O contents, for instance, of the biotite-schist and the biotite-sillimanite-gneiss are 0.05 and 0.033 per cent respectively. The SiO_2 percentages of these rocks do not differ very much, they are 53.05 in the former and 53.02 in the latter. Moreover, the SiO_2 contents of the chlorite- and the garnet-biotite-schist vary rather widely, being 60.52 and 68.05 per cent respectively. On the other hand their Rb_2O contents are the same (0.011 per cent). Nockolds and Mitchell (1948, p. 542) mention similar findings for the schists surrounding the Garabal Hill-Glen Fyne Complex.

Other major elements

The most important constituents in the psammo-pelitic metamorphis rocks under consideration are Al_2O_3, Fe_2O_3, FeO, MgO and K_2O. They are fundamental constituents of the different index minerals of the various metamorphic zones. CaO and Na_2O, however, are of less significance than these oxides. This is because (1) Ca and Na are not as important as Al, Fe, Mg and K in the composition of chlorite, biotite, almandine garnet, staurolite /

staurolite and sillimanite, and (2) the plagioclases and/or epidotes, in which Ca and Na are present in significant proportions, occur, when present, in the studied rocks only in minute amounts.

The relative proportions of Al_2O_3; FeO, MgO and Fe_2O_3 and K_2O are best represented graphically by the AKF triangular diagram introduced by Eskola (1915, p. 128). It is known that according to the facies classification of metamorphic rocks, the mineral assemblages in equilibrium vary with the grade of metamorphism. When plotted on the AKF diagram corresponding to the green-schist facies, the compositions of both the chlorite- and the biotite-schists are found to lie in the part of the diagram indicating the assemblage chloritoid-biotite-muscovite-quartz. It should be noticed that the position of chloritoid on the AF side of the triangle can be considered as equivalent to that of an aluminous species of chlorite; consequently, the mineral assemblage in these rocks can be regarded as chlorite-biotite-muscovite-quartz, which agrees to a great extent with their mineral composition. It is of interest to find that the small amount of biotite present in the chlorite-schist is greenish in colour with X = dark yellow, Y = Z = deep green, while the biotite of the biotite-schist is brownish with X = yellow, Y = Z = dark brown, and that of the sillimanite gneiss reddish /

reddish brown with X = pale yellow, Y = Z = reddish brown, confirming what has been observed by Tilley (1926, p. 40). The plot of the composition of the metamorphic schist of the garnet zone on the AKF diagram of the epidote-amphibolite facies corresponds to the assemblage chloritoid (chlorite)-almandine-muscovite-quartz. The plots of the compositions of the representative rocks of the staurolite and sillimanite zones on the AKF diagram of the amphibolite-facies indicate the assemblages: staurolite-muscovite-kyanite-quartz and staurolite-muscovite-almandine-quartz respectively. It is thought to be more convenient in our discussion to consider the representative rocks of the different zones as indicative of three grades of regional metamorphism. (1) The low grade is represented by the schist of the chlorite zone. (2) The medium grade is represented by the average of the rocks of the biotite and the garnet zones. This average, given in Table I, when plotted on the AKF diagram of the epidote-amphibolite facies, lies in the field showing the assemblage chloritoid (chlorite)-almandine-muscovite-quartz. (3) The high grade is represented by the average of the rocks of the staurolite and silimanite zones. This average, when plotted on the AKF diagram of the amphibolite facies, lies in the field showing the assemblage staurolite-muscovite-kyanite-quartz.

Al and Ga

In the rocks investigated Al_2O_3 varies from 15.69 to 28.86 per cent, the average being 21.42 per cent. This is higher than the average Al_2O_3 content of shales (15.40) cited by Pettijohn (1949, p. 271). The averages in the different grades of metamorphism are 17.45 in the low grade (chlorite-schist), 18.72 in the medium grade (average of the rocks of the biotite and garnet zones) and 26.11 in the high grade (average of the rocks of the staurolite and the sillimanite zones). The average Al_2O_3 content of five metamorphic rocks of Duchess County, New York (phyllites, a garnetiferous schist and a mica-schist) studied by Barth (1936, p. 802) is 18.14 per cent, approximating to the averages of both the low and medium grades of the Scottish Highlands but considerably lower than the average of the corresponding high grade.

It seems that the Al_2O_3 content in the high grade metamorphic rocks is relatively higher than that of rocks of both the low and medium grades. Staurolite, kyanite and sillimanite are species generally stable in the relatively high grade metamorphism and their Al_2O_3 contents are higher than those species indicative of low and medium grades of metamorphism, that is, chlorite, biotite and almandine garnet.

It is interesting to notice that the total of SiO_2 and Al_2O_3 /

Al_2O_3 does not vary much in the grades of metamorphism. It is 77.97, 79.27 and 77.93 in the low, medium and high grades respectively. Moreover, the average of the total of these two major oxides in the slates of the Duchess County, New York is 80.12 (Barth, 1936, p. 799). This average is very close to that of the phyllites, garnetiferous and mica-schists of the same locality (79.31). Also, the total of these two oxides in the quartz-muscovite-chlorite phyllite of the Stavanger region, Norway, is 78.32 (Goldschmidt, 1920, p. 110). The average of the total in the other metamorphic schists of this region which carry biotite and/or garnet is 79.41. This may indicate that the different reactions which take place in the various grades of metamorphism in order to produce their respective index minerals do not materially change the total of SiO_2 and Al_2O_3.

Ga is most commonly found substituting for Al in the crystal lattices of the different minerals. It is of significance that the relative decrease or increase of Al in the rocks of the different zones is accompanied by similar behaviour of Ga. The high grade metamorphic rocks contain the highest Al content and are also the richest in Ga (Fig. 1).

Fe^2, Fe^3 and Mg-- Cr, Co, Ni, V, Cu and Li.

The total of FeO, Fe_2O_3 and MgO of the rocks of the various /

various zones ranges from 8.87 to 11.10 per cent. Perhaps this difference is mainly to be attributed to the varying amounts of iron-ores present in these rocks. However, the variation in this total is only from 9.99 to 10.51 per cent in the different grades of metamorphism. The low grade metamorphic rock (chlorite-schist) is slightly richer in these oxides (10.48) than the medium grade metamorphic rocks (9.99), and is not appreciably different from that of the high grade metamorphic rocks (10.51).

The ratio FeO/Fe_2O_3 varies rather considerably in the rocks of the different zones as well as in the various grades of metamorphism. It reaches its highest value (14.5) in the low grade and its lowest value (2.1) in the high grade, the value in the medium grade being 3.5.

Average shale (Pettijohn, 1949, p. 271) has more Fe_2O_3 than FeO and therefore the ratio FeO/Fe_2O_3 is less than unity (0.3). In this respect the high grade metamorphic rocks are intermediate between average shale and low grade metamorphic rocks.

The distribution of both Co and V is almost uniform in the different grades of metamorphism. Li, Cr and Ni, however, show more marked variation. Li is richest in the medium grade metamorphism. The Li contents of the low and high grades do not /

not differ significantly, being 100 and 115 ppm. respectively. The high Li content of the medium grade metamorphism can perhaps be correlated with the relative richness in biotite produced under the P T conditions prevailing in this grade. However, there is an appreciable amount of Li in the staurolite-schist (120 ppm.) which contains 40 per cent of staurolite, 20 per cent muscovite, and only 5 per cent of biotite. Here it is more likely that most of the Li content occurs in staurolite where it would substitute for Fe^3 in the structure. Muscovite does not usually contain Mg and/or Fe which could be replaced by Li. The muscovite of the Caledonian plutonic rocks, for example, has only 10 ppm. Li, while the biotites of these rocks vary in their content of this element from 70 to 800 ppm. with an average of 360 ppm. (Nockolds and Mitchell, 1948, p. 84). The Li content of the sillimanite-gneiss is 110 ppm., that is, one-third of the amount in the biotite-schist, though the mineralogical composition of these two rocks is nearly the same (Table II), each having 40 per cent of biotite. Li, therefore, may be relatively enriched at the lower temperatures prevailing in the biotite zone.

Cr is lowest in the low grade (60 ppm.). The Cr content of the high grade (115 ppm.) is but little higher than that of the medium grade (100 ppm.). The Ni content of the rock of the low grade (55 ppm.) is slightly higher than that of the average of the medium grade metamorphic rocks (45 ppm.). Ni attains its highest value in the high grade metamorphic rocks (98 ppm.). The distribution of Cr+Ni is similar to that of Fe^3+Mg in the three grades of metamorphism.

The Cu content of the different schists - 6 to 15 ppm. - is relatively very low. The averages for both the medium and high grade rocks are similar (12 ppm.). The low grade rock has a lower Cu content (6 ppm.).

It is interesting to notice that the distribution of the total of Ti, Mn, Cr, Ni, Li, Co, V and Cu in the three different grades of metamorphism is similar to that of Fe^2, Fe^3 and and Mg, as graphically illustrated in Fig. 1.

The metamorphic rocks surrounding the Garabal Hill-Glen Fyne Complex examined by Nockolds and Mitchell (1948) also illustrate this correlation. Fe^2, Fe^3 and Mg are unfortunately not given, but their relative concentrations can be judged from the mineralogical constitution of the different rocks. The hypersthene-bearing hornfels (analysis No. 1, Table IV, p. 545) is the richest in Cr and Ni, and the diopside-bearing hornfels (No. 6, Table IV) comes next in the abundance of these elements. It is reasonable to assume that the Mg content of each of these hornfelses is higher than in any of the associated schists, and that /

that it is highest in the hypersthene-bearing hornfels.

Ti, Mn, Cr, Ni, Li, Co, V and Cu usually replace Fe^2, Fe^3 and Mg in favourable crystal lattices. During the progress of the crystallisation differentiation of volcanic rocks the total of Fe^2, Fe^3 and Mg tends to decrease. It has been found by the writer (Higazy, 1952b) that the total of the trace elements which can replace these major elements also decreases. In regional metamorphism, however, where there seems to be no regular decrease of the total of Fe^2, Fe^3 and Mg from high to low grades, the same behavious is found in the respective trace elements. In metasomatic-metamorphism this has also been found to be the case (Higazy, 1952a).

Ca; Sr, Y and La

The Ca content of the investigated rocks is relatively low. CaO ranges from 0.48 to 1.33 per cent. The average CaO content in these rocks (0.84) is much lower than that of shales (3.11). The average CaO content of the high grade metamorphic schists (1.13) is higher than the averages for the other two grades (0.93 in the low grade and 0.51 in the medium grade). As found in case of the ratio FeO/Fe_2O_3 , the CaO content of the high grade metamorphic rocks shows a closer resemblance to the average for shale than do the low and medium grades.

The /

The similarity between the distribution of Ca on one hand and of that of each of Sr, Y and La on the other is striking. Increase or decrease in Ca is accompanied by similar behaviour of both Sr and Y. If present, La is in amounts below its limit of sensitivity in the low and medium grades, but it occurs in detectable amounts (30 ppm.) in the high grade rocks which also possess the highest Ca content amongst the rocks examined. The similarity of behaviour between these trace elements and Ca can be readily understood if we consider that their ionic radii are all closely alike (Ca, 1.06; Sr, 1.27; Y, 1.06; and La, 1.22 Å).

K; Rb, Ba and Pb

K_2O varies from 2.23 - 6.59 per cent with an average of 3.64, close to that of the average shale (3.24). The K_2O content is almost the same in the chlorite-, garnet- and staurolite-schists, being 2.27, 2.23 and 2.25 respectively. It is relatively high in both the biotite- and the biotite-sillimanite-schists, being 6.59 and 4.89 respectively. Its distribution in the three grades of metamorphism is 2.27 in the low, 4.41 in the medium and 3.57 per cent in the high grades.

The distribution of each of Rb, Ba and Pb is very similar to that of K. These trace elements attain their highest amounts in the medium grade (Rb 275, Ba 2000 and Pb 22 ppm.) which /

which is also richest in K. They are lowest in the low grade (Rb 100, Ba 900 and Pb 10 ppm.) which is also poorest in K. It is significant that the metamorphic rocks surrounding the Garabal Hill-Glen Fyne Complex show similar tendencies. Ba and Rb are more concentrated in the schists which have biotite and potash feldspar among their major constituents (Nockolds and Mitchell, 1948, Analyses Nos. 2, 5 and 10, Table IV, p. 545), and which can therefore be expected to be relatively rich in K.

Zr

Zr varies considerably in amount and its abundance is most likely to be related to the amount of zircon found in the different rocks. The chlorite- and the biotite-schists have relatively high amounts of this element. Zircon as a minor accessory constituent is also relatively more abundant in these two rocks than in the other schists. The biotite of the sillimanite-gneiss is more heavily sprinkled with pleochroic haloes than that of the biotite-schist, yet the Zr content of the former rock is much lower than that of the latter. This may indicate that the nuclei of these haloes are for the most part radioactive minerals other than zircon.

Mo and Sc

Mo is found in very small amounts in the rocks of the different zones, 1 ppm. in the low grade and an average of 2 ppm. in each of the medium and high grades.

Sc, if present, is found in amounts below its limit of sensitivity in the rocks of both low and medium grades. The sillimanite-gneiss has 10 ppm. Sc and thus the average Sc content in the high grade metamorphic rocks is 5 ppm. Sc is related in its distribution to Mg, Fe^2 and Fe^3.

Be and Ag

The Be content of the rocks of each of the low and high grades is 5 ppm. In the medium grade Be, if present, is in amounts below its limit of sensitivity.

Ag is present in amounts ranging from 1 to 3 ppm.

The abundances of both Be and Ag in the rocks examined fail to suggest a definite relationship with any of the major elements.

Sn, Tl, Ge and In

Sn, if present, is in amounts below its limit of sensitivity in the investigated rocks. Cassiterite has not been found /

found among the minor accessory minerals of these rocks.

Tl, Ge and In, if present, are in amounts below their respective limits of sensitivity; relatively they are the rarest of the trace elements in the rocks under consideration. It is worth mentioning that although the Rb content is as high as 450 ppm. in the biotite-schist, Tl is undetectable in the same rock. The lepidomelane-skarn of Co. Donegal, Eire, studied by the writer (Higazy, 1952a), has 800 ppm. of Rb and its Tl content is also undetectable. However, the perthites of the Black Hills of South Dakota, recently analysed by the writer (Higazy, 1952c) ~~p.~~) which have a Rb content as high as 9500 ppm., contain 30 to 150 ppm. of Tl. This confirms the unique association of Tl and Rb in rocks and minerals already noted by Ahrens (1948).

Water

The H_2O- reaches its highest value 0.39 in the low grade and it is lowest in the high grade. The total H_2O- and H_2O+, however, is highest in the medium grade and lowest in the high grade. The metamorphic rock of the low grade has a total of these two oxides (3.87) which is very slightly lower than that of the average of the rocks of the medium grade (4.11), and higher than that of the average of those of the high grade (3.21).

BEHAVIOUR OF THE TRACE ELEMENTS IN REGIONAL METAMORPHISM

General statement

The average composition of all the investigated rocks (Table I) is considered to represent approximately the original composition before metamorphism. The SiO_2, MgO, Na_2O, K_2O and P_2O_5 contents of this average are similar to those of the average shale quoted by Pettijohn (1949). The total of Fe_2O_3 and FeO, however, (7.80) is slightly higher than that of the average shale (6.47); CaO (0.84) is much lower than in the average shale (3.11); and Al_2O_3 (21.42) is much higher than in average shale (15.40). It is assumed that this original composition would give rise under the different P. T conditions to the metamorphic rocks of the different grades. It is not overlooked that other factors such as primary local lithological differences, shearing stress and transference of mobile ions, are also involved in the processes of metamorphism.

The significant changes which took place in the proportions of the major elements during the production of the low grade chlorite-schist are: decrease in Al and K, and a slight increase in the total of Mg, Fe^2 and Fe^3. There has been also a corresponding decrease of Ga, and of Rb and Ba, and a slight increase in the total of Ti, Mn, Li, Cr, Co, Ni, Cu and V. The production of the medium grade metamorphic rocks (biotite

and /

and biotite-garnet schists) involved decrease in Al, Ca and the total of Mg, Fe^{2} and Fe^{3}, and increase in K. In the high grade rocks (staurolite-schist and sillimanite-biotite gneiss) there has been a slight decrease in K, and increase in Al, Ca and the total of Mg, Fe^{2} and Fe^{3}. Thus, in all these changes K behaves differently from the total of Mg, Fe^{2} and Fe^{3}. The trace elements behave like their respective major elements during the development of these medium and high grade rocks.

The inter-relationships of Cr, Ni and Co on the one hand and of Ba and Sr on the other in the different grades of metamorphism are very significant. In all three grades we find Cr $>$ Ni $>$ Co and Ba $>$ Sr. Thus, the different P T conditions corresponding to the various grades of metamorphism do not appear to have influenced the relative distribution of these trace elements. It may be stated that the distribution Cr $>$ Ni $>$ Co is found to be characteristic for the ultrabasic and basic rocks that form during early and intermediate stages of magmatic crystallisation (Lundegårdh, 1949; Higazy, 1952). The distribution Ba $>$ Sr, however, is found to characterise rocks that develop at the late and end stages of the magmatic history (Higazy, 1952b).

Significant /

Significant Ratios

It has been found (Higazy, 1952b) that certain ratios vary significantly during the formation of various kinds of volcanic rocks by the crystallisation differentiation of basic magma. The most important of these ratios are $(FeO+Fe_2O_3)/(MgO+FeO+Fe_2O_3)$, Fe^3/Fe^2 and $(Fe^3+Fe^2)/Mg$ all of which increase during the progress of differentiation and thus attain their highest values in the late stages; and $(Mg+Fe^3+Fe^2)/(K+Na+Ca)$, which has its highest value in the early stages and thereafter decreases.

The ratio $(FeO+Fe_2O_3)/(Mg+FeO+Fe_2O_3)$, however, is almost uniform in the metamorphic rocks here under discussion, being 0.73, 0.77 and 0.76 in the low, medium, and high grades respectively. These values lie within the range found for late magmatic rocks (0.7-0.8) by Walker and Poldervaart (1949). The value of Fe^3/Fe^2 increases from low grade (relatively low temperature) to high grade (high temperature), a result which is the reverse of that characteristic for a series of differentiated volcanic rocks. The value of $(Fe^2+Fe^3)/Mg$ shows only a slight increase in the medium and high grades of metamorphism relative to the low grade. Fe_2O_3/MgO increases regularly from low to high grade and attains its maximum value (1.43) in the staurolite-schist.

It /

It seems, therefore, as regards the variation of these ratios, that the regular tendencies characteristic of differentiated volcanic rocks are not followed by metamorphic types which have substantially different mineralogical constitution. This is also true with respect to the other ratios of the trace elements. Li/Mg, Rb/K, Ba/K, Li/Ni and Li/Cr do not show a regular increase towards the low grade of metamorphism yet they attain their highest values in the late magmatic rocks. Moreover, neither (Mg+Fe^2+Fe^3)/(K+Ca) nor the corresponding ratio (Cr+Co+Ni+Cu+V)/(Rb+Ba+Sr) exhibits a regular decrease towards the low grade metamorphic rock.

This contrast in ratio-tendencies for differentiated types and regionally metamorphosed psammo-pelitic rocks may be accounted for by considering the respective differences in their petrogenetic evolution, differences which culminate in the production of highly contrasted mineral assemblages in the two series of rocks.

The ratios in the biotite-schist and the sillimanite-biotite-gneiss show an interesting feature. These two rocks are similar in their modal mineral composition. Their most abundant minerals are biotite and quartz. This makes it quite likely that biotite in each of these rocks is the main source of the trace elements. The values of the ratios Li/Mg, Li/Ni, Rb/K /

Rb/K, Ba/Ca, Ba/(Ca+K) and Sr/Ca are all higher in the biotite-schist than in the sillimanite-bearing biotite gneiss. This is consistent with Goldschmidt's rules for the replacement of major by trace elements. The trace elements which have bigger ionic radii than their respective replaceable major elements should concentrate relative to them at the lower temperatures. The biotite of the biotite-schist (green schist facies) is known to recrystallise at a relatively lower temperature than that of the biotiteof the sillimanite bearing rock (amphibolite facies). Similarly Cr/Fe^3 is higher in the sillimanite-biotite-gneiss which forms at relatively higher temperature. Cr has a smaller ionic radius than that of Fe^3.

CONCLUSIONS

During the development of the well known zones of regional metamorphism of the Scottish Highlands, the behaviour of the trace elements resembles that of the major elements which have approximately the same ionic radii. The trace elements, therefore, culminate in the rocks which show culmination of certain major elements. Ga culminates with Al; Ti, Mn, Li, Cr,

Ni /

Ni, Co and V with Mg, Fe^2 and Fe^3; Sr, Y and La with Ca; and Rb, Ba and Pb with K. Similar inter-relationships between certain trace elements are found in all three grades of metamorphism; e.g. the distribution of Cr, Ni and Co in the three grades is Cr > Ni > Co and that of Ba and Sr is Ba > Sr, corresponding to the distribution of these elements in average shale, as recorded by Rankama and Sahama (1950, p. 226).

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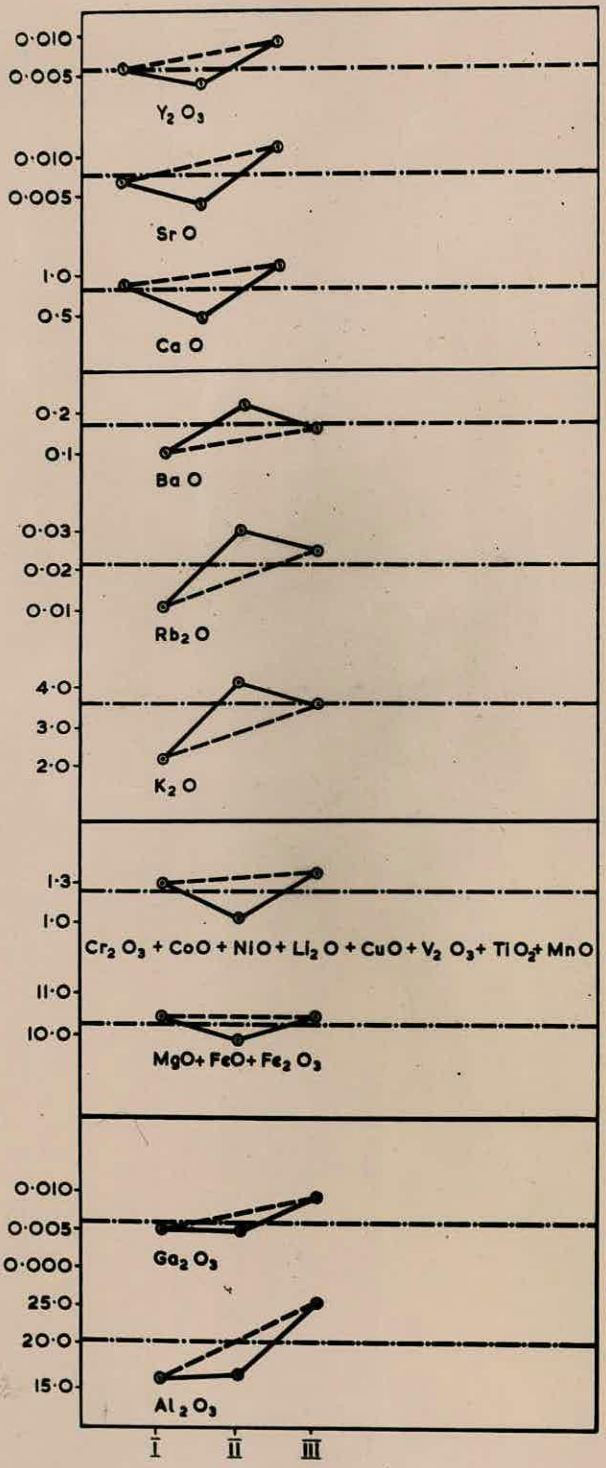

Fig. 1

Behaviour of major and trace elements in the three grades of metamorphism. -.-.-.-. represents the average composition of the analysed rocks. I = low grade, II = medium grade and III = high grade.

PART IV

TABLE IV

Significant ratios

	A	B	C	average BC	D	E	average DE
$(FeO+Fe_2O_3)/(MgO+FeO+Fe_2O_3)$	0.73	0.75	0.86	0.77	0.78	0.75	0.76
$(Fe^3+Fe^2)/Mg$	3.36	3.56	5.15	4.35	4.43	3.84	4.13
Fe^3/Fe^2	0.06	0.55	0.03	0.29	0.60	0.40	0.50
Fe_2O_3/MgO	0.17	1.09	0.15	0.62	1.43	0.72	1.08
K_2O/Al_2O_3	0.13	0.30	0.14	0.22	0.08	0.21	0.15
1000 Ga/Al	0.38	0.48	0.30	0.39	0.49	0.48	0.48
1000 Li/Mg	5.75	19.10	4.66	11.88	8.64	6.97	7.80
Li/Ni	1.82	6.60	1.25	3.93	1.00	1.47	1.24
Li/Cr	1.67	2.20	1.00	1.60	1.00	1.00	1.00
1000 Rb/K	5.05	8.22	5.40	6.81	8.02	7.39	7.70
100 Ba/K	4.78	5.50	5.40	5.45	5.08	4.92	5.00
100 Ba/(K+Ca)	3.5	5.1	4.5	4.8	3.7	4.0	3.8
Fe^2/Mg	3.17	2.29	4.96	3.63	2.76	2.92	2.84
$(Mg+Fe^2+Fe^3)/(K+Ca)$	2.98	1.35	3.00	2.18	2.98	1.53	2.26
(Cr+Ni+Co+V+Cu)/(Rb+Ba+Sr)	0.24	0.11	0.18	0.15	0.34	0.14	0.24
$100\ CR/Fe^3$	1.78	0.69	2.74	1.72	0.52	0.75	0.64

A - E as in Table I

A, BC and DE as in Table I

TABLE II

Trace element contents in ppm. of the analysed rocks

Element	A	B	C	average BC	D	E	average DE	average o all rocks
Rb	100	450	100	275	150	300	225	220
Li	100	330	50	190	120	110	115	142
Ba	900	3000	1000	2000	950	2000	1475	1570
Sr	60	50	20	35	80	120	100	66
Cr	60	150	50	100	120	110	115	98
Co	30	45	25	35	40	35	38	35
Ni	55	50	40	45	120	75	98	68
Zr	850	900	100	500	280	320	300	490
La	*	*	*	*	30	30	30	*
Y	50	35	30	33	60	100	80	55
Cu	6	15	8	12	15	8	12	10
V	110	110	80	95	110	115	113	105
Ga	35	55	25	40	75	60	68	50
Tl	*	*	*	*	*	*	*	*
Sn	*	*	*	*	*	*	*	*
Pb	10	35	10	23	15	20	18	18
Sc	*	*	*	*	*	10?	5?	*
Mo	1	1	3	2	2	2	2	2
Ge	*	*	*	*	*	*	*	*
Be	5	*	*	*	5	5	5	*
Ag	3	2	1?	1.5	1	2	1.5	2
In	*	*	*	*	*	*	*	*

A, B, C, BC, D, E and DE as in Table I.

Spectrographic analyst: R.A. Higazy

* = Element if present is in amount below its limit of sensitivity given in Table I.

TABLE III

Modal Composition of the examined rocks.

Mineral	A	B	C	D	E
Quartz	40	35	50	30	40
Chlorite	45	P	20	P	P
Sericite and Muscovite	10	17	10	20	15
Biotite	P	40	15	5	40
Staurolite	-	-	-	40	-
Garnet	-	-	P	P	P
Sillimanite	-	-	-	-	3
Iron-ores	5	8	5	5	2
Calcite	P	-	P	-	-
Albitic plagioclase	P	-?	-	P	P
Tourmaline	P	P	P	P	P
Apatite	P	P	P	P	P
Zircon	P	P	P	P	P

A - E as in Table I

P = present in amounts much less than 1 per cent

- = absent

PETROGENESIS OF PERTHITE PEGMATITES IN THE BLACK HILLS, SOUTH DAKOTA

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PETROGENESIS OF PERTHITE PEGMATITES IN THE BLACK HILLS, SOUTH DAKOTA[1]

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ABSTRACT

The study of some pegmatites of the Black Hills, South Dakota, has led to the conclusion that metasomatic replacement played a significant role in their formation. Microcline microperthites of these pegmatites were not products of magmatic crystallization but were formed by complex processes of perthitization. The hypothesis of the metasomatic origin of the perthites is supported by chemical analyses and microscopic features of the perthites and country rocks and by field observations.

STATEMENT OF PROBLEM

The origin of the potash-rich rocks, whether deep seated or extrusive, is still an unsolved problem. Some authors explain them as products of magmatic crystallization, whereas others believe in a secondary mode of origin of the potash. Final conclusions regarding the genesis of these rocks can be drawn only on the basis of field and laboratory investigations of individual occurrences.

The author studied some potash-rich pegmatites in T. 2 S., R. 6 E., near Glendale, Pennington County, South Dakota (fig. 1). Excellent outcrops and mine cuts facilitated the study. The pegmatite mines studied include the Glendale, in the northernmost portion of NW. ¼ Sec. 23, T. 2 S., R. 6 E.; the Soda Spar, in the SE. ¼ Sec. 22, T. 2 S., R. 6 E.; the Johnson Dike, in the SE. ¼ NW. ¼ Sec. 22, T. 2 S., R. 6 E.; and several smaller unnamed bodies. Several pegmatites, such as the Three Falls Lode in the SW. ¼ Sec. 22, T. 2 S., R. 6 E., previously mined, were also examined.

Smaller pegmatites are very numerous in this area. The map of pegmatites of the Beecher Rock Basin, T. 4 S., R. 4 E., in Custer County, South Dakota, made by Gwynne (1944) shows clearly their wide distribution.

Some of the largest pegmatites of the Black Hills in the neighborhood of both Custer and Keystone were also visited. These were the Buster, 2½ miles south-southwest of Custer, in the SW. ¼ Sec. 2, T. 4 S., R. 4 E.; the New York, in the NE. ¼ Sec. 18, T. 4 S., R. 4 E.; the Peerless, in the NE. ¼ SE. ¼ Sec. 8, T. 2 S., R. 6 E.; the Hugo, in the southernmost portion of SE. ¼ Sec. 8, T. 2 S., R. 6 E.; the White Cap, in the S. ½ Sec. 9, T. 2 S., R. 6 E.; and the Etta, in the NW. ¼ NW. ¼ Sec. 16, T. 2 S., R. 6 E.

The structure of most of these pegma-

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[1] Manuscript received October 8, 1948.

[2] On a study leave at the University of Chicago.

tites has been described by other writers: Apsouri (1940), Connolly and O'Harra (1929), Guiteras (1940), Fisher (1942 and 1945), Landes (1928), Lincoln (1927), Page and Norton (1946), and Tullis (1939). Few chemical or microscopic data have been published. The author, therefore, analyzed some perthites and country rocks and examined 65 slides of these rock types. Still more data are needed to make certain the conclusions drawn.

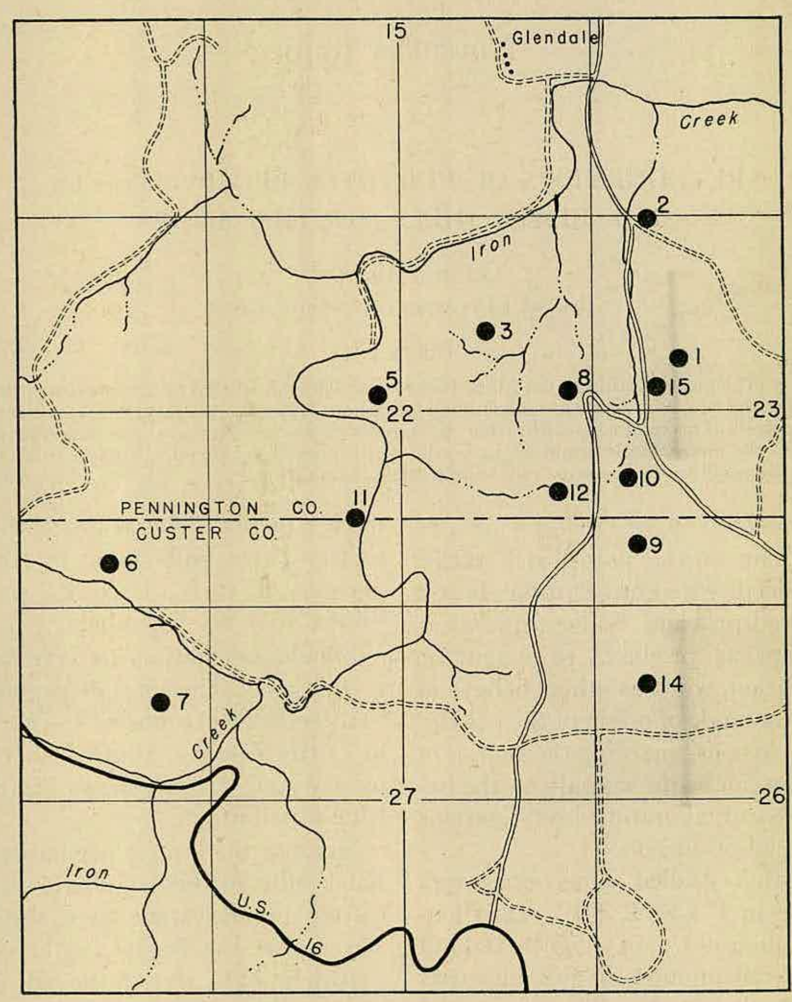


FIG. 1.—Glendale area, showing location of perthites

GEOLOGY OF PEGMATITE AREA

The general geology of the Black Hills has been discussed by Darton and Paige (1925). The Black Hills uplift, an outlier of the Rocky Mountains, is an elliptical area whose long axis trends northwest. The core is composed of metamorphic and eruptive rocks surrounded by concentric outcrops of Paleozoic and Mesozoic sediments. The pre-Cambrian central portion and the outwardly dipping sediments are overlain by Oligocene formations. Hypabyssal dikes and sills of Tertiary age intrude the pre-Cambrian metamorphic rocks and the Paleozoic and Mesozoic sediments (Kirby, 1932).

The pre-Cambrian rocks are metamorphosed sediments and basic igneous rocks, granites, and granite pegmatites. The sediments are conglomerate, quartzite, slate, phyllite, mica schist, garnet and staurolite schists, and marbles (Van Hise, 1890). The basic rocks, originally dioritic or gabbroic, are amphibolites and hornblende schists. In places metamorphism makes it difficult to distinguish between metabasics and metasediments (Connolly, 1927).

The pegmatite granite of Harney Peak is a coarse-grained potassic granite composed principally of microcline-perthite, quartz, and muscovite with an unusually large amount of tourmaline. The pegmatites are also rich in potash and consist chiefly of those minerals which form the pegmatitic granite.

Intense metamorphism and lack of fossils (Connolly, 1927) make it difficult to determine the age of the sediments. Most investigators assign these rocks to the Algonkian. Davis (1926) determined the age of the uraninite from the pegmatites of the southern Black Hills as 1,167 million years. The corrected age, applying Wickman's graphic chart (1943) of $U/(U + Pb)$ and $U/(U + Th)$, is 1,450 million years. The Black Hills pegmatites are, therefore, Archean.

FIELD RELATION OF PEGMATITE AND ASSOCIATED SCHISTS

Recent studies of the Black Hills pegmatites show that most of the mined pegmatites are zoned (Page and Norton, 1946). The zones occur in a definite sequence, and, although any number of different zones may be missing, the sequence of the existing zones will remain the same. Perthite may be either an essential constituent of the zones or may form one of the zones. The Hugo pegmatite and the High Climb Pit, 6 miles north of Custer (Fisher, 1942, pl. 19 and fig. 4) are examples of the first type. Perthite is the principal constituent of some of the different zones of the Soda Spar pegmatite, the Johnson Dike, and the Three Falls Lode.[3]

Examples in which perthite alone forms one of the zones are the White Cap and the John Ross Lode, 4 miles west of Custer (Fisher, 1945, pp. 80–82). The Glendale pegmatite consists of perthite only. Fisher (1945, p. 10) has shown that pegmatitic masses composed almost entirely of perthite are common.

Abundant pegmatitic pockets in numerous unzoned bodies in many cases are composed almost entirely of perthite, commonly associated with albitites.

Perthite is also found as metacrysts in the perthitized schists and as coarse phenocrysts in the granites of the area. The unaltered schist is composed essentially of muscovite, biotite, and quartz with minor amounts of garnet. The schist in places is feldspathized and/or tourmalinized.

The feldspathized schists contain from 25 to 80 per cent of feldspar. The feldspar may be a perthite, an albite, or a microcline.

An outcrop of the perthite schist (pl. 1, *A*, *D*) about 36 yards long, lies in the NE. ¼ Sec. 28, T. 2 S., R. 6 E. The foliation of the perthitic schist, of the schist inclusions commonly found in the pegmatites, and of the isolated schist outcrops all have the same trend. The perthite of the schist appears mainly along the schistosity as small ovoid masses less than 1 mm. in diameter, grading into masses more than 3 cm. long, which tend

[3] For location see p. 555 and fig. 1.

to assume the rectangular outlines of a true feldspar (pl. 1, *A*). Some of the larger metacrysts have biotite laminae curved around them, indicating that the growing feldspar crowded aside the folia of the schist. The ovoid masses sometimes join and form a pinch-and-swell structure. Perthites crowded with many megascopic schist inclusions grade into uncontaminated perthite (pl. 1, *B* and *C*). Replacement rather than viscous intrusion and magmatic crystallization seems to be the best explanation of these phenomena.

Microscopic features support this view. The inclusions in the perthite metacrysts are brown biotite and quartz. The biotite has the same optical properties as the schist. The quartz inclusions are more or less rounded and elongated in a direction parallel to that of the schistosity of the matrix. Some of them still

PLATE 1

A, Perthite of the perthite schist assuming the rectangular outline of the feldspars (white with dark schist inclusions). Pushing-aside of the schist foliae is best shown at the corners of the crystal *P*.

B, Perthite, uncontaminated crystal (*white*); another smaller crystal appears to the right of the figure. The groundmass is schist relic, showing black quartz and lighter-colored micas.

C, A crystal of perthite of the perthite schist, showing inclusions of the schist in a megascopic sieve texture. Parts of the crystal are uncontaminated (*white*). Inclusions are dark.

D, Perthite schist, showing many perthite crystals (white with light-gray schist inclusions). Schist relic is dark and forms the groundmass.

PLATE 2

A, Perthitic schist showing albite (*A*) and string perthite (*P*) with faint grating. Note (1) rounded quartz inclusions (schist relic) in both albite and perthite, (2) the cementing material between some quartz grains is still preserved (*C*), (3) the trend of the quartz inclusions is roughly northeast-southwest in the figure, and (4) biotite inclusions (*B*). 12×.

B, Feldspathized schist showing albite (*A*)—polysynthetic twinning—and potash feldspar (*PF*)—simple twinning, Carlsbad law. Notice (1) rounded inclusions of quartz in the feldspars (in some feldspar crystals the inclusions appear white, in others they are extinguished); (2) the trend of inclusions is the same in the different feldspar crystals—northeast-southwest; and (3) the pushing-aside of the biotite flakes of the original schist (*B*) at the corners of the feldspars. 12×.

C, Albitite. Notice the cementing material (*C*) between some quartz grains. Quartz (*Q*), albite (*A*), tourmaline (*T*). The albite crystals show polysynthetic twinning, all trending in a roughly parallel direction. Most of them do not show up clearly in the figure. 12×.

D, Section of a perthite parallel to (001), showing patch (*white*) and microcline (*grated*). Note the microcline island in the albite patch in optical continuity with host microcline. Note also the extinguished ungrated portion of the microcline. Albite and microcline edges show embayments. 41×.

E, Section of a perthite parallel to (010), showing albite veins and patches (*white*) with numerous microcline islands (*gray*). 12×.

F, Section of a perthite parallel to (001), showing patch albite (polysynthetic twinning) and microcline (*grated*). Note microcline relics in the patch, showing optical continuity with the host microcline, and irregular resorbed contacts. 12×.

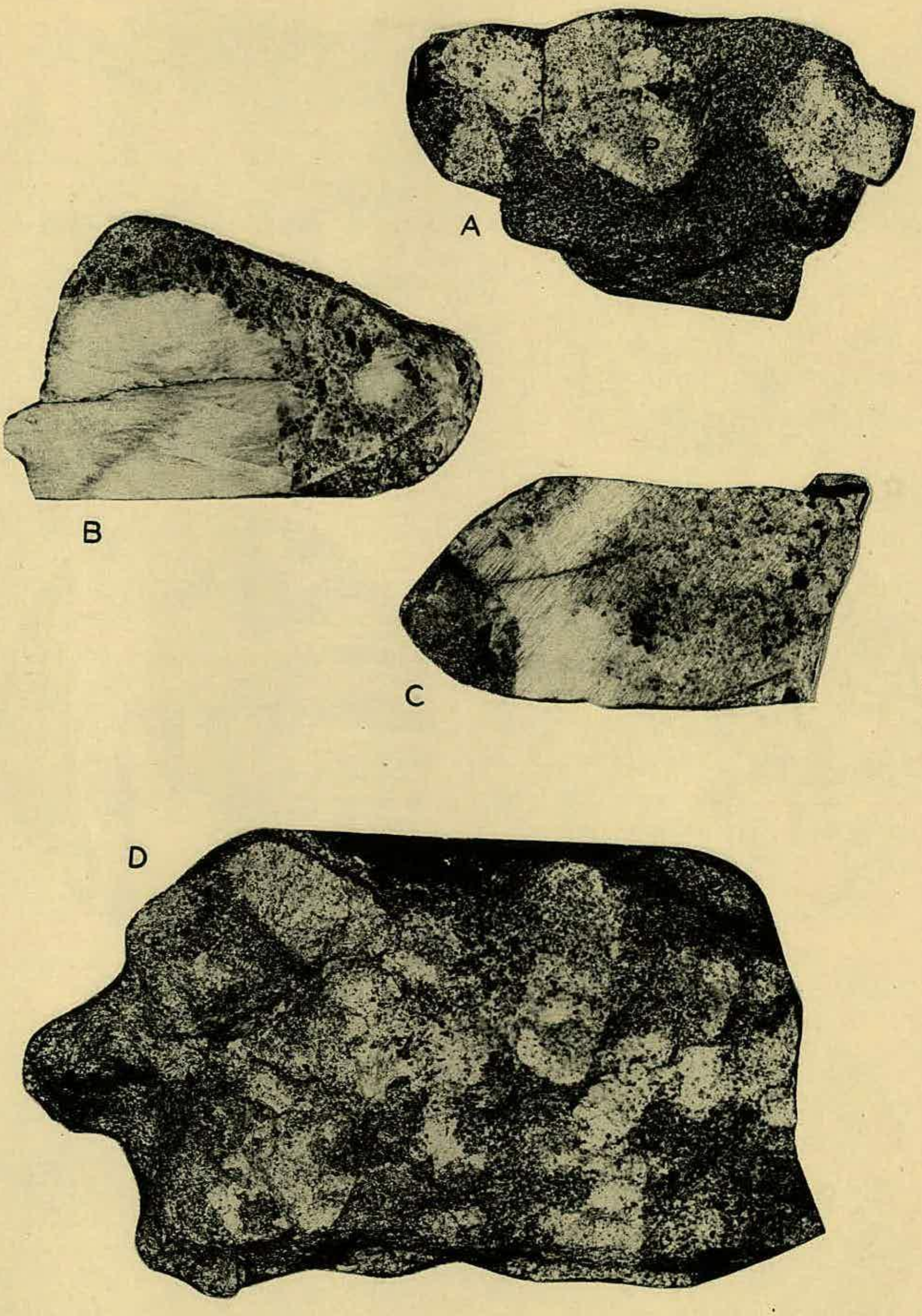
PLATE 3

A, Patch and vein perthite (no. 13, table 1), section parallel to (010), albite (*white*), microcline (*gray*). Note (1) fine strings and thin films between the veins, (2) grading of the strings and films into veins near the center, (3) grading of the veins into patches, and (4) microcline relics in the patch at the lower portion. 12×.

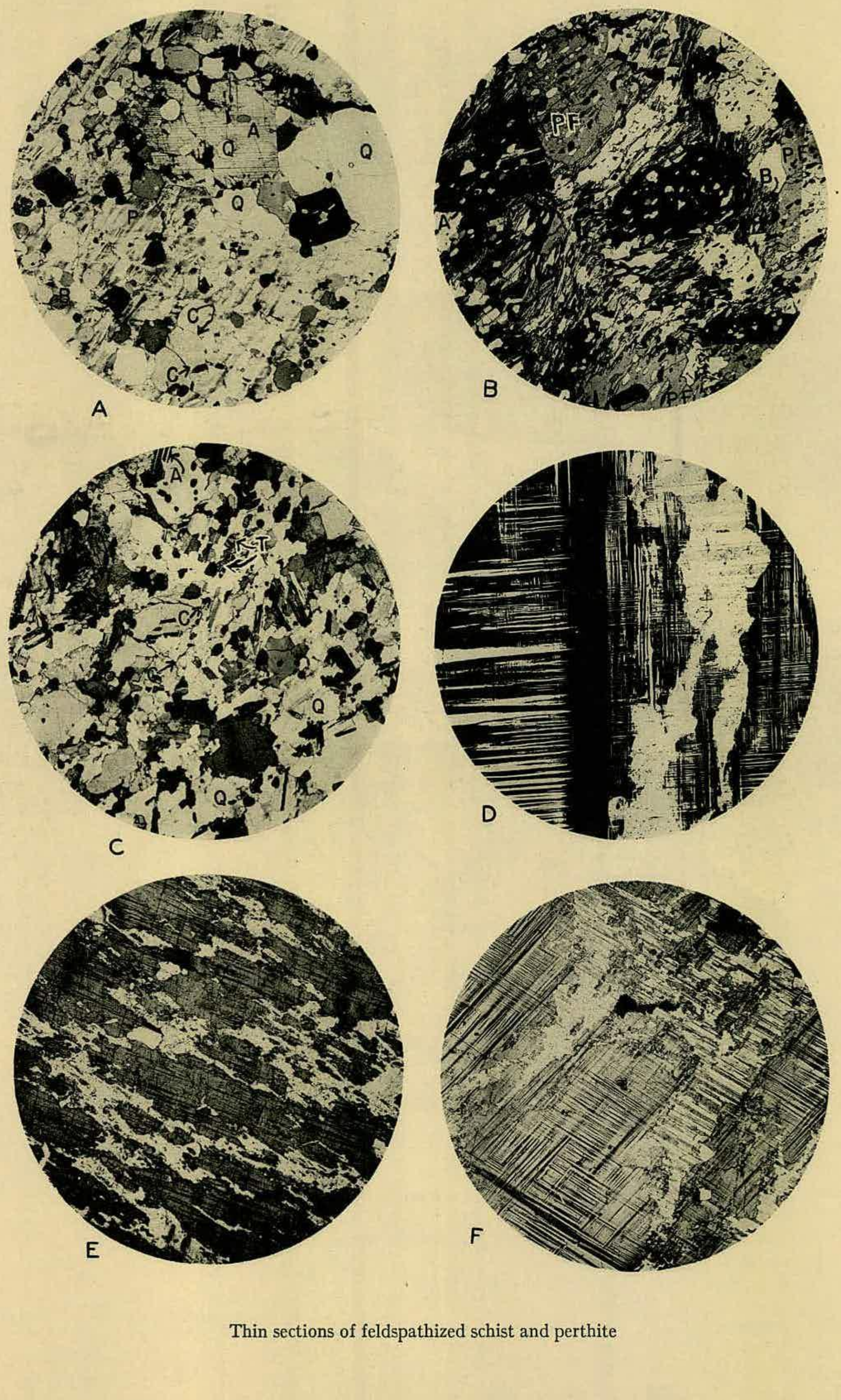
B, Film, vein, and patch perthite (no. 5, table 1), section parallel to (010), albite (*white*), microcline (*dark gray and black*). Note (1) abundance of thin films, (2) grading of the films into veins, (3) complex texture of the veins grading into patches, and (4) microcline islands in the patch near the center. 12×.

C, Film and vein perthite (no. 7, table 1), section parallel to (001), albite (*black*), microcline (*finely grated*). Note abundance of regularly elongated veins and thin films. The latter grade into the former. 12×.

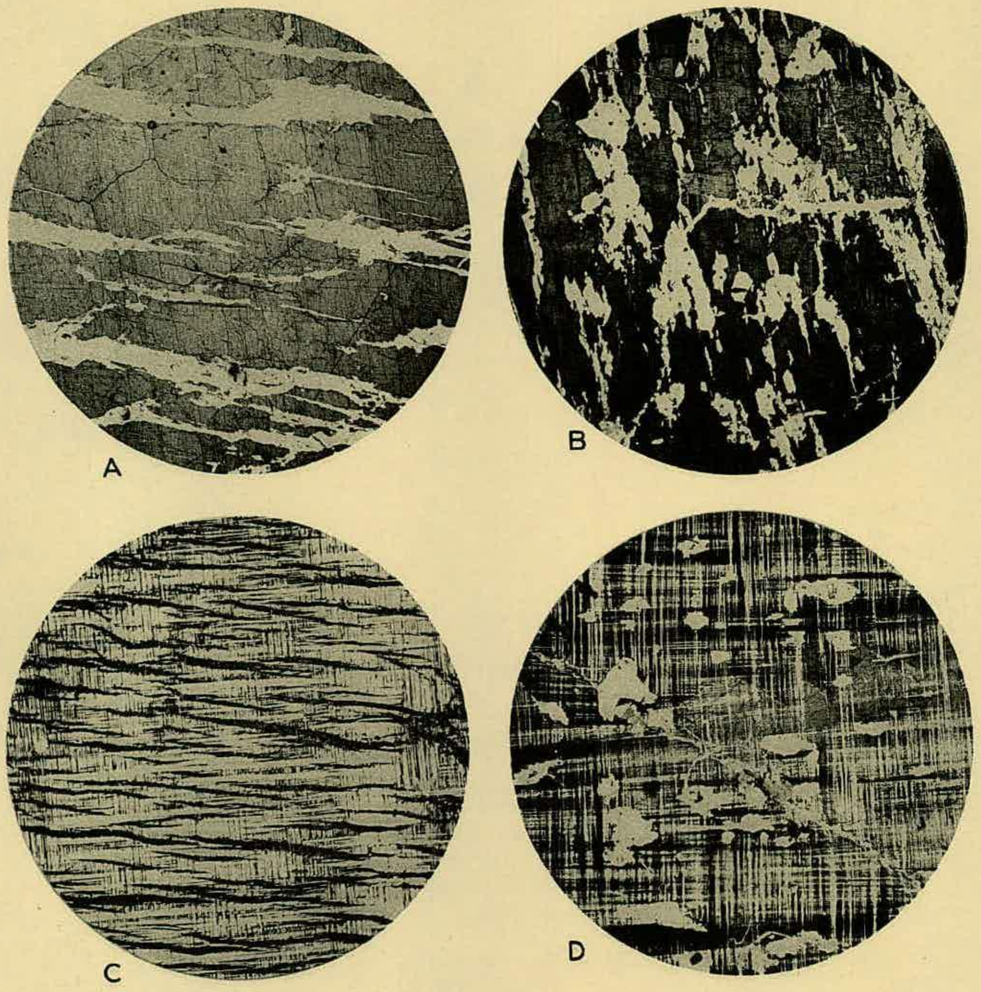
D, Vein perthite (no. 10, table 1), section parallel to (010), albite (*white*), microcline (*grated*). Note the roughly round cross section of veins. 12×.



Perthite of the perthitized schist



Thin sections of feldspathized schist and perthite



Thin sections of perthite

have the yellowish-green chloritic or the yellowish-brown ferriferous cementing material, like that of the quartz of the original unaltered schist (pl. 2, *A*). The albite of the schist has formed in the same manner as the perthite. Plate 2, *A* shows inclusions of rounded quartz of the schist in the albite. They are elongated in the direction of the schistosity. Albite from a schist in the NE. ¼ Sec. 8, T. 2 S., R. 6 E. (across the east-west road from the mill of Consolidated Feldspar Corporation near Keystone) contains abundant quartz inclusions which clearly show a sieve texture (pl. 2, *B*). All the inclusions in the feldspar crystals are elongated in a northeast-southwest direction in agreement with that of the schistosity and the quartz of the matrix. The albite schist in some cases grades into albitites composed essentially of albite, quartz, and micas. In these albitites the cementing quartz material can still be observed between some quartz grains, and the albite is generally elongated in the direction of the schistosity (pl. 2, *C*). These transitional rocks, containing some relic features of the schist, suggest a metasomatic origin for both the perthite schists and the albitites.

TABLE 1

ANALYSES OF PERTHITES*

Oxides	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	Average	16	17
SiO_2......	63.89	65.13	64.29	63.67	64.48	64.36	63.96	64.13	64.11	64.30	64.29	64.48	65.10	64.97	65.07	64.41	64.69	64.20
TiO_2......	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al_2O_3.....	21.61	20.70	19.40	20.08	19.54	19.53	19.39	18.92	19.62	19.37	19.76	19.66	19.55	19.41	19.04	19.72	19.79	19.38
Fe_2O_3.....	0.09	0.09	0.09	0.07	0.09	0.09	0.13	0.06	0.06	0.09	0.09	0.12	0.10	0.07	0.13	0.09	0.17	0.05
MgO.....	0.00	0.03	0.11	0.02	0.00	0.05	0.05	0.07	0.12	0.03	0.06	0.06	0.00	0.02	0.03	0.04	0.01	0.02
CaO......	0.78	0.25	0.32	0.49	0.79	0.82	0.46	0.15	0.37	0.27	0.27	0.21	0.07	0.26	0.17	0.38	0.02	0.02
BaO......	0.02	0.05	0.06	0.02	0.01	0.02	0.17	0.03	0.04	0.05	0.03	0.05	0.02	0.05	0.05	0.04	n.d.	n.d.
Na_2O.....	2.72	2.94	0.38	1.96	2.74	2.96	2.80	2.12	2.55	1.43	2.89	2.12	2.98	3.06	3.29	2.46	3.19	1.21
K_2O......	11.08	10.58	15.62	13.68	12.52	11.94	12.41	14.03	12.84	14.02	12.30	13.00	11.58	12.35	11.94	12.66	11.95	14.95
H_2O......	0.31	0.17	0.16	0.18	0.21	0.29	0.36	0.25	0.22	0.23	0.21	0.28	0.16	0.12	0.16	0.22	0.27	0.27
Total...	100.50	99.94	100.43	100.17	100.38	100.06	99.73	99.76	99.93	99.79	99.90	99.98	99.56	100.31	99.88	100.02	100.09	100.10

* 1–15: Perthites (see fig. 1 for location); analyst, R. A. Higazy. 16: Perthite (Hugo pegmatite); analyst, B. Bruun. 17: Microcline (Hugo pegmatite); analyst, B. Bruun.

COMPOSITION OF PERTHITES AND RELATED ROCKS

Fifteen perthites, one cleavelandite, and three samples of the country rocks were analyzed chemically by the writer at the University of Chicago. Specimens of perthite and microcline from the Hugo pegmatite, obtained from Dr. L. Page, of the U.S. Geological Survey, were analyzed by Mr. B. Bruun. The analyses of the sixteen perthites and the microcline appear in table 1, the analysis of the cleavelandite is given in table 2, and the analyses of the country rocks are shown in table 3.

The normative potassium feldspar (Or), sodium feldspar (Ab), and lime feldspar (An) of each of the analyzed perthites, microcline, and cleavelandite were calculated, using the equivalent molecular percentage instead of the molecular percentage (Niggli, 1936). This is shown in table 4. The Or is the molecule $KAlSi_3O_8$, composed of one atom of potassium, one of aluminum, and three of silicon; the Ab is the molecule $NaAlSi_3O_8$; and the An is $CaAl_2Si_2O_8$. The percentages of the three feldspar molecules do not differ much from those obtained with the weight percentages in calculating the norm. The sum of the three molecules forms in most cases 98 per cent of the total normative composition.

NORMATIVE COMPOSITION OF THE PERTHITES

The normative ratios Or:Ab and Ab:An of the feldspars shown in table 4 were plotted in figure 2. Perthite 1 has an Or:Ab ratio of 72.5:27.5, similar to that of perthite 13, which has the ratio 72.0:28.0. Yet the Ab:An is 88.5:11.5 in the former and 98.5:1.5 in the latter. The similarity of the Or:Ab ratio in the two perthites might indicate that their temperatures of formation were about the same, and, accordingly, one would expect them to have similar normative plagioclase composition. On the contrary, the normative plagioclase in the former is near oligoclase, whereas in the latter it is sodic albite. Similarly, perthite 14 and 6 have Or:Ab ratios of 73.1:26.9 and 73.2:26.8, respectively, and Ab:An ratios of 95.5:3.5 and 87.7:12.3, respectively. Moreover, figure 2 shows that there can exist perthites with similar normative plagioclase composition, but different Or:Ab ratios. Examples of this are: (1) perthites 15 and 8, which have Ab:An ratios of 97.0:3.0 and 96.5:3.5, respectively, and Or:Ab ratios of 70.7:29.3 and 81.3:18.7, respectively; (2) perthites 4, 5, and 6 with Ab:An ratios of 88.0:12.0, 87.4:12.6, and 87.7:12.3, respectively, and Or:Ab ratios of 82.0:18.0, 75.2:24.8, and 73.2:26.8, respectively.

TABLE 2

ANALYSIS OF CLEAVELANDITE*

Oxides	Per Cent Oxides
SiO_2	67.62
TiO_2	0.00
Al_2O_3	19.76
Fe_2O_3	0.09
MgO	0.08
CaO	0.50
BaO	0.05
Na_2O	11.03
K_2O	0.09
H_2O	0.40
Total	99.62

* Analyst, R. A. Higazy.

Perthite 13, found as a phenocryst in the granites of the area, has a normative plagioclase composition of Ab 98.5. This is more sodic than most of the perthites. If this phenocryst had crystallized from a granitic magma, it would have a normative plagioclase poorer in the albite molecule than that of the pegmatite perthites because it formed at a comparatively higher temperature. Moreover, the normative plagioclase composition of cleavelandite (No. 18, table 4) is Ab 97.5 An 2.5. This is richer in anorthite than is the perthite phenocryst of the granite. Also, perthite 2 has exactly the same normative plagioclase composition as that of cleavelandite. Perthite 13 has even a lower anorthite content than does cleavelandite. Therefore, it can be stated that such perthites might have formed at the same temperature as cleavelandite (the

TABLE 3

CHEMICAL ANALYSES OF THE COUNTRY ROCKS*

Oxides	1	2	3
SiO_2	68.83	70.85	69.93
TiO_2	0.46	0.21	0.00
Al_2O_3	14.63	15.48	17.84
Fe_2O_3	1.42	0.64	0.14
FeO	3.83	1.09	0.20
MnO	0.05	0.01	0.01
MgO	2.24	0.83	0.54
CaO	0.52	0.38	0.59
BaO	0.11	0.11	0.02
Na_2O	1.05	2.16	9.68
K_2O	5.01	6.45	0.42
P_2O_5	0.17	0.45	0.51
H_2O^+	1.52	1.18	0.23
H_2O^-	0.14	0.08	0.06
Total	99.98	99.90	100.17

* 1, Biotite schist; 2, microcline-perthite biotite schist; 3, albitite. Analyst, R. A. Higazy.

hydrothermal species), if not lower. Lastly, 17 is a microcline collected from the microcline-quartz zone of the Hugo pegmatite, and 16 is a perthite from the perthite zone. The perthite which is from an outer zone and supposed to have crystallized at an earlier stage than the microcline of the inner zone has a normative plagioclase composition of Ab 99.7 An 0.3; this is more sodic than that of the microcline, which has the normative plagioclase Ab 99.0 An 1.0.

COMPOSITION OF PERTHITE OF THE SCHIST

The similarity in composition of the perthite metacryst in the schist and the phenocryst in the granite with the perthites of the pegmatites is striking. Table 5 shows that the weight percentages of all the oxides of a perthite meta-

TABLE 4

RATIO OR: AB: AN OF THE DIFFERENT PERTHITES*

Number	Or	Ab	An	Ab: An	Per Cent Plag.	Or: Ab
1	70.4	26.2	3.4	88.5: 11.5	29.6	72.5: 27.5
2	69.4	29.3	1.3	97.5: 2.5	30.6	70.2: 29.8
3	94.7	3.5	1.8	66.0: 34.0	5.3	96.2: 3.8
4	80.1	17.5	2.4	88.0: 12.0	19.9	82.0: 18.0
5	72.5	24.0	3.5	87.4: 12.6	27.5	75.2: 24.8
6	70.5	25.9	3.6	87.7: 12.3	29.5	73.2: 26.8
7	72.8	24.9	2.3	91.6: 8.4	27.2	74.5: 25.5
8	80.7	18.6	0.7	96.5: 3.5	19.3	81.3: 18.7
9	75.5	22.7	1.8	92.7: 7.3	24.5	76.8: 23.2
10	85.3	13.3	1.4	90.6: 9.4	14.7	86.5: 13.5
11	72.7	25.9	1.4	95.0: 5.0	27.3	73.7: 26.3
12	79.0	19.3	1.7	92.0: 8.0	21.0	80.5: 19.5
13	71.7	27.9	0.4	98.5: 1.5	28.3	72.0: 28.0
14	72.1	26.6	1.3	95.5: 4.5	27.9	73.1: 26.9
15	70.0	29.1	0.9	97.0: 3.0	30.0	70.7: 29.3
Average	75.8	22.4	1.8	91.0: 9.0	24.2	77.2: 22.8
16	71.1	28.8	0.1	99.7: 0.3	28.9	72.2: 28.8
17	89.0	10.9	0.1	99.0: 1.0	11.0	89.0: 11.0
18	0.6	97.0	2.4	97.5: 2.5	99.4	0.8: 99.2

* 1–15, perthites; 16, perthite (Hugo pegmatite); 17, microcline (Hugo pegmatite); 18, cleavelandite.

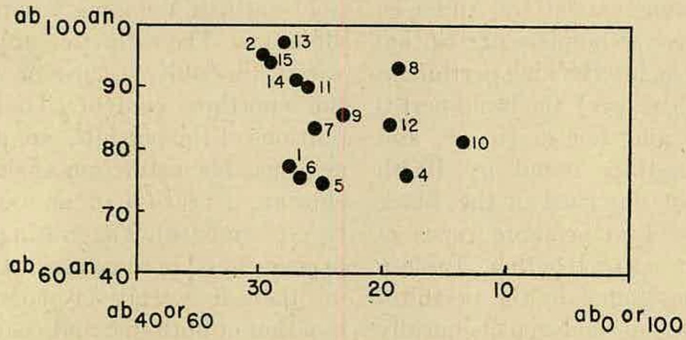


FIG. 2.—The normative ratios Or: Ab and Ab: An of the analyzed feldspars

cryst of the perthitized schist, with the single exception of baria and water, lie within the range of the oxides forming the perthites of the pegmatites. It also shows that the weight percentages of all the oxides of the perthite phenocryst of the granite, with the exception of lime, lie within the range of the oxides forming the perthites of the pegmatites.

TABLE 5

Oxides	Range in the Perthites (Per Cent)	1*	2†
SiO_2	63.89–65.13	65.10	63.96
TiO_2	0.00	0.00	0.00
Al_2O_3	18.92–21.61	19.55	19.39
Fe_2O_3	0.06– 0.13	0.10	0.13
MgO	0.00– 0.12	0.00	0.05
CaO	0.15– 0.82	0.07	0.46
BaO	0.01– 0.06	0.02	0.17
Na_2O	0.38– 3.29	2.98	2.80
K_2O	10.58–15.62	11.58	12.41
H_2O^+	0.12– 0.31	0.16	0.36

* Perthite phenocryst in granite.
† Perthite metacryst in schist.

TEXTURES OF PERTHITES

The analyzed perthites as well as a few others were examined microscropically. Four textural types have been recognized, namely,

1. Patch perthite
2. Vein perthite
3. Film perthite
4. String perthite

These types were named by Andersen (1928), who gave a complete description of each type. The interlocking perthite of Andersen (1928, p. 151), the braid perthite of Goldich and Kinser (1939), and the guttate perthite found by Barth (1930) were not observed in the Black Hills perthites. Two or more types of perthite always occur together. Table 6 shows the types found in the perthites analyzed. Those not analyzed chemically are similar to those analyzed.

Vein and patch types of perthite are abundant in practically all material studied. The patches reach 2.3 mm. or more in width and in most cases exceed 1.0 mm. In the patches of albite are islands of microcline, which exhibit complete optical continuity with the host microcline (pl. 2, *O*). They are well shown in sections parallel to both (010) (pl. 2, *E*) and (001) (pl. 2, *F*). Plates 2, *D–F*, and 3, *A* and *B*, illustrate these relations. In sections parallel to (001), regular bands of albite are commonly found which are parallel to the pericline twins of microcline and in many cases swell out perpendicular to this direction. Commonly the patches send out branches or offshoots which appear to have eaten their way into the microcline. These are irregular and in places have a complicated texture. In some cases the patches form lens-shaped or roughly rounded pools, which send off other patches which may run in any direction. The contacts between the albite of the patches and the microcline are commonly irregular and embayed (pl. 2, *E*). The amount of albite in the patches, estimated by microscopic areal measurements, is not the same in all perthites. In perthite No. 10 albite patches form about 8 per cent, whereas in perthite No. 11, albite patches form approximately 19 per cent of the whole specimen. Patch albite commonly shows polysynthetic twinning according to the albite law. The extinction angle on (010) varies, probably because of variation in the anorthite content. The microcline portions of the perthites are more homogeneous. The extinction angles of microcline are +15° to +16° on (001) and +5° to +6° on (010). The grating may differ in coarseness; in some cases it is fine, and in others it is relatively coarse. A combination of both fine and coarse gratings in a single perthite is common. Nearly all the microcline seen contains some areas, variable in width, which lack the characteristic grating (pl. 2, *D*). Some graphic granites, composed essentially of quartz and perthite, also show a patch type which displays the general characteristics mentioned above.

The vein type of perthite is closely associated with the patch type. In some places it is difficult to differentiate between them. The vein perthite generally shows intricate and irregular networks of anastomosing veins, which grade into the patch type. The veins commonly enclose microcline islands in complete optical continuity with the host microcline similar to those in the patch type. Albite of the vein type rarely exhibits polysynthetic twinning, and its edges are commonly irregular. Both the width and the length of the albite of the vein type vary in the different perthites, but they are decidedly less than those of the patches. The width varies from 0.05 to 0.2 mm., and the length reaches a few millimeters. The veins in some cases are more or less parallel to (100) (pl. 3, *C*), but more commonly they run irregularly through the whole perthite. They generally have numerous veinlets which possess smaller width and length. Veins which have circular cross-sections of a diameter of about 0.05 mm. are also present (pl. 3, *D*).

TABLE 6

TEXTURAL TYPES OF ANALYZED PERTHITES

No.	String	Film	Vein	Patch	Color[*]
1......	T[†]	T	X	X	Pale pink
2......	X	T	T	X	Grayish-white
3......	T	T	X	X	Pink
4......	...	...	X	X	Grayish-white
5......	T	X	T	X	Deep pink
6......	T	T	X	X	Pink
7......	T	X	X	T	Salmon-red
8......	...	X	X	T	Whitish-gray
9......	X	T	X	X	Grayish
10......	...	T	X	T	Grayish-white
11......	T	T	X	X	Deep pink
12......	T	...	X	X	Whitish-gray
13......	T	T	X	X	Pink
14......	X	...	X	T	Deep pink
15......	...	...	X	X	Pinkish-gray

[*] The perthites analyzed vary in color. The percentage of Fe_2O_3 may be the same in both pink and gray perthites. For example, perthites 1 and 2 are pink and grayish-white, respectively; yet each has 0.09 per cent Fe_2O_3. This indicates that the variation in color is not due to iron or apparently to any of the common elements but might be attributed to other rarer elements.

[†] Symbols: X = Present in abundance; T = Present in trace; . . . = Absent.

The film and string albites constitute a relatively small amount of the total albite of the perthite, or both films and strings may be absent. The strings and films are always accompanied by vein and patch types (pl. 3, *A*). Both of the latter form, on the average, 90 per cent of the total albite of the perthite, the rest being film and string types. The total albite, estimated by microscopic areal measurements, conforms closely to the normative plagioclase percentages of the various analyzed perthites given in table 4. The films are generally 0.01 mm. in width, rarely 0.04 mm., and several millimeters long. The strings have a width of about 0.003 mm. and a length of as much as 0.65 mm. Both film and string types commonly grade into the vein type. The strings make an angle of 76°–81° with (001). They commonly occur in groups between the veins. The grating of the microcline of the strings is relatively fine, but such fine grating can also be found in the other types.

SIGNIFICANCE OF PERTHITE TEXTURES

The perthitic intergrowth has been thought to be due to (1) simultaneous crystallization, (2) exsolution, or (3) replacement.

A detailed study of the textural features of perthites of southern Norway led Andersen to believe that each well-defined textural class corresponds to a particular mode of origin (1928, p. 163). The string and film types were believed to be the products of exsolution. The string forms at an early stage of the evolution of the feldspar, whereas the films form at a lower temperature in a later stage. The vein perthite was believed to be formed mainly by recrystallization of albitic solutions derived from the pegmatitic magma from which the host feldspar crystallized. These solutions fill the contraction cracks, believed by Andersen to be formed perpendicular to (010) and making an angle of about 70° with (001), where they crystallized without much replacement. Goldich and Kinser (1939, p. 423) thought the atomic structure was an important factor in determining the location of the openings in which the vein solutions would crystallize. In a later stage, Andersen says, these solutions work their way farther from the cracks, replacing the host microcline and forming networks of albitic material. The patch type was considered to be an advanced stage of replacement, transitional between the vein type and pure albite.

It is reasonable to accept the replacement hypothesis for the explanation of the origin of the patch type. It is difficult to believe that magmatic crystallization can give rise to the peculiar characteristics of this type. The microcline islands in complete optical continuity with the host microcline, the extreme irregularity of the contact between the patches and the host, the numerous embayments, the network-like forms and other complex textures without any regularity in the direction of elongation, the transition of veins into patches and of the latter into chessboard albites and albite in general, the variation in the amounts of albite of the patches of different perthites, and the pools and pods of albite with offshoots and tongues which appear to have worked their way by eating and digesting the host—all these features undoubtedly favor the replacement theory.

Vein perthite, which is next to the patch type in abundance, commonly shows microcline relics and irregular and embayed contacts with the host microcline. Intricate networks of arborescent and anastomosing veins are common. These generally grade into the patch type. It is, therefore, a product of metasomatic processes, that is, a crystallization of albitic materials circulating into the contraction cracks and/or the openings controlled by the atomic structure of the feldspar. Much replacement of the potash feldspar accompanies its precipitation.

Andersen's concept of origin of string and film types of perthites seems correct. These perthites are the rarest types. They are believed formed by exsolution in the solid state, that is, by diffusion of the constituents of albite to cracks in the host microcline. Both types show more uniform elongation than do the vein and patch classes. Transitional stages between string and film types, on the one hand, and the vein type, on the other, are not uncommon. Some veins cut the strings and films and are therefore younger than such strings and films. In the early stages of the evolution of the perthite, diffusion of the albitic material seems to have followed a certain preferred direction in the atomic structure of the feldspar forming the regularity in trend of the strings and films. Later in the evolution some of the albitic materials acted selectively in certain directions in the feldspar, giving rise to the regular veins. They might have started this action in the same direction as those of the strings and films, transforming these into the vein type. Perthite No. 15 is devoid of both the string and the film types. This may be because the transformation of strings and films into veins has been completed.

What is the origin of the homogeneous potash-soda feldspar and of the circulating albitic material? It has been proved experimentally that soda feldspar dissolves to a considerable extent in potash feldspar by prolonged heating somewhat below the melting temperatures (Dittler and Köhler, 1925). It has also been proved by X-ray analyses that homogeneous potash-soda feldspar may form cryptoperthite on heating slightly below its melting temperature (Kozu and Endo, 1921; Chao, Smare, and Taylor, 1939). It may be concluded, therefore, that at relatively high magmatic temperatures the potash-soda feldspar is homogeneous. On cooling, the solubility of the soda feldspar decreases rapidly, so that a once homogeneous substance separates into two solid phases, namely, a soda-rich and a potash-rich feldspar. The soda feldspar in this case would be found in fine or thin intergrowths, in other words, strings and films, but not in relatively coarse bands, like those of the veins and patches. The perthite obtained experimentally is a submicroscopic cryptoperthite having a greater similarity to the strings, and to a less extent to the films, than to any of the other classes.

Although the string perthite can be produced by exsolution from magmatic sources, some may have been formed by migration of material from the country rock to structurally favored places where they form rocks markedly unlike the original parent-rock. This process is described elsewhere in this paper. The perthite of the perthitic schists (pl. 1, *A–D*) could not be derived from a magmatic source. It shows megascopic and microscopic features, discussed above, which are difficult to explain by viscous intrusion and magmatic crystallization.

PERTHITE GENESIS

Magmatic pegmatites must, by definition, precipitate from the residual magmatic melt and are its final product of differentiation. The water content of this residual melt was probably less than 10–12 per cent. Such melts should obey the laws of crystal fractionation.

The concentration of lithium or sodium in certain pegmatites and the impoverishment of others in potassium seem to indicate that these rocks might not have been derived from the crystallization of a pegmatitic rest magma. The residual magma is known to be rich in the alkalies in the latest stages, and there is no way of separating the different alkali members by the differential crystallization of the liquor, letting one or another of them concentrate in certain more favorable structures.

In some places, as in the case of the Edison pegmatite in the Keystone area, potassium-bearing minerals are not found. This pegmatite has an interior zone of quartz and albite, surrounded by a zone of quartz, albite, and spodumene. In other cases, such as the Etta pegmatite of the Keystone area, in which spodumene, the dominant mineral, forms crystals several feet in length, lithium is present in abundance; in still other pegmatites, lithium is found only in traces.

Whenever perthite forms pegmatitic pockets or forms a zone in a pegmatite body, its chemical composition should closely approximate the mother-liquor from which it was crystallized. Walker and Mathias (1946) believe that the perthite at Bantry Bay (South Africa) represents the composition of the pegmatitic magma. If perthites crystallize from a magma, such magma should follow the course of crystallization expressed by the feldspar equilibrium diagram.

The orthoclase-albite equilibrium diagram suggested by Vogt (1926) does not satisfactorily explain the derivation of the perthites analyzed from a granitic magma. The orthoclase:albite ratio in these perthites (table 4) is far from that which should be attained (that is, Or 40:Ab 60) had they been formed in such a manner.

Spencer (1938) in his study also concluded that the orthoclase-albite binary diagram cannot explain satisfactorily the magmatic origin of the potash-rich pegmatites.

THE ORTHOCLASE-ALBITE-ANORTHITE TERNARY EQUILIBRIUM DIAGRAM

The ratio Or:Ab:An of the different perthites given in table 4 was plotted on the orthoclase-albite-anorthite equilibrium diagram as shown in figure 3. The cotectic curve, CD_1, in figure 3, after Bowen (1928), has C at the Or:An eutectic point and D at the Ab:Or eutectic point.

All the perthites analyzed lie in the field of the orthoclase or the potash-rich rocks. Those of Andersen (1928, p. 148) fall in the same field. In the normal course of crystallization, composition of the liquid cannot cross the cotectic curve. In the plagioclase field the crystallizing liquid must follow a certain path, such as that given by Nockolds (1946, p. 215) and plotted in figure 6 or that given by Barth (1944). The liquid, upon hitting the cotectic curve, would then follow it, so that in the last stages of crystallization the eutectic ratio Or:Ab would be attained. The Or:Ab:An ratio of the Black Hills rocks does not harmonize with this concept.

The author also plotted the Or:Ab:An content of some fifty rocks.[4] These are deep seated (graphic granites, granites, pegmatites, and a monzonite), hypabyssal (porphyries), and extrusive (rhyolites, liparites, pitchstones, comendites, and trachytes). The compositions of these fifty rocks also lie in the orthoclase field (fig. 4). An attempt to shift the Or:Ab eutectic point D of figure 4 to D^1, around which most of the plotted graphic granites and granites fall, and the Or:An eutectic point C to C^1, which represents the composition of a pitchstone,[5] would not solve the problem, as there are still other rocks[6] whose composition still lies in the orthoclase field (fig. 5). Why should these rocks, if of magmatic origin, not follow the regular course of crystallization that such an origin demands according to the feldspar ternary diagram?

[4] Of subrang Dopotassic Omeose, Order Quardofelic Britannare, and the subrang Dopotassic Magdeburgose and Sodipotassic Alaskose, Order Quarfelic Columbare, from Washington's tables (1917, pp. 109, 57, and 61, respectively).

[5] Belonging to the subrang Perpotassic, Order Quarfelic Columbare (Washington, 1917, p. 79).

[6] Of the subrang Dopotassic Omeose and the subrang Perpotassic Lebachose, Order Quardofelic Britannare (Washington, 1917, p. 107).

Bowen has proved (1937) that liquids at the latest stages of crystallization become enriched in the alkali silicates. The chemical analyses of some volcanic rocks have been shown to fall in the trough of his figure 9 (1937, p. 18), which he postulates for rocks formed in the last stages of crystallization. Some deep-seated rocks (granites and syenites) have been shown to lie also in this trough. However, most of the potash-rich rocks—extrusive as well as deep seated—do not lie in this trough. With respect to the origin of such rocks, Bowen referred to the work of R. Terzaghi (1935). She stated that some of the potash-rich rocks may have been formed by metasomatic alterations but that most of them are magmatic. The position of the latter rocks in the orthoclase field Or:Ab:An ternary diagram she attributes mainly to the reaction relation between anorthite and orthoclase, to pressure, or to devitrification.

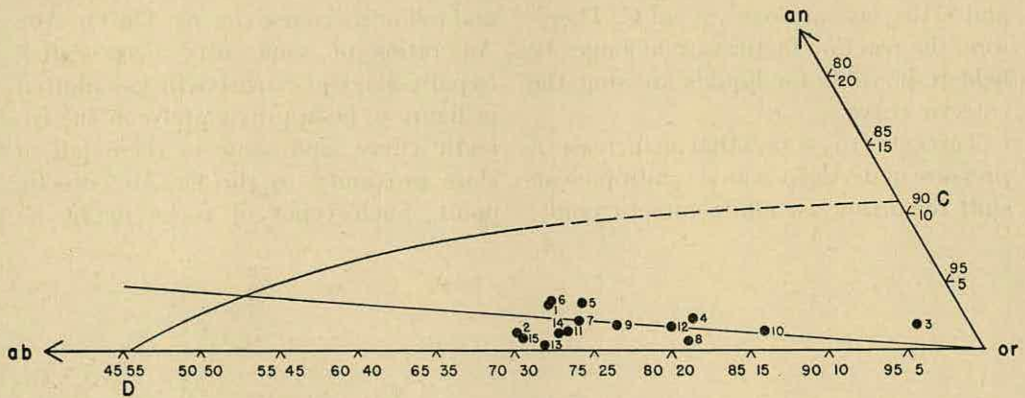


FIG. 3.—The Or:Ab:An ratio of the analyzed perthites

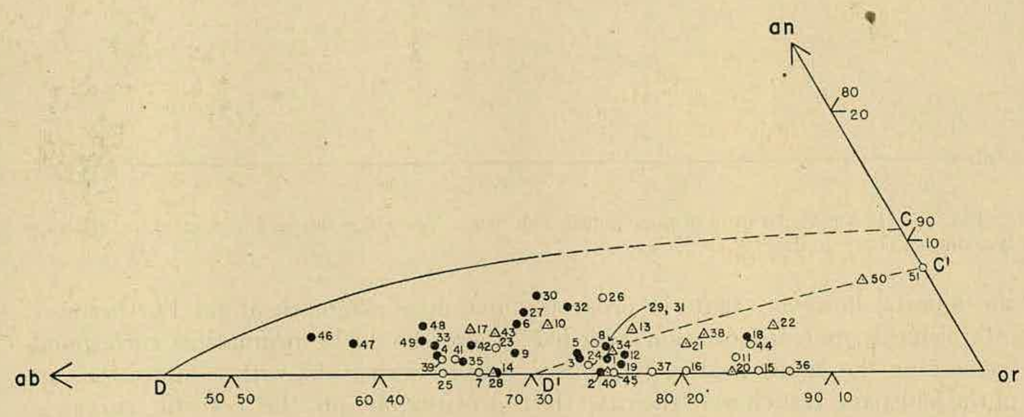


FIG. 4.—The Or:Ab:An ratio of some potash-rich rocks. Nos. 1–5 and 6–32 = nos. 1–5 and 7–33 of Washington (1917, p. 109). Nos. 33–45 = nos. 1, 2, 3, 11, 12, 13, 15, 18, 22, 25, 27, 30, and 31 of Washington (1917, p. 57). Nos. 46–49 = nos. 10, 31, 32, and 60 of Washington (1917, p. 61). Nos. 50–51 = nos. 1–2 of Washington (1917, p. 79). Solid circle = granite, pegmatite; open circle, rhyolite, trachyte, and other volcanics; triangle, porphyry.

The reaction relation between anorthite and orthoclase as suggested by Bowen (1928, pp. 227–233) was thought to enable the liquids to cross the cotectic curve. Recently, Schairer and Bowen (1947), in their study of the system anorthite-leucite-silica, found that such a reaction relation does not exist. There is, however, a eutectic between anorthite and orthoclase at 1040° ± 20° C. Therefore, the reaction factor can no longer be held responsible for liquids crossing the cotectic curve.

Terzaghi (1935) says that an increase of pressure under deep-seated conditions can shift the orthoclase-albite eutectic point; she admits, however, that, in order to establish this, more information is needed concerning the latent heat of formation of the feldspars. If such were the case, the plagioclase field would increase, and some of the potash-rich rocks would no longer lie in the orthoclase field. But, as has been mentioned above (p. 566), such a shift, on the basis of the position of most of the graphic granites (which closely approximates the amount of shift postulated by Terzaghi), is not adequate because other potash-rich rocks will still remain in the orthoclase field. The effect of pressure on the feldspar equilibrium diagram appears to be of little importance because some volcanic rocks, such as rhyolites and liparites, as well as some deep-seated granites and pegmatites, lie together in the same field. Furthermore, Nockolds (1946) found that there are deep-seated aplites, adamellites, and granites which lie on the cotectic curve and follow its course (fig. 6). The Or:Ab:An ratios of some fifty deep-seated, hypabyssal, and extrusive rocks,[7] plotted in figure 6, lie approximately on the cotectic curve, and some of them fall in close proximity to the Or:Ab eutectic point. Such types of rocks might be mainly of magmatic origin. Furthermore, there should be pegmatites corresponding to such rocks with compositions approximately on the cotectic curve, so that the position of this curve as given by Bowen in the orthoclase-albite-anorthite equilibrium diagram seems to be approximately correct.

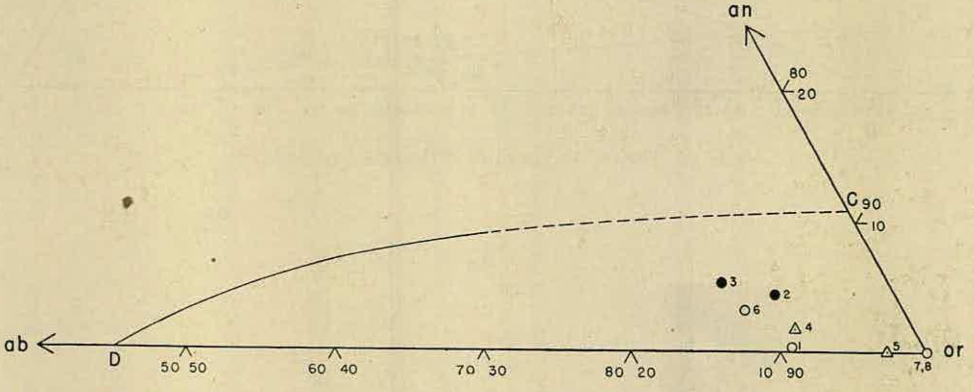


FIG. 5.—The Or:Ab:An ratio of some potash-rich rocks. Nos. 1–8 = nos. 4, 5, 7, 8, 9, 10, 11, and 12 of Washington (1917, p. 107).

Therefore, if pressure was not the factor responsible for throwing potash-rich rocks into the orthoclase field, would it not also have affected Nockolds' selected rocks and the others of figure 6 which do not lie in that field? Why, then,

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[7] Of the subrangs Sodipotassic Liparose, Dopotassic Mihalose, and Dopotassic Dellenose (Washington, 1917, pp. 145, 79, and 165, respectively).

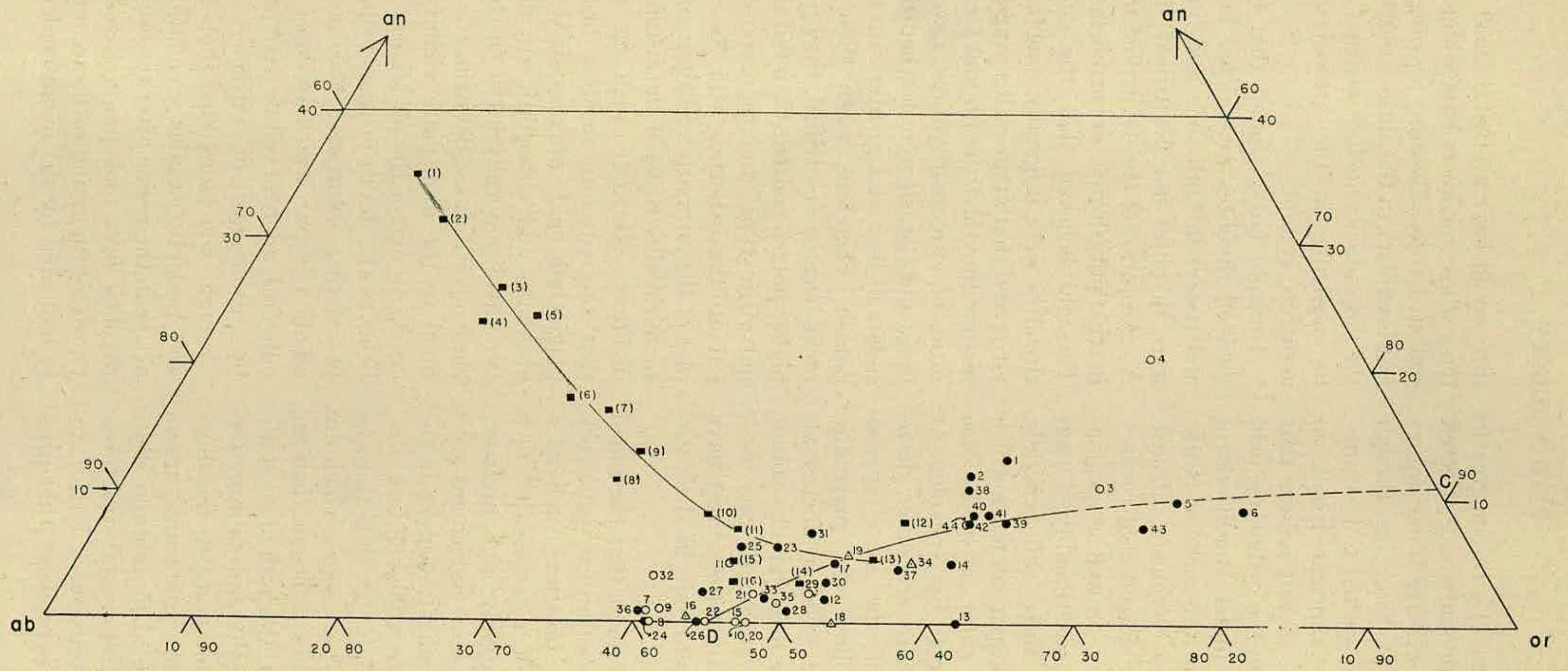

FIG. 6.—The Or : Ab : An ratio of some rocks following a course of crystallization in the plagioclase field and of rocks falling approximately on the cotectic curve. Nos. (1)–(16) = nos. 1–16 of Nockolds (1946). Nos. 1–6 = nos. 3–8 of Washington (1917, p. 79). Nos. 7–37 = nos. 248, 249, 250, 254, 255, 256, 257, 258, 260, 261, 262, 263, 264, 265, 267, 270, 276, 279, 280, 282, 283, 284, 285, 289, 290, 291, 292, 294, 296, and 297 of Washington (1917, p. 145). Nos. 38–44 = nos. 1, 5, 7, 8, 10, 17, and 22 of Washington (1917, p. 165). Square, granite, adamellite, and aplite of Nockolds (1946).

are they still governed by the magmatic rules? Why should pressure have affected some rocks and not others? If one argues that rocks studied by Nockolds, though deep seated, were subjected to less pressure than were the deep-seated rocks in the orthoclase field, then it follows that the volcanic rocks in the orthoclase field also were formed under conditions of higher pressure than the rocks of Nockolds—a conclusion obviously absurd. There probably are deep-seated rocks—granites and aplites, as well as pegmatites—which are unquestionably of magmatic origin; but these will generally have normative feldspar contents which follow the cotectic curve, as in the case of those rocks selected by Nockolds. At the same time, there are other deep-seated varieties of the same species which do not follow the magmatic crystallization rule. The orthoclase-albite-anorthite ratios of such rocks cannot result from strictly magmatic processes; thus metasomatic alterations must have played the significant role in their formation.

It is important to note that the zoned plagioclase crystals of an extrusive rock formed under low pressure, such as a basalt, and those of a deep-seated rock formed under relatively high pressure, such as a gabbro, show agreement with the course of crystallization given in the the albite-anorthite solid-solution diagram (Bowen, 1928, p. 34). In both rocks the zoned crystals have cores which are richer in the anorthite molecule than are the rims. Moreover, the path of crystallization of both basalts and gabbros terminates at the same point in the diopside-albite-anorthite equilibrium diagram (Bowen, 1928, p. 46). Diopside and albite exhibit quite different crystal structures: chain lattice and framework lattice, respectively. It seems probable that pressure would have a greater effect on systems whose members have different crystal structures. Because no pressure effect is evident in the albite-anorthite and the diopside-plagioclase systems, it must be negligible in the orthoclase-albite-anorthite system.

Terzaghi (1935) found that four devitrified rhyolites were richer in potash and poorer in both soda and lime than were rhyolites not devitrified. The Or: Ab: An ratios of the devitrified rocks fall in the potash-rich or orthoclase field. Terzaghi believed that the devitrified rhyolites were originally magmatic and vitric and that at an earlier stage of their history they had the normal Or:Ab:An ratios of vitreous rhyolites. Later, soda, lime, and potash were leached out—the soda and lime at a greater rate than the potash. Therefore, when these altered rocks became devitrified, they possessed higher potash content than did the original vitric type, and they consequently fell into the orthoclase field. Recently the plot of the normative feldspar content of some rhyolite rocks of the Esterel region in France (Terzaghi, 1948, fig. 1) shows that the vitreous obsidian lies in the plagioclase field, whereas six devitrified obsidians and spherulitic rhyolites and two rhyolite porphyries lie in the orthoclase field. Because devitrification is confined to the immediate vicinity of the cracks in one of the obsidians, Terzaghi believes the devitrification to be due to percolating solutions. The crystals of alkalic feldspar, which are most strongly euhedral, are believed to have originated by *replacement* of vitreous material. Terzaghi concludes that hot solutions and possibly gaseous emanations were active in the region after the eruptions of rhyolitic lava took place. Reactions between solutions and rocks are most clearly indicated by the microscopic features of the spherulitic rhyolites that she studied. The secondary potash which enriched the rhyolites during their devitrification either was introduced by hydrothermal solutions or gaseous emanations originating from an underlying body of magma or was derived by local leaching of the rhyolite itself. The potash leached from the rhyolite in one place was carried on in solution and was available for potash enrichment elsewhere. The possible dual origin of the secondary potash in the Esterel region is in harmony with the conclusions reached by Allen (1935), Allen and Day (1934), and Fenner (1936) in their studies of the thermal waters and the altered rhyolites of the Yellowstone Park region.

Fenner (1936, p. 278) observed that not only were orthoclase, analcite, heulandite, and calcite formed as replacements of original minerals by soluble salts (chlorides, carbonates, etc., of the alkalies), but all these difficultly soluble minerals were taken into solution to some extent, migrated rather freely, and were deposited in fissures and other open spaces. Elsewhere, Fenner (1936, p. 279) states that there may be many occurrences of similarly altered rocks in volcanic regions, which, in the absence of complete data, have been regarded as normal lavas. Even analyses of such rocks have been accepted as representing original compositions.

The high potash content of some rhyolites and extrusives may be due to secondary enrichment by potash-bearing solutions. The secondary potash might have been derived in part from these extrusives by leaching and migrating from one place to another. Possibly the potash transfer could take place in the solid state, especially so if evidence for the presence of solutions is lacking. If pressure causes differences in the chemical potentials of the elements in the various parts of country rocks, it is believed that the elements will migrate from areas of higher to areas of lower potentials until equilibrium is reattained (Ramberg, 1944).

Other factors may be responsible for potash-rich pegmatites—perhaps the concentration of volatiles in the last stages of crystallization. Andersen (1931, p. 25) gives two analyses of pegmatites whose projection points apparently lie in the plagioclase field. Others can be found in Washington's tables. On the other hand, some pegmatites lie in the orthoclase field. Though all magmatic pegmatites are supposed to have crystallized from residual solutions rich in volatiles, we find some on the cotectic curve, others in the plagioclase field, and still others in the orthoclase field. We can conclude, therefore, only that we have pegmatites of different origins and that in the case of the magmatic types the presence of volatile constituents has had no significant influence on the course of crystallization.

Moreover, the effect of volatile constituents on the course of crystallization is not too well known; their only important effect, however, seems to be a lowering of the temperature of crystallization, with no discernible influence on its course. Bowen states (1928, pp. 299–300) that the addition of 1 per cent H_2O (the most important volatile constituent) to a liquid composed of 50 per cent $K_2Si_2O_5$ and 50 per cent K_2SiO_3 does not change the course of crystallization or even the proportions of the separated phases from that of the dry melt. Moreover, in Bowen's nephelite-kaliophyllite-silica equilibrium diagram (1937), the lowest temperature of crystallization for a dry melt is 1038° C.; but granites rich in the volatiles and thought to have crystallized from a magma at 700° C. have chemical compositions which place them in the "trough" of this dry-melt diagram. The zoned plagioclase crystals of both peridotites poor in volatiles and granites relatively rich in these follow equally well the rules of plagioclase crystallization given by the albite-anorthite binary equilibrium diagram. One is therefore led to the conclusion that, although the presence of the volatile constituents will lower crystallization temperatures, it will not significantly change the course of crystallization. That is, although fusion surfaces might show differences in relief with increase or decrease of volatiles, the positions and relative reliefs of the cotectic "valleys" and boundary surfaces will remain approximately the same.

The immiscibility of water-rich siliceous liquids does not seem to be the solution. The initial compositions used by Tuttle and Friedman (1948) for the determination of the equilibrium relations of the system Na_2O-SiO_2-H_2O at 250, 300, and 350°, proving that the system possesses liquid immiscibility between 200 and 250°, consist of approximately 50 per cent H_2O. This is much higher than the 10 per cent of H_2O assumed to be in the pegmatitic rest magma. Smith (1948, p. 538) also dealt with solutions of a very highly specialized composition that do not represent a rest pegmatitic magma from which a perthitic rock could crystallize. Smith's solutions had 50 per cent H_2O and less than 1 per cent of K_2O. Goranson's work (1931) makes it unlikely that a perthitic liquid which approximates that of a granite could absorb more than 10 per cent H_2O.

Moreover, the potash-rich rhyolites cannot be explained because their temperature of crystallization is higher than that at which immiscibility occurs.

The experiments by Goranson (1931) have demonstrated a limited miscibility of H_2O in silicate melts. A consequence of this is that, near the end of the consolidation history of a magma, a hydrothermal solution may separate as an independent phase coexisting with the magmatic phase, on the one hand, and with the solid phase (the rock), on the other. The significance of Goranson's work and its implications have been discussed by many petrologists. The exudation of the hydrothermal solutions is believed to mark the final stages in the consolidation of the magma. It is important to note that they are separated from the magma through an immiscibility gap. The composition of the solutions is governed by the endomagmatic hydrothermal differentiation processes as described by Neumann (1948). Magmatic pegmatites are the precipitates from the residual magmatic melt prior to the hydrothermal stage.

It appears, therefore, that neither the reaction relation anorthite-orthoclase nor pressure nor the volatile constituents can account for the composition of the Black Hills perthitic pegmatites. Metasomatic alterations which were found by Terzaghi (1948) to be responsible for the presence in the orthoclase field of the potash-rich rhyolites that she studied might also be the reason why the Black Hills potash-rich pegmatites lie in the same field. It is uncertain whether all the potash-rich deep-seated, hypabyssal, and extrusive types plotted (figs. 4 and 5) are metasomatic rocks or were formed by some other processes. This is not discussed in this paper and will be the subject matter of another work by the author.

If it turns out that the hypothesis of potassium metasomatism is true, the orthoclase field of the orthoclase-albite-anorthite ternary diagram might well be named the "potassium metasomatism field." Perhaps also there are rocks which possess a higher albite normative composition than is consistent with a truly magmatic origin. Examples of these are the albite-rich granites and the albitites. A chemical analysis of an albitite from the Black Hills is given in table 3; this has an Or:Ab ratio of 3:97. These would be placed in a field nearer to the Ab corner of the Or-Ab-An ternary diagram; this field might be named the "sodium metasomatism field."

Whether the potash pegmatites of the Black Hills were once magmatic and have been metasomatized or are merely metasomatic is another subject and will be considered elsewhere.

GENESIS OF PERTHITE SCHISTS

Table 3 shows the chemical analyses of three country rocks. The rock formula introduced by Barth (1948) of each of the analyzed rocks—the average perthite, the cleavelandite, and the microcline—was calculated as shown in table 7. Table 8 shows quantitatively the gains and losses required to change the normal schist to a perthitized schist, albitite, and perthite. The normative compositions, using Von Wolff's method, were also calculated in table 9.

Figure 7 is a reproduction of figures 7 and 8 of Reynolds' work on the geochemical changes leading to granitization (1946). The schist of the Glendale area lies in the field of the aureole sediments of the Flamouth granite area. It lies also in the field of the aureole shales of the Dartmoor area (Reynolds, 1946, fig. 5). The perthitized schist falls in the fields representing the Flamouth granite, the granitization series of the Dartmoor area, and the granites of the latter region. The albitite and the average perthite lie in a separate field closer to the *L* of the diagram. This means that partial feldspathization of the schist could give rise to perthitic schist, which has a chemical composition similar to potash granites. If feldspathization is more complete, rocks will form that possess a chemical composition near that represented by *L* of the Von Wolff diagram.

Such rocks are the albitites and the perthitites (monomineralic rocks composed of perthite). The formation of such rocks is an end-stage in Reynolds' sequence of changes of pelitic and semipelitic rocks. These changes may take place by the reorganization of the atoms and molecules inside the schist. Table 8 would then refer to loss and gain inside certain volumes of the schist, whereas the whole schist complex may show little change in bulk chemical composition. The perthite crystals in this schist seem to grow and recrystallize at the expense of the schist material, similar to the formation of porphyroblasts in other metamorphic rocks. In places they seem to have pushed aside the schist which forms the groundmass of the rock (pl. 1, *A*). In places there are crystals exceeding 6 cm. in length, exhibiting megascopic sieve texture (pl. 1, *C*). A perthitic pegmatite which has approximately the same chemical composition and shows identical textures as those of the perthite of the schist may thus be formed in a similar manner. It is worth mentioning that Goldschmidt (1934) attributed the source of scandium, the rare element found in some pegmatitic pockets, to the country rocks which are mainly amphibolites and not to a pegmatitic magma. This was concluded from spectrographic studies. The amphibolites which could give their scandium lend support to the belief that the schist could contribute potassium to form the feldspars. If this be true, the change is illustrated by the following: Three schist "unit cells" (the least number of the schist "unit cell" to form a perthite is 3) are composed of: K 16.86, Na 5.37, Ca 1.62, Mg 8.76, Fe 11.43, Al 45.45, Ti 0.90, Si 181.35, P 0.39, H 26.85; and the average perthite "unit cell" consists of: K 14.45, Na 4.35, Ca 0.39, Mg. 0.05, Fe 0.07, Al 21.20, Ti 0.0, Si 58.80, H 1.37.[8] Therefore, the equation of the process of transformation will be

$$3 \text{ schist} \rightleftharpoons \text{perthite} + 2 \text{ schist relic.}^{9} \quad (1)$$

The "unit cell" of this schist relic is composed of: K 1.21, Na 0.51, Ca 0.62, Mg 4.36, Fe 5.68, Al 12.13, Ti 0.45, Si 61.28, P 0.20, H 12.74 (see Table 10).

TABLE 7

FORMULAE OF THE COUNTRY ROCKS

Rock	K	Na	Ca	Mg	Ba	Mn	Fe^{++}	Fe^{+++}	Al	Ti	Si	P	O	H
Schist	5.62	1.79	0.50	2.92	0.04	0.04	2.82	0.95	15.15	0.30	60.45	0.13	160	8.95
Perthitic schist	7.20	3.80	0.38	1.46	0.04	0.00	0.78	0.42	15.70	0.16	61.62	0.32	160	6.85
Albitite	0.48	16.30	0.54	0.70	0.00	0.00	0.15	0.10	18.34	0.00	60.51	0.38	160	1.32
Average perthite	14.45	4.35	0.37	0.05	0.02	....	....	0.07	21.20	0.00	58.80	....	160	1.37
Cleavelandite	0.11	18.37	0.47	0.11	0.01	....	....	0.06	20.24	0.00	59.21	....	160	2.42
Microcline	17.50	2.15	0.02	0.03	....	....	....	0.03	20.90	0.00	59.00	....	160	1.65

TABLE 8

GAINS AND LOSSES IN THE SCHIST

	Addition and Subtraction
Schist to perthitic schist	*Addition:* 1.58 K, 2.01 Na, 0.55 Al, 1.17 Si, 0.19 P
	Subtraction: 0.12 Ca, 1.46 Mg, 0.04 Mn, 2.57 Fe, 0.14 Ti, 2.10 H
Schist to albitite	*Addition:* 14.51 Na, 0.04 Ca, 3.19 Al, 0.06 Si, 0.25 P
	Subtraction: 5.14 K, 2.22 Mg, 0.04 Ba, 0.04 Mn, 3.52 Fe, 0.30 Ti, 7.63 H
Schist to average perthite	*Addition:* 8.83 K, 2.56 Na, 6.05 Al
	Subtraction: 0.13 Ca, 2.87 Mg, 0.02 Ba, 0.04 Mn, 3.70 Fe, 0.30 Ti, 1.65 Si, 0.13 P, 7.58 H

TABLE 9

NORMATIVE COMPOSITION AFTER VON WOLFF

Rock	Alk *f*	An	Mt	Aug	*Q*	*t*	*L*	*M*	*Q*
Schist	37.6	2.4	1.2	13.4	41.1	4.3	44.3	14.6	41.1
Perthitic schist	55.2	2.0	0.6	5.2	34.3	2.8	60.0	5.8	34.3
Albitite	84.2	2.8	0.1	2.0	10.9	0.2	87.2	2.1	10.9
Average perthite	94.7	3.9	0.1	0.1	0.1	1.1	99.7	0.2	0.1

Figure 8 shows a crystal of perthite about 2 cm. in length, forming a zone surrounded by another zone containing

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[8] Ba is taken into Ca, and Mn is taken into Fe.

[9] Material produced after the petroblastic formation of perthite from the schist.

schist relic material. Figure 9 is drawn to explain a mode of formation of such a crystal. The arrows indicate the direction of migration, and the amounts of the diffusing ions are shown. The three "unit cells" of equation (1) are called in figure 9 the "outer shell," the "inner shell," and the "core." Potassium and sodium migrated from both the outer and the inner shells toward the core, which acted as a receiver for the feldspathic material. The core, which possesses K 5.62 and Na 1.79, has thus gained K 5.62 and Na 1.79 from the inner shell and K 3.21 and Na 0.77 from the outer shell. The core also gained Al 6.05 migrating from the inner shell and at the same time lost the excess of other ions over and above those necessary to form the perthite. The inner shell has gained K 1.21, Na 0.51, and Al 3.03 migrating from the outer shell and the other ions

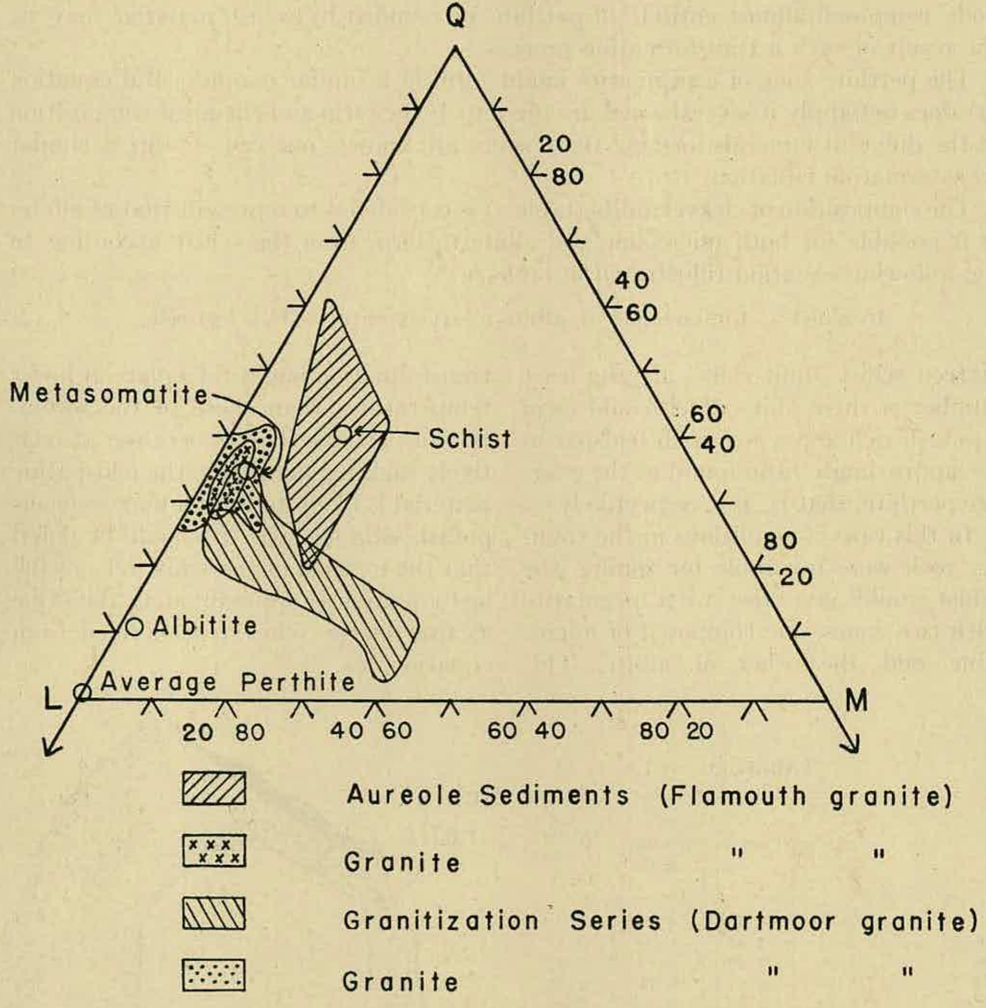

FIG. 7.—Von Wolff diagram showing the composition of the studied rocks

migrating from the core in the amounts indicated on the arrows. Lastly, the outer shell gained material migrating from the core as given in figure 9. In this case it is supposed that the outer and the inner shells have the same composition after the development of the perthite. If such were not the case, the outer and inner shells would form two zones different in composition. The development of a pegmatite body composed almost entirely of perthite surrounded by schist material may be the result of such a transformation process.

The perthite zone of a pegmatite might form in a similar manner. But equation (1) does not apply if several zones are present. If the ratio and chemical composition of the different minerals forming these zones are known, one can set up a similar transformation equation.

The composition of cleavelandite (table 2) is considered to represent that of albite. It is possible for both microcline and albite to form from the schist according to the following equation (illustrated in table 11):

$$16 \text{ schist} \rightleftharpoons 4 \text{ microcline}^{10} + \text{albite (cleavelandite)} + 11 \text{ schist relic} . \qquad (2)$$

Sixteen schist "unit cells" are the least number of these units which could form a potash-rich and a soda-rich feldspar in the approximate ratio found in the average perthite, that is, 4:1, respectively.

In this case, if conditions in the country rock were favorable for zoning, the schist could give rise to a pegmatite with two zones, one composed of microcline and the other of albite. This transformation might take place at lower temperatures than those of the formation of perthite. This is because, at relatively high temperatures, the feldspathic material is likely to form a homogeneous potash-soda feldspar. It should be noted that the formula of the schist relic of the last equation is approximately the same as that of the schist relic derived from equation (1).

TABLE 10

	3 Schist =	Perthite +	2 Schist Relic	Formula of Schist Relic
K.	16.86	14.45	2.41	1.21
Na.	5.37	4.35	1.02	0.51
Ca.	1.50	0.39	1.13	0.57
Mg.	8.76	0.05	8.71	4.36
Ba.	0.12	0.02	0.10	0.05
Mn.	0.12	....	0.12	0.06
Fe^{++}.	8.46	....	8.46	4.23
Fe^{+++}.	2.85	0.07	2.78	1.39
Al.	45.45	21.20	24.25	12.13
Ti.	0.90	0.00	0.90	0.45
Si.	181.35	58.80	122.55	61.28
P.	0.39	....	0.39	0.20
H.	26.85	1.37	25.48	12.74

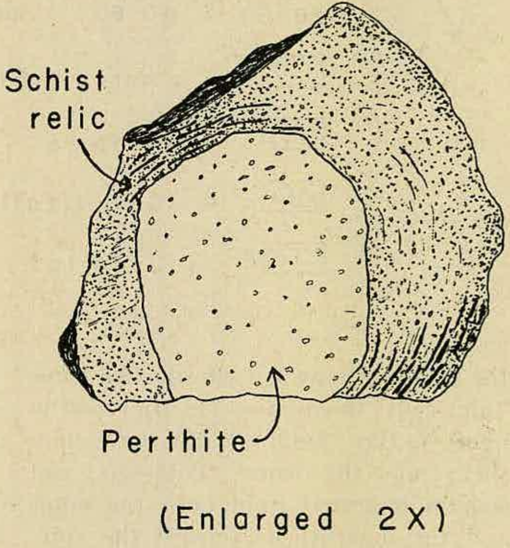

FIG. 8.—Perthite metacryst in the schist

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[10] The formula of microcline (table 1) of Hugo pegmatite is used here.

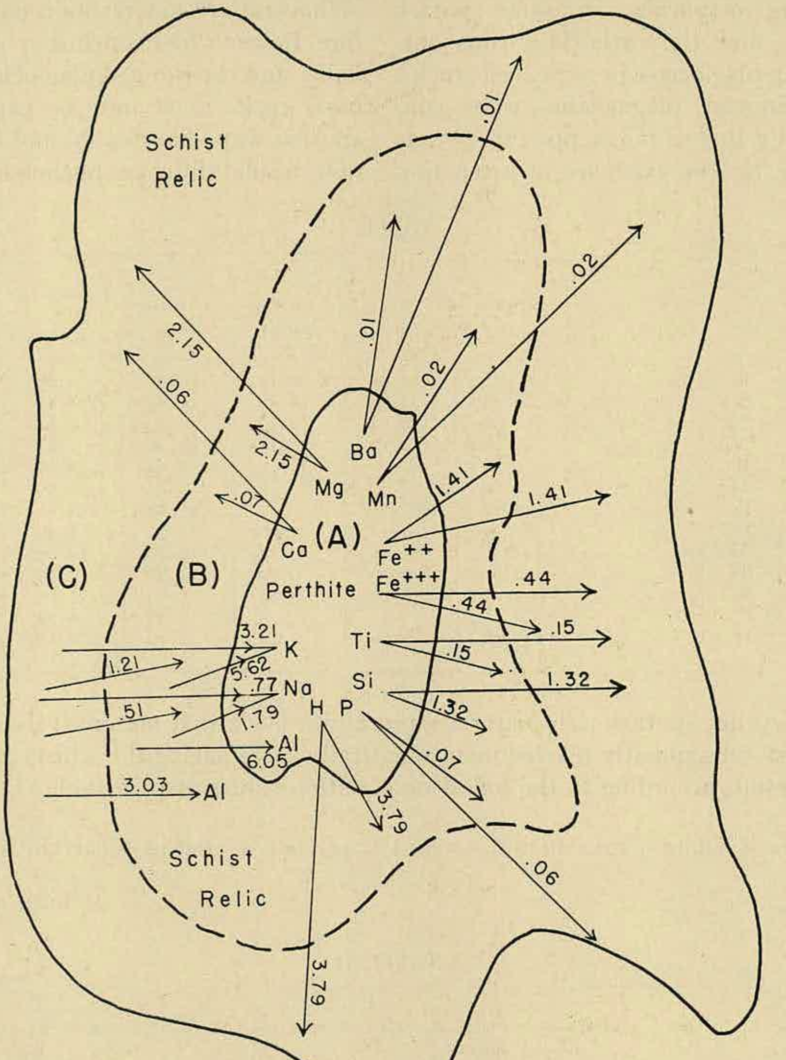

FIG. 9.—Reorganization of the schist material to form the perthite metacryst. *A*, core of innermost shell; *B*, inner shell; *C*, outer shell.

It is worth mentioning that the formation of microcline and albite suggests an explanation of the plagioclase rims surrounding orthoclase in some potash granites and the orthoclase rims surrounding plagioclase in some basic rocks. Such rimmed plagioclases were considered by Bowen (1928, pp. 227–233) as evidence for the existence of a reaction relation between anorthite and orthoclase. In a recent work, Schairer and Bowen (1947) found that anorthite and orthoclase are not reaction pairs; therefore, Bowen's first conclusion is no longer valid, and the rimmed plagioclases of the basic rocks must now be explained in another way. They could find their solution in solid diffusion phenomena.

TABLE 11

	16 Schist	= 4 Microcline	+ Cleavelandite	+ 11 Schist Relic	Formula of Schist Relic
K	89.92	70.00	0.11	19.81	1.80
Na	28.64	8.60	18.37	1.67	0.15
Ca	8.00	0.04	0.47	7.49	0.67
Mg	46.72	0.12	0.11	46.49	4.22
Ba	0.64	....	....	0.64	0.06
Mn	0.64	....	....	0.64	0.06
Fe^{++}	45.12	....	....	45.12	4.10
Fe^{+++}	15.20	0.12	0.06	15.02	1.40
Al	242.40	83.60	20.24	138.60	12.60
Ti	4.80	0.00	0.00	4.80	0.43
Si	967.20	236.00	59.21	671.99	61.09
P	2.08	....	....	2.08	0.19
H	143.20	6.60	2.42	134.20	12.18

If microcline (potash-rich material) and albite (soda-rich material) derived from the schist subsequently reacted metasomatically by replacing the schist, other rocks would result, according to the following equation (illustrated in table 12):

$$\text{Microcline} + \text{albite (cleavelandite)} + \text{schist} \rightleftharpoons \text{perthite} + \text{albitite} + \text{perthite schist} + \text{basic ions}\,. \tag{3}$$

TABLE 12

	Microcline	+ Cleavelandite	+ Schist	= Perthite	+ Albitite	+ Perthite Schist	+ Basic Ions
K	17.50	0.11	5.62	14.45	0.48	7.20	....
Na	2.15	18.73	1.79	4.35	16.30	3.80	....
Ca	0.02	0.47	0.50	0.37	0.54	0.38	....
Mg	0.03	0.11	2.92	0.05	0.70	1.46	0.85
Ba	....	0.01	0.04	0.02	0.00	0.04	....
Mn	....	....	0.04	....	0.00	0.00	....
Fe^{++}	....	....	2.82	....	0.15	0.78	1.89
Fe^{+++}	0.03	0.06	0.95	0.07	0.10	0.42	0.45
Al	20.90	20.24	15.15	21.20	18.34	15.70	....
Ti	0.00	0.00	0.30	0.00	0.00	0.16	0.14
Si	59.00	59.21	60.45	58.80	60.51	61.62	....
H	1.65	2.42	8.95	1.37	1.32	6.85	....

The amounts of potassium, sodium, aluminum, and silica of the reactants are approximately equal to those of the products; however, basic ions are released in the reaction and are thus free to migrate to other parts of the country rock, where they may, by reaction, give rise to other basic rocks. Perhaps they migrated to the north of the studied area, where they may have played a role in the formation of some amphibolites outcropping there. Another working hypothesis is that they might have diffused to lower levels in the gravitational field. A combination of both explanations is also a possibility. Figure 10 is a summary of the reactions discussed above.

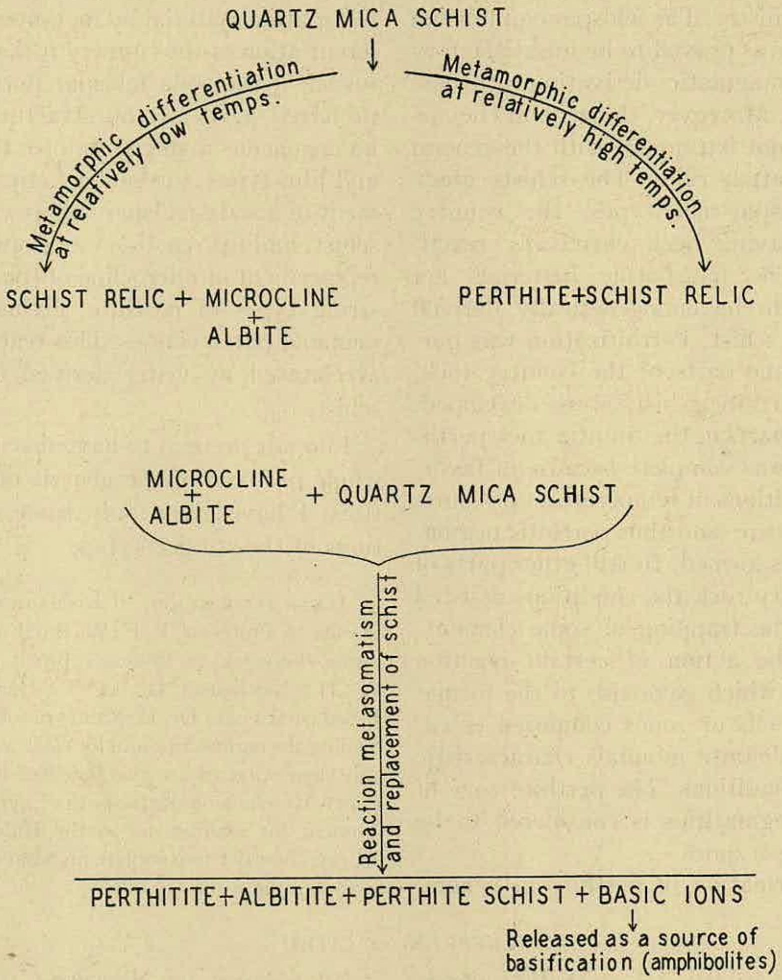

FIG. 10.—Metasomatic development of the Black Hills perthite

SUMMARY AND CONCLUSIONS

Some pegmatitic perthites and country rocks of the Glendale area of the Black Hills of South Dakota were chemically analyzed and microscopically studied in order to explain the origin of the perthites of this area. The textures of the perthites and the microscopic features of the country rocks do not seem to be of a magmatic nature; rather, they support metasomatic activities. Evidence of metasomatic derivation of the perthites was given in the discussion of their chemistry. The feldspar equilibrium diagram was proved to be unsatisfactory for the magmatic derivation of these perthites. Moreover, the general chemistry does not harmonize with the general crystallization rules. The schists grade into feldspar-rich types, the country schists having been chemically reactivated. The feldspathic materials are thought to be endogenetically derived from the schist. Perthitization was partial in some parts of the country rock, where perthite schists were developed. In other parts of the country rock perthitization was complete because of favorable conditions of temperature, pressure, and structure, and thus perthitic pegmatite bodies formed. In still other parts of the country rock the conditions assisted both in the trapping of some elements and in the action of certain reaction processes which gave rise to the formation of shells or zones composed essentially of definite minerals characteristic of such conditions. The perthite zone of certain pegmatities is considered to be one of these zones.

The formation of perthite in general was a complex metasomatic process which took place in various stages. The following steps are believed to have taken place during the evolution of the studied perthites: (1) endogenetic development of homogeneous potash-soda feldspathic material by metamorphic differentiation of the country rocks; (2) diffusion of the soda feldspar portion into preferred parts of the structure of the homogeneous material to form the string and film types; (3) endogenetic development of a soda-feldspar (albite) from the schist; and (4) reaction metasomatism or replacement of microcline of the film and string types of perthite, giving rise to vein and patch classes. This reaction was accelerated by water derived from the schist.

I do not pretend to have discussed the whole problem of the genesis of pegmatites. I have given only some explanations of the studied types.

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PART V

OBSERVATIONS ON THE DISTRIBUTION OF TRACE ELEMENTS IN THE PERTHITE PEGMATITES OF THE BLACK HILLS, SOUTH DAKOTA

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ABSTRACT

The trace-element contents of the Black Hills perthites have been determined spectrographically. Their chief trace elements are found to be Rb, Ba and Sr. The distribution and relative proportions of the different trace elements are discussed. They seem to support the metasomatic derivation of the perthites from the schists of the country rocks in which the pegmatites occur.

STATEMENT OF PROBLEM

The perthite pegmatites of the Black Hills, South Dakota, have been considered by the writer (Higazy, 1949) to have been formed not by magmatic crystallization but mainly by replacement processes. The chemical composition of these perthites as well as their textural and microscopic features support their metasomatic derivation. Moreover, field observations seem also to be in favor of the replacement origin of these pegmatites. The trace-element contents of the perthites and of some of the country rocks were determined spectrographically in order to study the significance of such elements in the petrogenesis of these perthites.

SPECTROGRAPHIC ANALYSIS AND DATA OBTAINED

Portions of the powders used previously for chemical analysis were spectrographically analysed by the writer at the Macaulay Institute for Soil Reserach at Aberdeen, Scotland, using the semi-quantitative method described in detail by Mitchell (1948). The determined trace elements, and the wave lengths /

lengths of their respective diagnostic lines have already been recorded by the writer (Higazy, 1952a).

The trace-element contents of the analysed perthites and cleavelandite are listed in Table 1; and those of the other country rocks are given in Table 2. For the exact location of these rocks, and their chemical composition and petrographic description, reference should be made to an earlier paper (Higazy, 1949, Fig. 1, p. 556, p. 559 and pp. 562-564).

MAJOR ELEMENTS

The average ratio Or:Ab:An in the analysed perthites is 75.8:22.4:1.8 (Higazy, 1949, p. 561). The most important major elements in their composition are, therefore, Si, Al and K. Na and Ca may also be significant but not to the extent of that of K. The ranges of K_2O, Na_2O and CaO in these perthites are 10.58 - 15.62, 0.38 - 3.29 and 0.15 - 0.82 per cent respectively.

Small amounts of Mg and Fe are usually present in the composition of perthites. MgO and total iron oxides (as Fe_2O_3) in the perthites of the Black Hills vary from 0.00 - 0.12 /

0.12 and 0.06 - 0.13 per cent respectively. The exact mode of occurrence of these elements, namely, Mg, Fe^{2} and Fe^{3}, in the structure of potash feldspar is not yet perfectly known. Among the major elements of the perthite, Na possesses the closest ionic radius (0.98 Å) to that of Mg (0.78) and that of Fe^{2} (0.83). It is not certain that Mg and/or Fe^{2} replace Na in the feldspar lattice since (a) Na usually has a higher co-ordination number and (b) Mg and Fe^{2} appear to have much higher activation energy values (E-value). Mg is known to replace Al in biotite and hornblende. Although these species have different structures from that of the feldspars, yet the possibility of such replacement in the latter should not be disregarded. If, however, Mg and Fe^{2} have no definite position in the structure of the feldspar, it may then be conjectured that they are either dispersed through the structure or present in minute mineral inclusions in the perthite. A combination of these two alternatives is also a possibility.

Fe^{3} has an ionic radius of 0.67 Å, not very different from that of Al^{3} (0.57), and both have the same valency. If the feldspar lattice is favorable for the admission of Fe^{3}, it may be surmised that it replaces Al, since Wickman (1943, p. 381) points out that Fe^{3} may be considered as so immobile that it could be incorporated in a suitable lattice under any conditions.

TRACE /

TRACE ELEMENTS

The different trace elements in the perthite pegmatites are classified according to their abundance into four categories: abundant, present in small amounts, rare and very rare.

Abundant:

Rb, Ba and Sr.

Present in small amounts:

Li, Pb, Ga and
Tl.

Rare:

Mn, V, Cu;
Be, Ge and
Zr

Very rare:

Cr, Co, Ni, Sc;
Sn, Ag, Mo;
La, Y and
In.

Rubidium, barium and strontium

The Rb content in the analysed perthites (Nos. 1 - 15) varies from 600 to 9500 ppm. and the average is 2665 ppm.

(Table /

(Table 1). The average in the two analysed microcline-perthites from the Hugo pegmatite is 3600 ppm. The Rb content of the potash feldspar of the Caledonian granodioritic rocks of Scotland studied by Nockolds and Mitchell (1948), Table XXI, p. 571 varies from 60 to 800 ppm., the highest being in potash feldspar from aplite, Garabal Hill-Glen Fyne Complex, Scotland. But the perthite found as phenocrysts in the granites of the Glendale area of the Black Hills (analysis 13, Table 1) has 900 ppm. Rb. On the whole, the Rb content of the Black Hills perthites seems to be higher than that of the Caledonian feldspars.

Ahrens (1945b) examined the Rb content of 67 specimens of potash feldspars (microcline, orthoclase and perthite). Most of these, however, were collected from pegmatites of widely different occurrence. Their Rb content varies from 40 to 2560 ppm. with an average of 295 ppm. The range in the 16 green microcline (amazonite) examined also by him, is from 640 to 11,880 ppm. with an average of 3670 ppm. The average in perthites of the Black Hills (2665 ppm.) is not appreciably lower than that of the green microcline. Among the fifteen analysed perthites of the Black Hills, one is grayish in color (No. 9), five are grayish-white (Nos. 2, 4, 8, 10 and 12) and other nine are pinkish (Higazy, 1949, p. 563). The grayish perthite is relatively /

relatively the richest in Rb (9500 ppm.). The average Rb content of the six grayish and grayish-white samples is 4835 ppm., while that of the nine pinkish perthites is only 1220 ppm. This seems to be a fairly reliable indication that the pink varieties of potash feldspar contain relatively less Rb than the grayish types. The average Rb of the grayish perthites (4835 ppm.) lies within the range given by Ahrens (1945b, p. 229) for amazonite (4570-5485 ppm.) and closer to the minimum limit, while the average for the pink types is notably less than for the green species being only 1220 ppm.

Ba in the Black Hills perthites is less abundant than Rb except in the perthite porphyroblast (No. 7) found in the perthitized schist. It is interesting to notice that the color of this Ba-rich perthite is salmon red and that it contains 0.13 per cent of total iron oxides as Fe_2O_3, an amount similar to that of perthite No. 15, which is pinkish. Moreover, perthites Nos. 10 and 11 are grayish-white and deep pink, respectively; yet each has 0.09 per cent Fe_2O_3. But the Ba content of the grayish-white perthite (380 ppm.) is less than that of the deep pink (1500 ppm.). The reddish coloration, therefore, seems to be related to relative enrichment in Ba rather than in Fe.

The Ba content ranges from 20 to 10,000 ppm. The highest abundance for the pegmatitic perthites excluding the perthite porphyroblast of the schist is 1500 ppm. while the average is 965 ppm. The average Ba content of the microcline-perthites of the Hugo pegmatite is 290 ppm. In the potash feldspars of the Caledonian granodioritic rocks Ba ranges from 2000 to 8000 ppm. and is more abundant than Rb, as in the porphyroblast of the perthitized schist of the Glendale area of the Black Hills. But the Ba content (50 ppm.) of the potash feldspar from aplite, Garabal Hill-Glen Fyne Complex (Nockolds and Mitchell, 1948, p. 571) is lower than that of Rb (2000 ppm.), as in the pegmatitic perthites and the perthite phenocryst of the granite of the Black Hills. Although the data for the Black Hills perthites do not show a regular relationship between Rb and Ba, yet they suggest that the relatively Rb-rich perthite (No. 9) possesses a relatively low content of Ba.

Sr varies from 20 to 1500 ppm. with an average of 270 ppm. It is less abundant than Ba in most of the analysed perthites, as in the potash feldspars of the Caledonian rocks and those of the Pre-Cambrian granites of Boulder Creek, Overland Mtn. and Silver Plume, Jamestown, Colorado, examined by Bray (1942).

That Rb, Ba and Sr are concentrated in the K-rich feldspars is very obvious, especially when comparison is made with /

with the content of these three elements in cleavelandite. This Na-rich species has only 0.09 per cent K_2O and its Rb, Ba and Sr contents are 2, 5 and 100 ppm. respectively. Rb and Ba are thus present in negligible amounts compared with their respective average abundances in the perthites. Sr, however, is relatively high. But cleavelandite has 0.50 per cent CaO. Its Or:Ab:An ratio is 0.6:97.0:2.4 (Higazy, 1949, p. 561). It is quite likely that Sr (1.27 Å) substitutes for Ca (1.06) in cleavelandite.

Lithium, Lead and Gallium

Li is present in all the analysed perthites but in widely variable amounts, the range being from 2 to 230 ppm. and the average, 60 ppm. It seems that the relatively Rb-rich perthites (Nos. 8, 9 and 10 of Glendale area pegmatites and No. 16 of the Hugo pegmatite) are also rich in Li. But this relationship cannot be generalised since perthite No. 12 has 2000 ppm. Rb and 130 ppm. Li, while perthite No. 4 has 5000 ppm. Rb and only 7 ppm. Li. Moreover, the potash feldspar of the adamellite, Morven-Strontian Complex, Scotland (Nockolds and Mitchell, 1948) has 600 ppm. Rb and 8 ppm. Li, while the range of the Rb content of the other Caledonian potash feldspars is from 60 to 2000 ppm. and their Li is below its limit of sensitivity (1 ppm.).

The /

The position of Li in the feldspar lattice is debatable. Li feldspars do not exist in nature, and according to Ahrens (1945a, p. 82), a Li content greater than 2 - 5 ppm. is exceptional in the feldspars. However, the Li content of the micas is generally appreciable. There are good grounds for assuming that Li replaces Mg in biotite. Both elements have the same ionic radius (0.78 Å) and the same coordination number. On the other hand, muscovite does not usually contain Mg. But Hendricks (1939, p. 763) mentions that Li can enter the muscovite structure giving rise to lithium muscovite. Moreover, Ahrens finds as much as 1.2 per cent Li_2O in the muscovites of Uranoop River Area, Namaqualand, S. Africa (Ahrens, 1945a). He suggests that Al may be replaced by Li in the muscovite structure providing that electrostatic balance is restored by a concomitant replacement elsewhere in the lattice. The proposed substitution of Al by Li in muscovite may possibly imply that such replacement could also take place in the feldspar lattice as Lundegårdh suggests (1947, p. 108). It should also be mentioned that Li (0.78 Å) may replace Na (0.98). Cleavelandite has 150 ppm. Li, but this Na-rich species also possesses a high amount of Al. On the other hand the analysed albitite (Table 2) is relatively poor in Li (10 ppm.). This makes the replacement of Na by Li rather uncertain.

Pb /

Pb is present in all the analysed perthites. Omitting No. 15 it ranges from 10 to 40 ppm. with an average of 25 ppm. Perthite No. 15 is exceptionally high in Pb (450 ppm.) and if it is taken into account, the average rises to 53 ppm. It is interesting to notice that the total of Rb, Ba and Sr in the exceptionally high Pb perthite (No. 15) is the lowest among all the samples tested. Pb ores were not detected microscopically in the thin section of this perthite. Pb is below its limit of sensitivity (10 ppm.) in cleavelandite. It is most likely replacing K in the lattice of the potash feldspars; the association of Pb and K in silicic rocks has been pointed out by Sandell and Goldich (1943, p. 169).

Ga occurs in the analysed samples rather uniformly, the range being from 30 to 50 ppm. and the average 33 ppm. Cleavelandite has 70 ppm. Ga. The geochemical relationship between Ga and Al is unique. Ga feldspars, $KGaSi_3O_8$ and $NaGaSi_3O_8$, in which Ga completely replaces Al, have been synthesized by Goldsmith (1950).

Thallium

The abundance of Tl in the perthites of the Black Hills is very interesting. The average Tl content of the fifteen perthites of the Glendale area is 29 ppm. It is found /

found in amounts below its limit of sensitivity (30 ppm.) in some perthites and in others it may be present up to 150 ppm. Shaw (1952, p. 128) reports 84 and 21 ppm. Tl in the microcline-perthites of Custer Mt. and the High Climb pegmatites of the Black Hills respectively. The microcline of the Hugo pegmatite has 80 ppm. Tl. In the five perthites which possess less than 1000 ppm. Rb (Nos. 6, 7, 11, 13 and 15) Tl is below its limit of sensitivity. Moreover, the lepidomelane-skarn of Co. Donegal, Ireland, examined by the writer (Higazy, 1952a) has as much as 800 ppm. Rb and its Tl content is undetectable. Of the four perthites (Nos. 2, 5, 14 and 16) in which Rb varies from 1000 to 1500 ppm. Tl is present in detectable amount (40 ppm.) only in No. 5. All the remaining perthites (Nos. 1, 3, 4, 8, 9, 10, 12 and 17) contain appreciable amounts of Tl together with at least 2000 ppm. of Rb. This clearly shows that there is a geochemical relationship between Rb and Tl as suggested by Ahrens (1948). It should be stated that Cs (8079.02 Å line) was detected qualitatively in only the spectrum of the perthite No. 9 which possesses the relatively highest contents of both Rb (9500 ppm.) and Tl (150 ppm.). There may be, therefore a relationship between Cs on the one hand and Rb and Tl on the other, especially if we consider that the caesium mineral pollucite examined by Ahrens (1945b) also contains appreciable /

appreciable amounts of both Rb and Tl. However, more data from several other Rb-rich potash feldspars are needed to establish the suggested relationship.

The Rb/Tl ratio in the perthites of the Black Hills varies from 25 to 93 with a mean of 60. Ahrens (1945b) concluded that the mean weight ratio Rb_2O/Tl_2O is 110 and that the limits of variation are 30 and 650. He also mentions that this ratio can vary in the same type of mineral from one area to another. The mean value of this ratio for the perthites of the Black Hills is 64, with variation from 28 to 98. The log. per cent relationship between Rb_2O and Tl_2O is represented graphically in Fig. 1. The results are practically the same as those plotted by Ahrens (1945b, Fig. 3) and the slope of the graph in both cases is nearly 45°.

Rb and Tl have the same ionic radii (1.49 Å) and are concentrated in potash-rich minerals, where they enter into the lattices with about the same ease, replacing K.

Manganese, vanadium and copper

Each of the elements Mn, V and Cu is found in almost uniform amounts. Mn varies from 7 to 15 ppm. with an average of 10 ppm.; V from amounts below its limit of sensitivity (5 ppm.) to 20 ppm. with an average of 6 ppm.; and Cu from 3 to /

to 5 ppm. with an average of 4 ppm. The exact position of each of these elements in the lattice of the potash feldspar is not known. Judging from the ionic radii of Mn^2 and Cu^2, 0.91 and 0.83 Å, respectively, it may be surmised that they replace Na (0.98), and that V^3 (0.65) substitutes for Al (0.57).

The contents of V (10) and Cu (5 ppm.) in cleavelandite are within the range of these elements in the perthites. However, the Mn content in this Na-rich feldspar (40 ppm.) is much higher than in any of the perthites.

Beryllium and germanium

Be is found in all the analysed perthites except one (No. 6). It varies from 5 to 8 ppm. Ge, however, is found in only five perthites of the Glendale area and in the microcline of the Hugo pegmatite. Its range is 10 to 15 ppm. It is likely that both Be and Ge replace Si in the feldspar lattice, since the ionic radius of Be (0.34 Å) and that of Ge (0.44) are close to the radius of Si (0.39). Moreover, Ge feldspars, in which Ge completely replaces Si, have been synthesized by Goldsmith (1950). Cleavelandite is richer in both Be and Ge than the perthites, having as much as 120 ppm. of Be and 20 ppm. of Ge.

Zirconium

Zr is found only in one perthite (No. 5) and there it is present in rather high amount (300 ppm.). This makes it very likely that minute inclusions of zircon are responsible for the Zr present in No. 5.

The very rare trace elements

Among the very rare trace elements in the analysed perthites are Cr, Co and Ni. Cr is found in eight perthites in amounts varying from 1 to 5 ppm., but below its limit of sensitivity in the others. Co and Ni, if present at all, are below their limits of sensitivity (2 ppm.) in all the analysed samples. In six of the perthites it can be stated that the relative distribution of Cr, Co and Ni is $Cr > Co = Ni$.

Sc, if present is in amounts below its limit of sensitivity in all the perthites.

Cr, Co, Ni and Sc are elements which generally replace Mg, Fe^2 and Fe^3 in crystal lattices. The relative deficiency of the perthites in these major elements explains the impoverishment of their replaceable trace elements.

Ag is present in most of the analysed perthites in amounts ranging from < 1 to 4 ppm. The ionic radius of Ag is 1.13 Å, very close to that of K. It is possible that the relatively /

relatively small amount of this trace element replaces K in the lattice.

Sn is found in detectable amount in only one sample (No. 16), collected from the Hugo pegmatite. The high content of Sn (200 ppm.) present in this perthite appears to be accidental, being attributable to very minute inclusions of Sn minerals, possibly cassiterite.

Mo is found in one perthite from the Glendale area and in another from the Hugo pegmatite, the Mo content in each being only 1 ppm.

La, Y and In, if present, are each in amounts below the respective limit of sensitivity.

SIGNIFICANCE OF THE DISTRIBUTION OF THE TRACE ELEMENTS

The petrogenetic significance of the distribution of the various determined elements in the perthites can be studied with regard to (a) the composition of the different perthites and (b) the trace-element contents of the associated country rocks: namely, the unaltered schist (quartz-muscovite-biotite-schist), the perthitized schist, the granite and the perthite pegmatites.

(a) Bray (1942) estimated certain trace elements in the potash feldspars of both Pre-Cambrian granites and their corresponding pegmatites. These rocks were supposed to be of magmatic origin. He (Bray, 1942, p. 797) remarked that the pegmatite minerals usually contain less of almost every minor element than the corresponding minerals from the parental granitic rocks. The statement that pegmatitic minerals should be relatively less enriched in almost every minor element, is too broad a generalisation; it is not in complete harmony with Goldschmidt's principles of the replacement of major by trace elements (Goldschmidt, 1937 and 1945), replacement being a process which is mainly governed by the electrostatic charges and the ionic radii of the elements concerned. According to these principles, there should be certain elements which become relatively concentrated in the pegmatite minerals, provided that such minerals also occur in the parental rocks. In such cases the ratio of the content of the trace element to that of its replaceable major element should be higher in the pegmatite mineral. Rb is an example of this, since its ionic radius (1.49 Å) is greater than that of K (1.33). The potash feldspar of aplite from the Garabal Hill-Glen Fyne Complex in Scotland has 2000 ppm. Rb, while the average of this element in the potash feldspars of the granodioritic rocks supposed to have crystallized /

crystallized earlier from the magma is only 425 ppm. (Nockolds and Mitchell, 1948). Moreover, the average Rb_2O content of the potash feldspars from granites studied by Ahrens (1948) is 0.0073 per cent, while that of the pegmatitic species is 0.0319 per cent and that of the hydrothermal microclines from pegmatites is as high as 0.433 per cent. Amongst the perthites of the Black Hills Nos. 6 and 15 have the lowest Rb_2O content, 0.066 per cent. The perthite phenocryst (No. 13) from granite, however, has a higher Rb_2O content (0.099 per cent). The Rb/K ratio of the phenocryst (9.4) is also higher than that of the perthites Nos. 6 and 15 (6.1). Moreover, the perthite porphyroblast of the schist has 0.088 per cent Rb_2O and its Rb/K ratio is 7.7. Supposing, for the sake of argument, that these perthites were derived from strictly magmatic sources, that is by differentiation of a basic magma, then their Rb contents, as well as the values of their Rb/K ratio, would seem to imply that the pegmatite perthites were formed at an earlier stage than the perthite phenocryst from the granite, and that the porphyroblast was developed at an intermediate stage - conclusions that are obviously not feasible.

There are other pegmatitic perthites, especially Nos. 4, 8, 9 and 10 of the Glendale area and No. 17 of the Hugo pegmatite /

pegmatite, which have unusually high Rb contents. These perthites cannot be considered as primary products of magmatic crystallization since such products generally have a much lower Rb content. The relatively high Rb and Li contents in these perthites may support the hypothesis that the latter were formed at the hydrothermal stage during which replacement processes become dominant.

There are also certain features in the distribution of the other trace elements which are not in favor of the magmatic mode of genesis. The Ba content of the phenocryst from granite and the value of its Ba/K (1000 Ba/K = 1.6) are much lower than those of (a) most of the pegmatitic perthites (1000 Ba/K ranges from 1.9 to 14.7) and (b) of the perthite porphyroblast of the schist (100 Ba/K = 97.0). But according to Goldschmidt's principles, divalent Ba should be more concentrated relative to K in the early formed crystals. Moreover, Engelhardt (1936) has pointed out that Ba is relatively enriched in potash feldspars which form at the earlier stages of crystallization compared with those formed later.

It is important to trace the source of the replacing materials which gave rise to the pegmatitic perthites. They may be the residual hydrothermal solutions which usually remain at the end of the magmatic history. These solutions subsequently /

subsequently replace the magmatic minerals of the pegmatites. But the relative distribution of Cr, Co and Ni leads to the belief that such magmatic hydrothermal solutions cannot be responsible for the development of the Black Hills perthites. It has been found that the relative abundances of these trace elements in the rocks that form during the end stages of magmatic crystallization is Co > Ni > Cr (Ludegardh, 1949, p. 21) or Ni > Co > Cr (Higazy, 1952b). Consequently the hydrothermal magmatic solutions as well as the magmatic pegmatites or even the granites that crystallized immediately before the hydrothermal stage should have a lower Cr content than that of either Co or Ni. The question now arises, why the Black Hills pegmatites and granite, if of strictly magmatic ancestry, have the relative distribution Cr > Ni > Co which is inconsistent with this mode of origin? Why do we find wide fluctuations in the Rb, Li and Ba contents of the different perthites? It may be argued that the composition of the hydrothermal replacing solutions varies from place to place in the same locality, that is to say, the solutions may have been Rb-rich in one part of the country rocks and Li-rich in another. But then the separation of such differing solutions from the original magmatic liquor calls for explanation. These problems seem to find their solution if we seek the origin of the replacing material in the country rock itself. In the first place, the analysed schist has /

has the relative distribution $Cr > Ni > Co$, like that of the associated granite and pegmatites. In the second place, the trace-element contents in the country schists are quite likely to differ from one part to another. Landergren (1945), studying the boron content of sediments, points out that this content varies horizontally as well as vertically in the stratigraphic column from one district to another. Such local differences in the trace-element contents of the country rocks would undoubtedly show up in the corresponding granitization products. This would be so quite apart from the fact that the mobilities of the different elements also vary and would therefore tend to give rise to different concentrations of such elements in the various parts of the rocks through which they pass. Moreover, it seems that each element would tend to follow preferential paths determined by the structural features of the area and therefore, for this additional reason, the relative concentrations would vary in different parts of the same locality.

(b) The trace-element contents of the various country rocks.

The chemical composition and the trace-element contents of the country rocks, namely, the unaltered schist, the perthite-schist, the granite and the albitite are recorded in Table 2.

It /

It is important to notice that the schist does not lack any of the trace elements present in the granitic country rocks. Moreover, they all have Cr > Ni > Co and Ba > Sr. This is the same relationship as that found in the psammo-pelitic schists of the different metamorphic zones of the Scottish Highlands (Higazy, 1952c). Here, also, the relative distributions Cr > Ni > Co and Ba > Sr persist in the analysed rocks of the chlorite-, biotite-, garnet-, staurolite- and sillimanite-zones.

The essential mineral constituents of granites, wherever they occur, are substantially the same. Yet the distribution of the rarer elements in these granites varies rather markedly. The trace-element contents of the Pre-Cambrian granites of the Black Hills (S. Dakota), the rapakivi granite of Finland and the Caledonian granites (adamellites) of Moy and Morven-Strontian (Scotland) are listed in Table 3. It will be noticed that the rapakivi granite has 1000 ppm. Rb, while the Scottish rocks have 500 and 400 ppm., and the Black Hills granite only 240 ppm. Furthermore, both the rapakivi and the Black Hills granites are relatively poor in Sr, having 39 and 50 ppm. respectively while the Scottish granites have 1200 and 1500 ppm. of this element. The values of Ba/Sr in the granites of Finland (rapakivi), Black Hills, Moy and Morven-Strontian are 12, 15, 2.5 and 1 respectively. These marked differences cannot be entirely attributed to the different /

different ages of these granites, since Sahama and Rankama (1939, p. 8) point out that the Pre-Cambrian granites in the different parts of Finland show a remarkable variation in their rarer-element contents, a discovery which led them to the belief that not all the granites could be of magmatic origin.

It is difficult to see how residual granitic melts which might form at the late stages of differential crystallization of basic magma could exhibit such wide variations in their trace-element contents from one geographical occurrence to another. It is a more reasonable inference from the data available that the granites concerned formed either by metasomatic processes within the country rocks or by a further extension of such processes - leading to refusion, whereby granitic ichors might be formed. Moreover, if the normative composition of several granitic and pegmatitic rocks supposed to have crystallized at the late stages of the differentiation history of basic magma be plotted on the orthoclase-albite-anorthite and the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagrams, the distribution is inconsistent with the hypothesis of their derivation from a differentiating basic magma (Higazy, 1950). The normative feldspar contents lie in the orthoclase field of the orthoclase-albite-anorthite equilibrium diagram and their salic normative constituents place them outside the region of low temperature in the $NaAlSiO_4$ /

$NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagram. It has been generally assumed that the discrepancy between the chemical composition of such rocks and the results of high temperature studies of analogous systems is mainly due to the effect of water vapor which usually concentrates towards the end of the magmatic history. However, this explanation is considered, on theoretical grounds, to be inadequate (Higazy, 1949). Moreover, Bowen and Tuttle (1950, p. 497) have recently established that water vapor has no discernible effect on the fundamental course of crystallization in the albite-orthoclase binary system, i.e. in the system which is the most important one concerned in the problem of the perthite.

The discrepancy between the normative composition of the Black Hills perthites and the orthoclase-albite-anorthite equilibrium diagram, together with the textural features, were considered as criteria supporting a metasomatic origin for these perthites (Higazy, 1949). Metamorphic differentiation, which is responsible for the development of the perthite porphyroblasts in the schist, was thought to give rise to chemically similar perthite pegmatites in parts of the country rock where favorable physical and structural conditions prevailed. Experimental data, given by Jagitsch, (1949) however, suggested that the depth affected by solid diffusion is only a few metres in /

in 10^8 years. Although so slow a rate could satisfactorily account for the formation of the perthite porphyroblasts yet it cannot explain the development of large pegmatitic bodies by "solid" diffusion. But the state under which diffusion takes place may not necessarily be that of a perfect solid; moreover, we do not yet know the exact effect on diffusion rates of the very complicated pressures and stresses that attend orogenesis. Such conditions may change an apparently solid rock into a state concerning which our knowledge is so far negligible (Bridgman, 1951). However, it is quite common to find appreciable amounts of water in sediments and especially in the pelitic types. Garrels, Dreyer and Howland (1949) report a rate of penetration for ions during their diffusion through intergranular spaces in water-saturated rocks, of two and a half miles in a million years at a temperature of 100°C. Moreover, they mention that the rate of diffusion increases with temperature. These findings add strength to the view that water might have accelerated the reactions and transformations during the metamorphic differentiation of the country schist which is regarded as having given rise to the perthites (Higazy, 1949, p. 580).

The significance of isotopic composition of the oxygen in silicate rocks in petrogenesis has been pointed out by Beartschi (1950). Silverman (1952) has recently determined the /

the relative abundances of the oxygen isotopes in different types of rocks. He has found that granites have higher O^{18} abundances compared to the basic rocks. This fact implies that the granites he investigated are not late crystallizing fractions of a differentiating basic magma. Furthermore, he finds that the rocks which are supposed to be the late differentiates have variable isotopic abundances which can be correlated with variation in their parental sedimentary materials (Silverman, 1952, p. 35). The variation in the trace-element contents of the perthites of the Black Hills and the appreciable differences of these contents in the granites of various geographical regions can also be ascribed to corresponding variations in the lithological and chemical constitution of the original country rocks already noted on p. 22.

GAINS AND LOSSES OF THE TRACE ELEMENTS DURING THE METASOMATISM OF THE COUNTRY SCHIST

If the hypothesis of the metasomatic derivation of the Black Hills perthites is true, it is of special interest to ascertain the behavior of the trace elements during the reorganisation of the atoms and molecules inside the schist to give rise to /

to these perthites. The additions and subtractions of the major elements which were inferred to have taken place during the metasomatism have already been given by the author (Higazy, 1949, Table 8, p. 574).

The metasomatic alteration of the quartz-muscovite-biotite-schist to perthitic schist comprised

addition of K, Na, Al and Si,

and subtraction of Mg, Fe^2, Fe^3 and Ca.

Reference to Table 2 shows that, as regards the trace elements, there was

addition of Rb, Ba, Sr and Pb; Ga; Be; Li and Zr

and subtraction of Cr, Co, Ni, Cu and Mo; and Y.

Thus Rb, Ba, Sr and Pb behaved similarly to K, while Ga followed Al and Be most probably accompanied Si. Li usually follows Mg, but in this particular case Li was added while Mg was subtracted. It has already been mentioned (p. 10) that Li may replace Al in the feldspar lattice. Since we here find that both Li and Al were added, it appears that replacement of Al by Li is highly probable. Cr, Co, Ni, Cu and Mo followed their replaceable major elements Mg, Fe^2 and Fe^3; and Y behaved similarly to Ca.

The geochemical changes of the major elements involved in the transformation of the country schist into average perthite /

perthite are mainly the same as those concerned in the formation of the perthite-schist. K, Na and Al were added; and Ca, Mg and Fe were subtracted. The K-replacing trace elements which were added are Rb, Sr, Pb and Tl. Again Tl shows its geochemical coherence to Rb. Ba, however, was subtracted; but since Ba can substitute for both K and Ca it seems that it followed Ca in this case, particularly as the gain in K (8.83)[x] is far greater than the loss in Ca (0.13)[x]. Similarly the total amount of added Rb, Sr, Pb and Tl is greater than the amount of the subtracted Ba. Cr, Co, Ni, Cu, V and Mo followed Mg, Fe^2 and Fe^3 in being subtracted; and La and Y decreases with Ca.

During the formation of the Black Hills perthites the trace elements therefore behaved as they have been found to do (a) in the metasomatic-metamorphic development of skarn rocks from an epidiorite in the Malin Head district of Co. Donegal, Ireland (Holmes and Reynolds, 1947; Higazy, 1952a) and (b) in the development of the various metamorphic zones of the Scottish Highlands (Higazy, 1952c). It is important to mention that the diffusion /

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[x] Amount of gain or loss is calculated from Barth's (1948) rock formulae (based on a unit cell for each rock of 160 oxygen atoms) and recorded by Higazy (1949, p. 574).

diffusion coefficients (D, in cm^2/day) recorded by Garrels, Dreyer and Howland (1949, p. 1819) show that the trace elements have the same or very similar diffusion coefficients as those of their replaceable major elements. Considerable confidence can be placed, therefore, in suggesting the addition of diffusion coefficient as a new significant factor in controlling the distribution and behavior of the trace elements during the progress of metasomatic and metamorphic processes.

CONCLUSIONS

The Black Hills perthites contain appreciable amounts of Rb, Ba and Sr. These elements have approximately the same ionic radii as that of K and are known to substitute for it in the crystal lattices. Tl is present in detectable amounts in the perthites which are relatively rich in Rb. Li, Pb and Ca are present in amounts notably less than those of Rb, Ba and Sr. Mn, V, Cu, Be and Ge are relatively rare; and Ag, Cr, Co, Ni, Sc, Mo, La and Y are very rare. The pink and reddish perthites seem to be relatively poor in Rb but relatively rich in Ba, while the grayish types show the reverse relationship.

The trace-element contents are variable in the different /

different perthites. The Black Hills granite and perthite pegmatites have $Cr > Ni > Co$ and $Cr > Ni = Co$ respectively which is not consistent with either a magmatic or a hydrothermal mode of origin. The replacing materials seem to have been derived endogenetically from within the country schist which also has $Cr > Ni > Co$.

During the metasomatic development of the Black Hills perthites the trace elements behave similarly to the major elements which respectively have approximately the same diffusion coefficients, and ionic radii and are known to be replaced by them in favorable crystal lattices.

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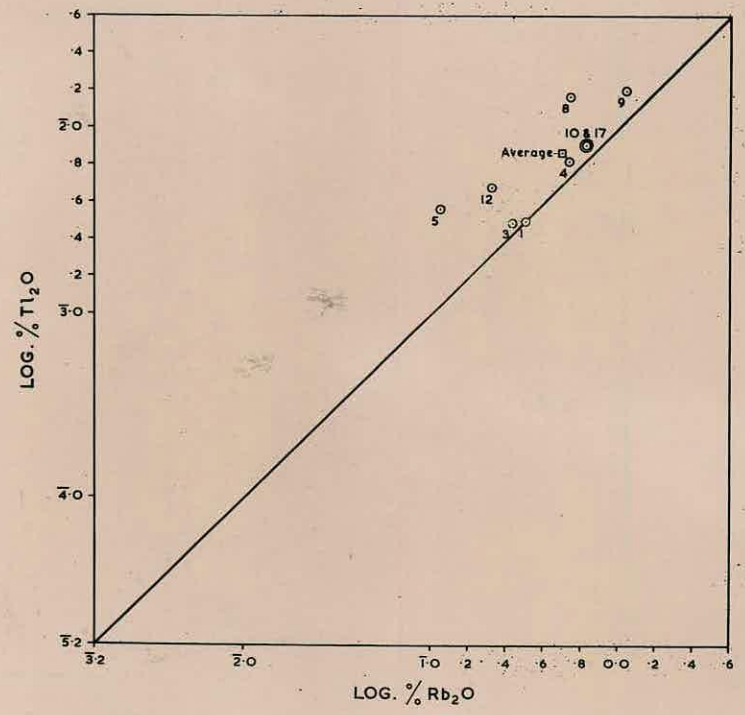

Fig. 1

Relationship between Rb and Tl in the analysed perthites of the Black Hills.

TABLE 1

Trace-element Contents in ppm. of the Analysed Perthites and Cleavelandite

Element	sensitivity	1	2	3	4	5	6	7	8	9	10	11
Rb	1	2800	1500	2500	5000	1000	600	800	5000	9500	6000	800
Li	1	40	4	9	7	25	3	2	170	300	100	8
Ba	5	45	80	25	260	200	400	1%	1000	20	380	1500
Sr	5	1500	12	20	180	45	70	750	400	600	90	60
Cr	1	*	*	*	*	*	*	*	*	5	3	3
Co	2	*	*	*	*	*	*	*	*	*	*	*
Ni	2	*	*	*	*	*	*	*	*	*	*	*
Zr	10	*	*	*	*	300	*	*	*	*	*	*
La	30	*	*	*	*	*	*	*	*	*	*	*
Y	30	*	*	*	*	*	*	*	*	*	*	*
Cu	3	3	3	4	5	4	3	3	3	4	4	3
V	5	5	5	*	5	*	5	5	5	20	10	10
Ga	1	35	30	40	35	50	30	30	40	45	30	30
Tl	30	30	*	30	65	40	*	*	140	150	80	*
Sn	5	*	*	*	*	*	*	*	*	*	*	*
Pb	10	10	18	15	50	15	30	35	20	40	10	40
Sc	10	*	*	*	*	*	*	*	*	*	*	*
Mn	5	8	10	10	10	10	12	8	7	8	10	10
Mo	1	*	*	*	*	*	*	*	*	1	*	*
Ge	10	*	*	*	*	*	*	*	15	10	*	*
Be	5	8	*	*	10	*	*	*	*	8	*	8
Ag	1	*	*	*	*	1	*	*	*	1	1	3
In	10	*	*	*	*	*	*	*	*	*	*	*

Nos. 1 to 11 correspond to numbers of chemical analyses by R.A. Higazy recorded by the writer (Higazy, 1949, p. 559).

Spectrographic analyst: R.A. Higazy.

*Element if present is in amounts below its limit of sensitivity.

TABLE 1 (Contd.)

Trace-element Contents in ppm. of the Analysed Perthites and Cleavelandite

Element	sensitivity	12	13	14	15	Average	16	17	Cleavelandite
Rb	1	2000	900	1000	600	2665	1200	6000	2
Li	1	130	25	55	2	60	35	160	150
Ba	5	100	150	200	100	965	30	550	5
Sr	5	240	25	50	35	270	800	90	100
Cr	1	3	1	3	1	1.5	1	1	1
Co	2	*	*	*	*	*	*	*	*
Ni	2	*	*	*	*	*	*	*	*
Zr	10	*	*	*	*	*	*	*	30
La	30	*	*	*	*	*	*	*	*
Y	30	*	*	*	*	*	*	*	*
Cu	3	3	5	4	3	4	4	4	5
V	5	5	5	8	5	6	5	15	10
Ga	1	30	30	35	30	35	35	40	70
Tl	30	45	*	*	*	39	*	80	*
Sn	5	*	*	*	*	*	200	*	*
Pb	10	20	25	20	450	53	10	10	*
Sc	10	*	*	*	*	*	*	*	*
Mn	5	15	10	12	10	10	12	8	40
Mo	1	*	*	*	*	*	*	1	*
Ge	10	10	*	*	*	*	*	10	20
Be	5	*	*	*	*	*	8	*	120
Ag	1	*	1	4	1	1	3	1	*
In	10	*	*	*	*	*	*	*	*

Nos. 12 to 17 correspond to numbers of chemical analyses by R.A. Higazy recorded by the writer (Higazy, 1949, p. 559).

Spectrographic analyst: R.A. Higazy.

*Element if present is in amounts below its limit of sensitivity.

TABLE 2

Chemical Composition and Trace-element Contents of the Country Rocks

	A Biotite-schist	B Perthite-schist	C Granite	D Albitite
Chemical composition as weight per cent of the oxide				
Oxide				
SiO_2	68.83	70.85	73.48	69.93
TiO_2	0.46	0.21	0.10	0.00
Al_2O_3	14.63	15.48	15.10	17.84
Fe_2O_3	1.42	0.64	0.41	0.14
FeO	3.83	1.09	0.82	0.20
MnO	0.05	0.01	0.02	0.01
MgO	2.24	0.83	0.60	0.54
CaO	0.52	0.38	0.80	0.59
Na_2O	1.05	2.16	3.34	9.68
K_2O	5.01	6.45	4.31	0.42
P_2O_5	0.17	0.45	0.13	0.51
H_2O	1.52	1.18	0.94	0.23
H_2O-	0.14	0.08	0.08	0.06
Trace elements as parts per million of the element				
Element				
Rb	240	600	240	1
Li	30	70	150	10
Ba	2000	3500	750	25
Sr	35	150	50	5
Cr	80	60	3	4
Co	10	3	*	2
Ni	40	20	*	*
Zr	220	250	250	50
La	30	30	30	*
Y	120	60	40	30
Cu	9	3	8	6
V	50	60	20	12
Ga	35	40	50	60
Tl	*	*	*	*
Sn	5?	*	5?	*
Pb	12	18	12	*
Sc	*?	*	*	*
Mo	1	*	*	*
Ge	*?	*	*	*
Be	5	8	25	10
Ag	<1	<1	<1	<1
In	*	*	*	*

Chemical and Spectrographic analyst: R.A. Higazy.

Chemical analyses A, B and D are taken from Higazy (1949, p. 560).

*Element if present is in amounts below its limit of sensitivity given in Table 1.

TABLE 3

Trace-element Contents in ppm. of Granites

Element	Rapakivi granite (1)	Black Hills granite	Morven-Strontian, Scotland adamellite (2)	Moy, Scotland adamellite (2)	Average granite (3)
Ba	480	750	1500	3000	445
Sr	39	50	1500	1200	85
Rb	1000	240	400	500	550
Li	25	150	40	25	185
Co	0	< 1	< 1	10	8
Ni	0	< 1	8	10	2
Cr	28	3	10	20	2
Ga	75	50	15	15	15
V	2	20	70	20	--

(1) Amounts taken from Sahama (1945, p. 59).

(2) Amounts taken from Nockolds and Mitchell (1948, p. 549 & p. 550).

(3) Amounts taken from Wager and Mitchell (1943, p. 287).

-- No data

PART VI

THE TRACE ELEMENTS OF THE PLUTONIC COMPLEXES OF LOCH DOON AND SPANGO (SOUTH SCOTLAND) AND THEIR PETROGENETIC SIGNIFICANCE

To be submitted for publication in Trans. Roy. Soc. Edinburgh.

ABSTRACT

The trace elements of the chief plutonic rocks of the Loch Doon (norite, diorite, granodiorite and adamellite) and the Spango (diorite and granodiorite) Complexes, Scotland, have been determined spectrographically. The distribution and relative proportions of the determined elements are discussed. Relationships appear to be consistent with the hypothesis that the investigated rocks developed metasomatically.

STATEMENT OF PROBLEM

The genesis of most granitic complexes is still a matter of acute controversy. Each complex may be considered to be the result of different processes by different investigators. The Loch Doon and the Spango granitic complexes of Scotland provide examples. They are considered to be derivatives of magmatic differentiation by some authors, whereas others interpret the evidence to imply a metasomatic mode of origin. This paper is a study of the geochemistry of the trace elements of a series of analysed rocks from each of these complexes with a view to assessing the significance of trace elements in the attempt to solve petrogenetic problems.

THE LOCH DOON COMPLEX

PREVIOUS WORK

The Loch Doon complex, which is probably of Lower Old Red Sandstone age, occurs in the Southern Uplands of Scotland, in the Counties of Ayr and Kirkcudbright. Walker (1928, Fig. 1, p. 154) gives a map showing its location as well as that of several other smaller complexes of the Southern Uplands.

Gardiner /

Gardiner and Reynolds (1932) cite earlier work dealing with this complex; and mention that its rocks range from true granites in the central portion to norite at the north-west and south-east margins, the major part of the complex being a tonalite. They (Gardiner and Reynolds, 1932, Pl. IV) give a geological map showing the distribution of these main rocks as well as transitional types between norite and tonalite and others between tonalite and granite. They also deal with the petrography and recorded the chemical composition of some of the rocks. They conclude that the three main plutonic types, namely, norite, tonalite, and granite seem to be the result of three successive intrusions in order of decreasing basicity. Later, however, McIntyre (1947) studied the north-west part of the Loch Doon complex and showed that the magmatic hypothesis cannot explain the fundamental features of his examined rocks. His evidence supports the alternative hypothesis that the granites of the area were produced by granitisation of the country-rock sediments. The pyroxene-bearing rocks which were thought by Gardiner and Reynolds (1932) to be intrusive norites, were considered by McIntyre to be basic-front representatives. McIntyre's interpretation is supported by a series of chemical analyses of rocks representing different stages of feldspathisation and basification. Rutledge (1950) studied the southern portion /

portion of the complex, and arrived at conclusions, similar to those of McIntyre (1947), favouring the metasomatic derivation of the rocks of the complex.

SPECTROGRAPHIC ANALYSIS AND DATA OBTAINED

Portions of the powders of the Loch Doon rocks, used previously for chemical analysis, were kindly provided by Dr D.B. McIntyre and Dr H. Rutledge. They were spectrographically analysed by the writer at the Macaulay Institute for Soil Research at Aberdeen, Scotland, using the semi-quantitative method described in detail by Mitchell (1948). The determined trace elements, and the wave lengths of their respective diagnostic lines have already been recorded by the writer (Higazy, 1952a, p. 171).

The analysed powders provided by Dr McIntyre are of rocks outcropping in the north-west part of the Loch Doon complex:

No. of analysed rock	Name
485	Greywacke
506	Slightly feldspathised greywacke
507	Highly feldspathised greywacke
685/5	Opdalitic pod in the aureole
333	Fine-grained opdalite
18	Coarse-grained opdalite
206	Potash-feldspar - poor "norite".

Those provided by Dr Rutledge are of rocks outcropping

in /

in the southern portion of the complex:

No. of analysed rock	Name
414	Biotite-hornblende-plagioclase-hornfels
214	Mobilised sediment
404	Contact quartz-diorite
401	Marginal hornblende-biotite-granodiorite
666	Adamellite

The chemical analyses of all these rocks are recorded in Table 1a,while their trace-element contents are given in Table 1b.

DISTRIBUTION OF THE TRACE ELEMENTS: DISCUSSION

Rubidium, barium, strontium and lithium

Rb is present in amounts varying from 50 ppm. in the basified sediment (biotite-hornblende-plagioclase-hornfels No. 414) to 380 ppm. in the adamellite. In the slightly feldspathised greywacke (No. 506) Rb is 90 ppm., increasing to 180 ppm. in the highly feldspathised greywacke (No. 507). Similarly, the quartz-diorite (No. 401) and the granodiorite (No. 404) have 120 and 110 ppm. respectively, while the adamellite, which represents a more advanced stage of granitisation (feldspathisation) has 380 ppm.

It is important to notice that the Rb content of the "norite" (100 ppm.) is appreciably higher than that normally found /

found in basic volcanic rocks. The averages of Rb in the basaltic and doleritic rocks of the Braefoot Outer Sill, Fife, are 4 and 16 ppm. respectively (Higazy, 1952b). Moreover, the Kokstad and the Perdekloof types of Karroo dolerite, S. Africa, contain only 18 ppm. Rb (Walker and Poldervaart, 1949, p. 644). Furthermore, some deep-seated gabbros which are probably of magmatic origin, are very much poorer in Rb than the Loch Doon "norite". The gabbros of Southern Lappland contain no perceptible Rb (Sahama, 1945, Table XII, p. 30). In the Skaergaard series, hypersthene-olivine-gabbro to fayalite-ferrogabbro, Rb varies from 20 to 30 ppm. (Wager and Mitchell, 1951, Table C). On the other hand, the Caledonian gabbros of the Garabal Hill-Glen Fyne Complex (Nockolds and Mitchell, 1948, p. 539) show exceptionally high Rb content, like the Loch Doon "norite". The range of Rb in these Garabal Hill rocks is from <20 to 500 ppm. with an average of 160 ppm. It is significant that the Rb content of the fine-grained gabbro of this area (500 ppm.) is higher than that of any of the six analysed diorites, four of the five analysed granodiorites, and one of the two analysed aplites (Nockolds and Mitchell, 1948, Table II, pp. 538-539). Furthermore, the value of Rb/K is higher in this gabbro (31) than in any of the rocks which are supposed to lie further down on the liquid line of descent and are believed by Nockolds /

Nockolds to form at a later stage of the magmatic crystallisation. This is obviously the reverse of what would be expected in a normal case of magmatic differentiation, since Rb is known to have a bigger ionic radius (1.49 Å) than that of K (1.33) and therefore K would concentrate relative to Rb in the latest fractions (Goldschmidt, 1937 and 1945). The high Rb content of the Garabal Hill gabbros is therefore inconsistent with the hypothesis of magmatic origin, a conclusion which applies equally to the "norite" of the Loch Doon complex.

Ba varies from 600 ppm. in the sediment (No. 214) to 2000 ppm. in the granodiorite. The adamellite has 1800 ppm., a content not noticeably lower than that of the granodiorite (2000 ppm.). Ba shows an increase from 750 ppm. in the greywacke (No. 485) to 1400 ppm. in the slightly feldspathised type (No. 506), and is as high as 2000 ppm. in the highly feldspathised greywacke (No. 507).

The Ba content of the Loch Doon "norite" (1000 ppm.) - like that of Rb - is exceptionally high compared with other basic rocks. The average Ba contents of Karroo dolerites (Walker and Poldervaart, 1949), Southern Lappland gabbros (Sahama, 1945) and various Skaergaard (Wager and Mitchell, 1951) are 180, 180 and 62 ppm. respectively. Moreover, the Ba content of average gabbro is given by Wager and Mitchell (1943,

p. /

p. 286) as 62 ppm. while Engelhardt (1936) reports 60 ppm. Ba for gabbros and anorthosites.

The following data show that Rb + Ba increases with K:

Rock	Rb + Ba in ppm.	K_2O in wt. per cent
Sediment	758	1.60
Basified sediment and the pyroxene-bearing rocks (norite and opdalites)	1288	1.93
Feldspathised greywackes and granitic types	1936	3.03

Sr varies from 200 in the greywacke to 2200 ppm. in both the "norite" and the granodiorite. Generally the Sr content of the basified rocks is slightly higher than that of the feldspathised types, the average Sr content of the biotite-hornblende-plagioclase-hornfels and the pyroxene-bearing opdalitic rocks being 1500 ppm. while it is 875 ppm. in the feldspathised greywackes. Similarly, the "norite" has 2200 ppm. Sr while the average of this element in the more feldspathic granitic types (quartz-diorite, granodiorite and adamellite) is 1430 ppm.

Li varies from 15 ppm. in the opdalitic rock (No. 685/5) to 350 ppm. in the adamellite. Most of the samples, however, have Li content ranging from 70 to 100 ppm. The average /

average in the granitic types and feldspathised greywacke (141 ppm.) is higher than that in the pyroxene-bearing rocks and basified sediment (75 ppm.).

The "norite" has 100 ppm. Li: very much higher than the amounts found in basic volcanic rocks and gabbroic types of probable magmatic origin. The Karroo dolerites (Kokstad and Pedekloof types) average only 2 ppm. (Walker and Poldervaart, 1949) and the basalts and dolerites of the Braefoot Outer sill, Fife, only 20 ppm. (Higazy, 1952b). The average Li contents for the Deccan Traps and for andesites are given by Strock (1936) as 7.4 and 15.2 ppm. respectively. The gabbros and dolerites of Southern Lappland (Sahama, 1945, p. 30) and the different gabbros of the layered series of the Skaergaard intrusion both average only 6 ppm.

Chromium, nickel, cobalt, vanadium and copper.

Cr ranges from 70 ppm. in the highly feldspathised greywacke (No. 507) and the adamellite to 450 ppm. in the biotite-hornblende-plagioclase-hornfels (basified sediment). Generally the content is lower in the granitic types and feldspathised greywackes (average 216 ppm.) than in the pyroxene-bearing types and basified sediment (average 320 ppm.). The average in the unaltered sediments is 250 ppm.

The general distribution of Ni is similar to that of Cr. Ni varies from 35 ppm. in the adamellite to 200 ppm. in the opdalitic rock (No. 18). The average in the granitic and feldspathised types (89 ppm.) is lower than that of the pyroxene-bearing rocks (134 ppm.). The average in the unaltered sediments is 108 ppm.

It is important to notice that the adamellite is unusually rich in both Cr and Ni. Normally, rocks that form at the latest stages of magmatic crystallisation have negligible amounts of these elements. The late magmatic microsyenite of the Braefoot Outer sill, Fife, has $<$ 1 ppm. Cr and 40 ppm. Ni (Higazy, 1952b). The silicic rocks ($SiO_2 > 63$ per cent) from different parts of the U.S.A. have Ni contents ranging from 2 to 10 ppm. (Sandell and Goldich, 1943, p. 182). In the granitic rocks of the Oliverian magma series, New Hampshire, Cr varies from 7 to 14 ppm. and Ni from $<$ 8 to 8 ppm. (Billings and Rabbitt, 1947, Table 3, analyses 4, 5 and 6, p. 577). Moreover, Lundegårdh (1949, Table 4, p. 41) reports $<$ 1 to 6 ppm. Cr and $<$ 1 to 50 ppm. in porphyry, rhyolite and similar acid rocks of Swedish occurrences For the late differentiates of the Skaergaard intrusion, Wager and Mitchell (1951, Table F, analyses G, H and I) report averages of Cr and Ni of $<$ 1 and 4 ppm. in the hedenbergite-granophyre of the layered series, 8 and 10 ppm. in the transgressive hedenbergite-granophyre, and 14 and 8 ppm. in average acid granophyre. They /

They (Ibid, p. 200) mention that fractionation of the basic magma, as exemplified by the Skaergaard intrusion, gives rise to intermediate and acid rocks which are almost entirely depleted of both Cr and Ni. This has been found by the author (Higazy, 1952b) to be true for the corresponding rocks in the Braefoot Outer sill, Fife. The high Cr and Ni contents of the diorite and granodiorite of the Loch Doon complex (average 350 and 130 ppm respectively) and those of the adamellite of that complex (70 and 35 ppm. respectively) therefore provide strong evidence against their origin from a differentiating basic magma, noritic or otherwise.

The averages of Co for unaltered sediment (48 ppm.), basified sediment and pyroxene-bearing rocks (46) and intermediate rocks (43) are closely similar. The feldspathised greywackes (35 ppm.), and especially the adamellite (5 ppm.), are poorer in Co.

Lundegårdh (1949) has mentioned that rocks which form at the early stages of the crystallisation of the basic magma have the relative proportion Cr > Ni > Co whereas those which form at the latest stages have Co > Ni > Cr. The rocks of the Braefoot Outer sill, Fife, show Cr > Ni > Co in the early basaltic and doleritic differentiates and Ni > Co > Cr in the late microsyenitic differentiate (Higazy, 1952b). The Cr content of late /

late magmatic rocks, therefore, is relatively lower than that of both Ni and Co. But the granodiorite and quartz-diorite and even the adamellite of the Loch Doon area have Cr > Ni > Co which is obviously not consistent with expectations from crystallisation differentiation. It is highly significant that the unaltered sediments of this area have the same relative proportion of these elements as the granitic types, that is Cr > Ni > Co. Moreover, the relative proportion Cr > Ni > Co has been found to persist through the well known regional metamorphic zones of the Scottish Highlands (Higazy, 1952c). It is quite likely, therefore, that metasomatic-metamorphism of the sediments played an important role in the development of the granitic rocks of the Loch Doon Complex.

V ranges from 100 ppm. in the adamellite to 200 ppm. in the "norite". There is no marked difference in the average contents of the various rocks studied. The average of the basified sediment and the pyroxene-bearing rocks (166 ppm.) is slightly higher than that of the feldspathised greywacke and the granitic types (120 ppm.). The average in the unaltered sediments is 138 ppm.

The V content of the adamellite (100 ppm.) is very much higher than that of acidic volcanic types; the latter contain only 8 ppm. of V (Higazy, 1952b).

Cu varies from 3 ppm. in both the sediment (No. 214) and the adamellite to 320 ppm. in the "norite". There is a general tendency for Cu to be relatively enriched in the basified rocks compared to the granitised types. The average in the former is 195 ppm. while it is 85 ppm. in the latter.

An interesting geochemical feature in the distribution of Cu in the Loch Doon area is its enrichment in the feldspathised greywacke (average 205 ppm.) relative to the granitic types (average 5 ppm.). This suggests that further granitisation of the analysed sediments might lead to the release of Cu and its subsequent concentration as ores. Naturally, this could only take place where Cu has been sufficiently abundant in the sediments to give rise to such ores. The same suggestion has been made by the author on the basis of evidence found during an investigation of the metasomatic-metamorphism of certain Dalradian rocks in Co. Donegal, Ireland (Higazy, 1952a, p. 184).

Lanthanum and Yttium

The variation in La is from $<$ 30 to 60 ppm. while that of Y is from 40 to 100 ppm. All the analysed rocks have $Y > La$ except the adamellite which has Y = La (60 ppm.).

The content of Y in the "norite" (70 ppm.) is higher than that of the quartz-diorite, granodiorite and adamellite (60 ppm. in each). Since there is tendency for Y to be relatively /

relatively concentrated in the later magmatic fractions (Higazy, 1952b), this suggests that the acidic types seem not to be the result of differentiation of a basic magma.

Gallium

The range in Ga is from 25 ppm. in the sediment (No. 214) to 45 ppm. in the adamellite. Generally, the distribution of Ga is uniform since the content of this element in the different rocks, does not noticeably vary from the mean content (35 ppm.) of all the analysed types.

Zirconium

Reference to Table la shows that the distribution of Zr seems to be erratic. It reaches 1200 ppm. in the opdalitic rock No. 18 (basic rock) whereas it is only 350 in another opdalite (No. 333). Similarly, it is as high as 1100 ppm. in the quartz-diorite, but falls to 400 ppm. in the adamellite. On average there is an increase in the average Zr content from the pyroxene-bearing rocks and basified sediment (610 ppm.) to the granitic types and the feldspathised greywackes (780 ppm.).

Scandium, molybdenum: tin, lead and silver

The variations of Sc and Mo are undetectable since

most /

most of the analysed rocks contain < 10 ppm. of Sc and < 1 ppm. of Mo.

The contents of both Sn and Pb show more variation than those of both Sc and Mo. Reference to Table 1b indicates that the pyroxene-bearing rocks contain slightly higher amounts of both Sn and Pb than the granitic types. As in the case of Cu, both Sn and Pb are more enriched in the feldspathised greywackes (18 ppm. Sn and 24 ppm. Pb) than in the more granitised types (< 5 ppm. Sn and 13 ppm. Pb). This would suggest a release of these ore-forming elements during the development of granitic rocks.

The distribution of Ag indicates a slight enrichment in the granitic types and feldspathised greywackes (average 4 ppm.) relative to the pyroxene-bearing rocks and basified sediment (average 1.6 ppm.).

Thallium, germanium, beryllium and indium

Tl, Ge, Be and In, if present, occur in amounts below their respective limits of sensitivity. This indicates that these trace elements are relatively the rarest trace elements in the silicate rocks of the Loch Doon area. In view of the very low limits of sensitivity, Mo and Ag should also be added to the list of very scarce trace elements in these rocks.

The /

The trend of the different trace elements

So far we have discussed the distribution of the different trace elements in the various rocks of the Loch Doon Complex. The so-called "norite" of this complex has been found to have a trace-element constitution which is highly anomalous compared either to that of volcanic rocks of corresponding composition or to that of gabbroic types thought to be of magmatic origin. Moreover, the Cr, Ni and V contents of the adamellite are of an entirely different order from those commonly remaining in the late differentiates of a fractionating basic magma.

In metasomatic processes, however, it has been found (Higazy, 1952a; and 1952d) that the trace elements follow such replaceable major elements as have approximately the same ionic radii and, possibly, similar coefficients of diffusion. The behaviour of the trace elements in the investigated rocks from the Loch Doon Complex is in close agreement with this principle. The total $Mg+Fe^2+Fe^3$ decreases in the sequence: "norite", diorite and granodiorite and adamellite, whereas K increases. In accordance with expectation, the total (Mn+Ti+Cr+Ni+Co+Li+V+Cu) decreases, whereas the total Rb+Ba increases:

Rock /

Rock	$Mg+Fe^2+Fe^3$ in wt. per cent	Mn+Ti+Cr+Ni+Co+Li+V+Cu in ppm.	K in wt. per cent.	Rb+Ba in ppm.
"Norite"	8.62	11,795	1.48	1100
Diorite and granodiorite	6.92	6459	2.19	1915
Adamellite	2.26	2783	3.56	2180

The same trend prevails in passing from the slightly feldspathised greywacke (No. 506) to the highly feldspathised greywacke (No. 507). In the former both $Mg+Fe^2+Fe^3$ (6.60 per cent) and Mn+Ti+Cr+Ni+Co+Li+V+Cu (8525 ppm.) are higher than in the latter (5.75 per cent and 7480 ppm.). Furthermore, the slightly feldspathised greywacke has lower K (1.63 per cent) and correspondingly lower Rb+Ba (1490 ppm.) than the highly feldspathised type (3.00 per cent and 2180 ppm.).

The von Wolff value "L" increases in the more advanced stages of granitisation (Reynolds, 1946). The values of the ratio L/M in the "norite", diorite and granodiorite, and adamellite are 1.7, 2.5 and 9.0 respectively. Accordingly, we find a corresponding increase in the values of L_{tr}/M_{tr}, when L_{tr} = Rb+Ba+Sr, the main trace elements of the common leucocratic minerals, and M_{tr} = Cr+Ni+Co+Li+V+Cu, the chief trace elements in the melanocratic minerals. The values of L_{tr}/M_{tr} are 3.4 in the "norite", 5.1 in the diorite and granodiorite, and 6.2 in the adamellite.

Evidences /

Evidences which add confidence to the inference that the sequence: "norite" (basic)--quartz-diorite and granodiorite (intermediate)-- and adamellite (acidic) did not result from a differentiating parental basic magma, can be found in the trends of the more important trace elements in this sequence. Reference to Table 1b in which the trace elements of the rocks concerned are listed show that:

(1) Cr and Ni are more concentrated in the intermediate rocks than in the basic rock. In contrast, the data concerning the relative distribution of Cr and Ni (a) in the different types of igneous rocks recorded by Lundegårdh (1949); (b) in the various rocks of the Skaergaard complex, Greenland (Wager and Mitchell, 1951, p. 199); and (c) in those of the Braefoot Outer sill, Fife (Higazy, 1952b) seem to leave no doubt that these two elements are enriched in the basic rocks relative to the intermediate types. Furthermore, the ionic radius of Cr (0.64 Å) is smaller than that of Fe^3 (0.67), and accordingly Cr should be concentrated relative to Fe^3 in the earlier rocks (Goldschmidt, 1937; and 1945). In the Loch Doon rocks, however, we find that Cr/Fe^3 in the "norite" (0.08) is lower than in the intermediate rocks (0.11).

(2) Both Li and Li/Mg are lower in the intermediate than in the basic rocks, but Strock (1936) has shown that both should increase /

increase during the progress of fractional crystallisation.

(3) Both Sr and Y are more abundant in the intermediate than in the basic rocks. This is the reverse of expectation from magmatic differentiation (Higazy, 1952b).

Moreover, it has been found that during the progress of crystallisation of the Braefoot Outer sill, Fife, the ratio Cr/Fe^3 decreases, whereas the ratios Li/Mg, Rb/K and Rb/Ba increase (Higazy, 1952b). The values of these ratios in the Loch Doon sequence are:

Ratio	"Norite"	Diorite and Granodiorite	Adamellite
Cr/Fe^3	0.08	0.11	0.03
1000 Li/Mg	3.1	2.9	48.0
1000 Rb/K	6.7	5.2	10.0
Rb/Ba	0.10	0.06	0.21

There is a significant break in the trend from "norite" to adamellite which is completely inconsistent with the hypothesis that the rocks are of co-magmatic origin. It should be remembered that in connection with metasomatic processes, there would be no necessity for a sorting out of the trace elements in the same manner as happens in a fractionating magma. The identity in the relative proportion of Cr, Ni and Co in the granites and their country rocks is strong evidence supporting the hypothesis of the metasomatic derivation of the former from the latter (Higazy, 1952d).

THE SPANGO COMPLEX

PREVIOUS WORK

The Spango complex, which is smaller than that of the Loch Doon, is probably of Old Red Sandstone age. It occurs on the border of Dumfriesshire and Lanarkshire. Walker (1928) summarises earlier work concerning this complex, and mentions that its main rock is a basic hornblende-biotite-granodiorite or quartz-diorite showing very little variation. He favoured the derivation of the rocks from a magma of quartz-dioritic composition. In an unpublished thesis Sarkar (1948) gives a detailed gelogical map of the area, showing the distribution of the main granodioritic rock of the complex as well as its surrounding sediments, together with detailed petrographic descriptions and chemical analyses of the rocks. His observations led him to conclude that the granodioritic types of the complex are products of metasomatic-metamorphism of the aureole sediments.

SPECTROGRAPHIC /

SPECTROGRAPHIC ANALYSIS AND DATA OBTAINED

Representatives of the Spango complex rocks were kindly provided by Professor Arthur Holmes for the spectrographic determinations of their trace elements. They include:

Metamorphosed mudstone (S/186);
Cordierite-biotite-hornfels (S/41);
Biotite-amphibole-plagioclase-hornfels (S/162E);
Porphyritic micro-diorite (501/D); and
Hornblende-biotite-granodiorite (501/G).

The chemical analyses of these rocks are assembled in Table 2a, while their trace element contents are given in Table 2b.

GENERAL GEOLOGY

The Spango granitic complex and its metamorphic aureole comprise Ordovician and Lower Old Red Sandstone rocks. Their sequence can be summarised as follows:

Lower Old Red Sandstone	(Lava conglomerate (Red Sandstone (Contemperaneous flows of andesite and olivine-basalt and ash beds Plutonic complex; granodiorite and diorite Minor dykes of porphyrite (metamorphosed)

Caradocian /

Ordovician	Caradocian	(Greywackes, mudstones and (haggis rocks (Glenkiln black shales.
	Arenig	Radiolarian cherts and mudstones

The Ordovician sediments are folded along axes with the normal Caledonian trend, south-west to north-east. The folds form part of the north-western flank of the great anticlinorium which is the dominating structure of the Ordovician and Silurian sediments in the Southern Uplands.

The plutonic complex is elliptical in form (3¼ x 1¼ miles) with the major axis approximately parallel to the strike of the Ordovician sediments. The width of the metamorphic aureole varies from 1/6 of a mile to 1 1/3 miles in the different parts (Sarkar, 1948).

Metamorphosed porphyritic dykes of Lower Old Red Sandstone age cut the Ordovician beds within the metamorphic aureole. They are earlier than the plutonic complex.

GENERAL PETROGRAPHY

(a) Arenig cherts and mudstones

The Arenig group is formed of radiolarian cherts of different /

different colours interbedded with mudstones. The unmetamorphosed chert is composed of crypto-crystalline silica with various bands containing ferruginous and argillaceous material (Sarkar, 1948, p. 18). The silica occupying the radiolarian tests is of slightly coarser grain than that of the groundmass. Different grades of metamorphosed chert are represented. The low-grade types contain quartz, minute flakes of biotite, small octahedra of magnetite, rare garnet and incipient cordierite. In the medium-grade the minerals remain the same but increase in grain size. Orthoclase, plagioclase, diopside and enstatite appear in the high-grade types in addition to the minerals already mentioned.

The unmetamorphosed mudstones are composed chiefly of fine chloritic and sericitic material, minute grains of quartz and ferruginous matter (Sarkar, 1948). Together with these constituents, the analysed sample (S/186) contains small needles of rutile and grains of zircon. In the low-grade metamorphosed mudstones minute blebs of pale green biotite appear, together with occasional acicular, colourless or pale green amphibole and incipient crystals of cordierite. The medium-grade types consist of cordierites of irregular shape in a matrix of brown biotite and minute quartz grains. Sample S/41 is representative of this type. The high-grade types consist of dark brown flakes /

flakes of biotite; cordierite, occasionally showing pleochroic haloes; acicular or lamellar crystals of amphibole; and skeletal enstatite.

(b) The Caradocian group

The Caradocian group is composed of (i) pebbly grits (Haggis rocks) and (ii) greywackes and mudstones.

(i) A general description of the constituent pebbles, fragments and grains of the Haggis rocks is given by Sarkar (1948, p. 43). The chief materials present include quartz, feldspars and amphiboles, Arenig cherts and mudstones; and spilites, andesites, alkali-trachytes, micro-granites, granophyres and tuffs. The groundmass in which these different ingredients are embedded, consists of a much finer-grained matrix of similar materials. The spilitic, andesitic and other volcanic pebbles closely resemble those found in the Arenig rocks of the Southern Uplands.

As a general rule the metamorphism of the Caradocian sediments increases towards the margin of the granitic complex, but numerous exceptions have been observed (Sarkar, 1948). In places, conspicuous enrichment of the Haggis rocks in hedenbergite and plagioclase is noticeable. This enrichment is believed to be brought about by introduction and fixation of cafemic constituents (Sarkar, 1948, p. 71).

(ii) /

(ii) The detrital constituents of the Caradocian greywackes vary in size from 0.1 to 2.0 mm. The grains are subangular in the coarser greywackes and angular in the finer types. They are composed of materials similar to those in the Haggis Rocks.

Quartzo-feldspathic pods and lenticles exhibiting granitic texture are occasionally present in the metamorphosed greywackes. The hornfels surrounding these pods and lenticles shows relative enrichment in biotite.

The Caradocian mudstones are similar in composition to the Arenig types; and the similarity naturally extends also to the different metamorphic products (chiefly cordierite-biotite-hornfels). Hornfelses unusually rich in biotite are notably developed.

The Plutonic Complex

The Spango complex is composed mainly of granodiorite with a subsidiary development of diorite. The two types are intimately connected and inclusions of dioritic composition of variable size are ubiquitous in the granodiorite.

Two varieties of diorite are recognised by Sarkar: (i) a porphyritic micro-diorite which exhibits crystalloblastic textures and (ii) a medium-grained diorite which is of more even grain.

The /

The most significant feature in the plagioclases and biotites of these diorites is their striking similarity to those developed in the high-grade hornfelses near the margin of the complex. Moreover, relics of fine-grained hornfelsic material arranged either zonally or at random are commonly met with in the plagioclases of the diorites (Sarkar, 1948, p. 113). The detailed mineralogical study carried out by Sarkar of numerous samples of diorite and aureole hornfelses shows that all transitional stages between these two extreme types are commonly represented.

The granodiorites are fine- to medium-grained hornblende-biotite-bearing varieties with abundant dark coloured hornfelsic and dioritic inclusions. These inclusions vary in size from a few millimetres to several yards across, and in shape from round or elliptical to irregular; their contacts with the granodiorite are usually sharp. Both the granodiorite and its inclusions have plagioclase and biotite with respectively similar characters (Sarkar, 1948, p. 157). Orthoclase forms up to one-third of the total feldspars in the granodiorite, and commonly contains relics of plagioclase with textures indicating that it was formed at the expense of the plagioclase. The approximate modes of the analysed granodiorite (501/G) and diorite (501/D), as recorded by Sarkar (1948, p. 177) are:

	Porphyritic micro-diorite	Granodiorite
Quartz	4.7	22.1
Plagioclase	57.6	42.5
Orthoclase	4.2	14.5
Amphibole	12.1	10.6
Biotite	18.5	8.9
Pyroxene	0.5	0.3
Accessories	2.0	1.0
	99.6	99.7

PETROGENESIS

Field and Petrological Evidence

Walker (1928) accepted the traditional magmatic origin for the Spango complex. Under this hypothesis, the diorite and granodiorite are interpreted as successive differentiation products of a single magma. Sarkar (1948), however, reports a wealth of field and petrographic evidence which is completely inconsistent with such a mode of origin. The predominant textures of the diorite and granodiorite are crystalloblastic. Many of the feldspars of both these types contain hornfelsic relics as inclusions. In addition, plagioclase crystalloblasts exhibiting properties similar to those of the rocks of the complex are widely distributed in the hornfelses of the aureole. The /

The biotites have properties similar to those of the adjoining hornfelses. Such features obviously cannot be explained by magmatic processes; they are, however, consistent with a metasomatic mode of origin.

Detailed study of the hornfelses reveals that in some places they become enriched in cafemic constituents (basified), while in others they become enriched in feldspathic constituents, culminating in the formation of rocks of dioritic and/or granodioritic composition (granitisation). A typical sequence worked out by Sarkar (1948) to illustrate successive stages in the evolution of granodiorite from mudstone is:

> (S/186) mudstone →(S/41) cordierite-biotite-hornfels → (S/162E) biotite-amphibole-plagioclase-hornfels (basified hornfels →(501/D) porphyritic micro-diorite → (501/G) biotite-hornblende-granodiorite.

Geochemical Evidence

The geochemical migrations and fixations of the major elements involved in the transformation processes have been found by Sarkar (1948) to be similar to those established by D.L. Reynolds (1946) for basification and granitisation processes.

As demonstrated by the data recorded in Table 2b the trace-element contents of the diorite and granodiorite are also inconsistent /

inconsistent with a magmatic ancestry for these rocks. In the first place, their respective contents of Cr (120 and 90 ppm.) and V (130 and 110 ppm.) are very much higher than those of felsic rocks developed by magmatic fractionation; the latter, as would be expected, are found to contain negligible amounts of these elements (Higazy, 1952b). Moreover, the relation Cr $\geq$ Ni > Co, which characterises both the diorite and granodiorite, is different from that of late magmatic differentiates; these have less Cr than either Ni or Co (Lundegardh, 1949; Higazy, 1952b). The fact that the country sediments of the Spango complex have the same relation (Cr > Ni > Co) strongly suggests that the sediments played an essential role in the development of diorite and granodiorite.

The behaviour of the trace elements in the basification and granitisation processes by which the rocks of this complex developed is also highly significant. Chemical and trace-element compositions of the greywackes - which played as essential a role in the development of the diorite and granodiorite as the hornfelses - are unfortunately lacking. In the absence of such data, the exact behaviour cannot be recognised. Judging by the hornfels data, however, basification and granitisation involved introduction of Rb, Zr, Sr and Y (see Table 2b). Table 2b also shows that the total of Li, Cr, Ni, Co, Cu and V in the average /

average basified hornfelses (931 ppm.), is higher than the corresponding average for diorite and granodiorite (389 ppm.). This follows the behaviour of the corresponding replaceable major elements, namely, Mg, Fe^2 and Fe^3, for which the respective totals are 9.58 and 5.75 per cent. Moreover, the total of Rb, Ba and Sr in the average granitised types (4360 ppm.) indicates an enrichment of these elements relative to their abundance in the basified types (3735 ppm.). This is in accordance with the total of K and Ca, which is higher in the diorite and granodiorite (5.39 per cent) than in the basified hornfelses (4.07 per cent). The major elements, therefore, were followed in a general way by the trace elements which are known to replace them in favourable crystal lattices. The data are too few for firm conclusions to be drawn, but it is worthy of notice that the pattern of behaviour is similar to that found by the writer in other metamorphic and metasomatic rocks (Higazy, 1952a; c; and d).

CONCLUSIONS

The chief rocks of the Loch Doon complex are pyroxene-bearing rocks of noritic composition, diorite, granodiorite and adamellite. /

adamellite. The pyroxene-bearing types are considerably richer in Rb, Ba and Li than basalts and dolerites. The adamellite, like the diorite and granodiorite, contains unusually high contents of Cr, Ni and V, and has the relation $Cr > Ni > Co$, which it shares with the country sediments. Late magmatic differentiates possess less Cr than either Ni or Co.

The pyroxene-bearing (basic) types contain lower Cr and Ni but higher Li than the diorite and granodiorite (intermediate types). Furthermore, in the basic types Cr/Fe^3 is lower and Li/Mg is higher than in the intermediate types. These relationships are inconsistent with an immediate magmatic ancestry for these rocks.

The trace elements are found to have behaved like their replaceable major elements during the development of the Loch Doon complex. The basified types have relatively higher totals of Mg, Fe^2 and Fe^3 and correspondingly of Li, Cr, Ni, Co, Cu and V; while the granitised types have relatively higher contents of K and Ca and accordingly of Rb, Ba and Sr.

The chief rocks of the Spango complex are diorite and granodiorite. These types have very much higher Cr and V contents than magmatic types of similar composition. Moreover, they have the relation $Cr > Ni > Co$ which is inconsistent with a magmatic origin.

The /

The relation $Cr > Ni > Co$, moreover, persists in the granitic types of the Loch Doon and Spango complexes; the same relation characterises their respective country rocks. This strongly suggests that in each complex the country rocks have played an essential role in the development of the granitic rocks.

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Dr R.A. HIGAZY made the following written contribution: "I have determined spectrographically the amounts of 22 trace elements in representative rocks from the Loch Doon complex. A detailed study of these determinations is in progress. In connection with Dr. Rutledge's paper it is interesting to mention that $\mathrm{Cr} > \mathrm{Ni} > \mathrm{Co}$ both in the plagioclase-biotite-hornblende-hornfels and mobilized sediment on the one hand, and in the quartz-diorite and marginal granodiorite on the other. This suggests that the former rocks may have played a significant role in the development of the latter."

The AUTHOR, in reply, said that he was gratified that Dr. Higazy's work on trace elements supported the close relationship which had been shown petrographically to exist between the sediments and the marginal granodiorite.

TABLE 2a

Chemical composition of the chief rocks of the Spango complex.

	A	B	C	D	E
	S/186	S/41	S/162E	501/D	501/G
SiO_2	56.62	57.26	54.24	58.68	65.18
Al_2O_3	17.88	18.42	18.03	17.57	16.93
Fe_2O_3	2.64	0.24	0.96	1.17	0.94
FeO	6.74	7.82	8.08	4.96	3.42
MgO	5.72	4.71	5.72	3.64	2.18
CaO	tr.	1.64	3.19	5.66	2.63
Na_2O	2.04	2.65	4.02	3.64	3.53
K_2O	2.58	2.69	2.94	2.79	3.04
H_2O+	4.27	2.45	0.87	0.96	0.98
H_2O-	0.49	0.48	0.16	0.05	0.14
TiO_2	0.87	1.37	1.26	0.84	0.72
P_2O_5	0.06	0.07	0.06	0.07	0.04
MnO	0.17	0.05	0.14	0.09	tr.
	100.08	99.85	99.67	100.12	99.73

Analyst: W.H. Herdsman.

A = Unmetamorphosed mudstone, near Fingland Farm, about 900 ft. from the Knockenshag diorite (Sarkar, 1948, Table 1, Analysis 1)

B = Cordierite-biotite-hornfels, a metamorphosed mudstone of medium grade, 250 ft. from the Knockenshag diorite border (Sarkar, 1948, Table 1, Analysis 2).

C = Biotite-amphibole-plagioclase-hornfels from near the Bucht Hill diorite margin (Sarkar, 1948, Table 1, Analysis 3).

D = Porphyritic micro-diorite inclusion within the granodiorite from the right bank of Brocklaw Burn (Sarkar, 1948, Table 1, Analysis 4).

E = Hornblende-biorite granodiorite from the right bank of Brocklaw burn (Sarkar, 1948, Table 1, Analysis 5)

TABLE 2b

Trace-element contents in ppm. of the chief rocks of the Spango complex.

Element	Sensitivity	A S/186	B S/41	C S/162E	Average BC	D 501/D	E 501/G	Average DE
Rb	1	85	150	220	185	180	140	160
Li	1	70	500	100	300	90	80	85
Ba	5	1700	1200	2800	2000	2200	2000	2100
Sr	5	120	600	2500	1550	2200	2000	2100
Cr	1	160	180	350	265	120	90	105
Co	2	30	25	50	38	30	15	23
Ni	2	150	150	190	170	60	30	45
Zr	10	180	200	280	240	1000	800	900
La	30	*	<30	<30	<30	<30	40	33
Y	30	70	90	150	120	160	120	140
Cu	3	30	50	5	28	10	12	11
V	5	110	120	140	130	130	110	120
Ga	1	35	35	45	40	35	40	37
Tl	30	*	*	*	*	*	*	*
Sn	5	*	*	*	*	*	*	*
Pb	10	<10	20	<10	12	10	12	11
Sc	10	<10	20	25	23	12	<10	<10
Mo	1	1	1	2	1.5	*	*	*
Ge	10	*	*	*	*	*	*	*
Be	5	*	*	*	*	*	*	*
Ag	1	*	<1	*	*	3	4	3.5
In	10	*	*	*	*	*	*	*

Analyst: R.A. Higazy.

* = Element if present is in amounts below its limit of sensitivity.

A - E are as given in Table 2a.

PART VII

THE TRACE ELEMENTS OF THE VOLCANIC ULTRABASIC POTASSIC ROCKS OF SOUTH-WESTERN UGANDA AND THE ADJOINING PART OF THE BELGIAN CONGO, AND THEIR BEARING ON PETROGENESIS

To be submitted for publication to the Geological Society of America.

ABSTRACT

The trace-element contents of the volcanic ultrabasic potassic rocks from South-western Uganda and the adjoining part of the Belgian Congo are discussed. The trace-element constitution of the various types investigated supports Holmes' hypothesis of their derivation from reactions between carbonatite magmas and sialic crustal material.

I. INTRODUCTION

Of the many assemblages of alkali igneous rocks described in recent years those of the Toro-Ankole volcanic fields of South-western Uganda and the Birunga-Bufumbira or North Kivu field, further to the south, are amongst the most remarkable for their petrographic constitution and the most interesting for their petrogenetic significance. By far the greater part of the work so far accomplished on these rocks has been carried out by the late A.D. Combe in the field in collaboration with Professor A. Holmes in the laboratory. A large number of rocks from the above areas have already been analysed chemically and samples of the analysed powders of many of them have been made available to me by Professor Holmes for spectrographic determination of the trace elements. This communication deals with (a) the distribution of the trace elements in characteristic rocks from both the Toro-Ankole and Birunga volcanic fields, and (b) the petrogenetic significance of the unique geochemical features which have been revealed.

The Toro-Ankole fields, East and South-east of Ruwenzori, comprise several areas of tuffs and explosion craters accompanied, in places, by lava-flows or near-surface plugs and sheets. The investigated specimens were collected by Combe from /

from the following areas:

(a) Katunga, an isolated extinct volcano, situated in the plateau country in the southern portion of the Toro-Ankole province. A general description of Katunga has been given by Combe (1937).

(b) Bunyaruguru, extending south of Lake George across the Western Rift and adjoining plateau. Reference should be made to Combe (1930, 1933 and 1939) for a general description of this field. The different explosion craters and lava occurrences of part of this field are shown in a map published by Combe and Holmes (1945, Fig. 2).

(c) Katwe-Kikorongo, within the Western Rift, between Lake Edward and Lake George.

Reference is also made in the present paper to the Fort Portal area, still further north. The exact locations of these volcanic areas can be seen in recent editions of the geological map of Uganda and also on maps compiled by Holmes (1950, Fig. 1, and 1952, Fig. 1).

The volcanic activity in Toro-Ankole, though now apparently extinct, dates from the Middle Pleistocene to almost the present time. The rocks underlying the volcanic products are mainly (1) the Kaiso series, composed of Pleistocene lacustrine and fluviatile deposits, and (2) Pre-Cambrian rocks comprising (a) the Post-Karagwe-Ankolean Granites, (b) the Karagwe-Ankolean System formed chiefly of argillites, phyllites and quartzites, and (c) the Toro System composed principally of schists, quartzites, amphibolites, gneisses and granites.

Except /

Except the Fort Portal area lava flows are very rare, pyroclasts being the dominant products. Katungite, a potassic volcanic rock with abundant olivine and melilite is the commonest type of lava. It occurs as lava-flows only at Katunga, the type locality; elsewhere, it is found almost ubiquitously as bombs, ejected blocks and lapilli in the agglomerates and tuffs. Each area, however, has its own peculiarities. At Katunga, katungite occurs by itself. In Bunyaruguru there is a greater variety, the two chief additional types being ugandite (a melanocratic olivine-rich leucitite) and mafurite (a rock differing from ugandite in having kalsilite instead of leucite). Mafurite obviously requires a very high K_2O/Na_2O ratio; otherwise potash nepheline appears instead of kalsilite. In the Katwe-Kikorongo area K is generally only a little higher than Na and consequently the place of mafurite is taken by potash ankaratrite. The latter type is linked to olivine-poor ugandite and mela-leucitite by leucite-ankaratrite, all the rocks of this series being richer in augite than the mafurite-ugandite series of Bunyaruguru.

In the Fort Portal area none of the above types except katungite is present. Lava-flows are abundant, but all are highly altered to calcium carbonate and only sparse relics of fresh minerals now remain. The original lavas seem to have been nepheline-leucite-melilite types not unlike those of Ninagongo (Birunga) and north shores of Lake Kivu.

It /

It may be noted here that these unique volcanic rocks and the sub-volcanic types, such as biotite-pyroxenite, that are invariably associated with them, present unusually difficult problems in petrogenesis. The recent hypothesis advanced by Holmes (1950) to account for the genesis of the most ubiquitous type, katungite, advocates that the latter was produced by reactions between a carbonatite magma and sialic crustal material such as granite and its associates. The magmatic carbonatite is regarded as the source of the cafemic material present in the rock, while the sialic material is considered to provide the alk-aluminous constituents and silica. This hypothesis has been successfully extended to the potash ankaratrite-mela leucitite series of Katwe-Kikorongo (Holmes, 1952).

Bufumbira is the eastern and Uganda part of the very extensive volcanic field of Birunga, which stretches across the Western Rift valley for nearly 50 miles north and north-east of Lake Kivu, for the most part covering regions in the Belgian Ruanda and the Belgian Congo. The positions of its major volcanoes are illustrated in the map given by Holmes (Holmes and Harwood, 1937, Fig. 2). The physiography and general geology of this field have been dealt with by Combe, in Combe and Simmons (1933, Chapters I-VI; see also the geological map at the end).

Simmons in Combe and Simmons (1933) gave preliminary petrographic /

petrographic descriptions of the volcanic rocks of Bufumbira. More detailed petrography, accompanied by chemical analyses and instructive petrological discussions has been published by Holmes in a valuable series of papers and memoirs (1936, 1937, 1942, 1945, 1950 and 1952; also Holmes and Harwood, 1932 and 1937; and Combe and Holmes, 1945).

Unlike the Toro-Ankole fields, the Birunga-Bufumbira field has many plagioclase-bearing rocks, kivite being the typical leucitic type and absarokite the potash feldspar-bearing type. In Bufumbira, ugandite is common and links the area to Bunyaruguru. In the south of Birunga nepheline-leucite-melilite rocks characterise Ninagongo and some of the small volcanoes along the north shore of Lake Kivu. This feature recalls the Fort Portal field, but there is a striking difference the Ninagongo rocks are beautifully fresh, whereas those of Fort Portal are heavily carbonated.

It is noteworthy that basalts are absent from both the Toro-Ankole and Birunga-Bufumbira fields, unlike the South Kivu field which is mainly basaltic with associated trachytes and rhyolites.

II /

II. GENERAL PETROGRAPHY

Holmes' investigations of the volcanic and associated rocks of Toro-Ankole and Birunga include a wealth of information with regard to (a) their detailed petrography; and (b) their classification and nomenclature according to their microscopical features and chemical composition. A brief summary of these investigations, with special emphasis on the general petrography of the rocks considered in the present study may be useful.

The constituents of the pyroclasts include fragments (a) of pre-volcanic crustal rocks (accidental) and (b) of a sub-volcanic (cognate) suite of rocks consisting of various combinations of the minerals augite, biotite and olivine. Representatives of both groups occur in the lavas - flows, blocks and lapilli - as xenoliths and xenocrysts. Each group will be briefly considered in turn before dealing with the lavas themselves.

(A) Accidental Constituents

The accidental xenoliths and xenocrysts and the accompanying ingredients of the tuffs and agglomerates are composed of the underlying crustal rocks. These are mainly granites, phyllites /

phyllites and quartzites; and other schists, amphibolites &c. belonging to the Karagwe-Ankolean and the Toro Systems. A full list of the varieties of such accidental blocks and xenoliths from Katwe crater has been given by Holmes (Holmes and Harwood, 1932, Table VIII, p. 403). Some of these crustal materials exhibit transfusion phenomena. Specimen K 9, considered in the present investigation, is a partially transfused microcline-granodiorite-gneiss from Katwe crater. It shows channels consisting of a dense, buff coloured, glassy or cryptocrystalline material with black inclusions, separating aggregates of granular quartz from large crystal of feldspar. The invading materials are tongues of a pyroxene-rich melilite-basalt (Holmes and Harwood, 1932, pp. 411-412). Holmes (1936) has also described from Bufumbira several interesting cases of transfused vein quartz or quartzite, accompanied in all cases by marked changes of composition. Moreover, he has demonstrated that granitic xenoliths enclosed in volcanic ejectamenta from Kariya crater (Bunyaruguru) have been transformed during the volcanic activity into leucite, leucitite and olivine-leucitite (Holmes, 1945).

(B) /

(B) Cognate Sub-volcanic Rocks

The sub-volcanic rocks are represented both as (a) ejected blocks in tuffs, agglomerates &c. and (b) xenoliths in lavas, lapilli and bombs. These rocks consist essentially of one or more of the minerals olivine, biotite and pyroxene; for brevity they are conveniently referred to by Holmes (1950) as the "O.B.P." series, after the initials of their dominant minerals.

Monomineralic inclusions composed almost entirely of olivine (dunite) occur locally in Bufumbira, but they are so friable that they cannot be collected without falling to pieces (Combe and Simmons, 1933, p. 69).

Monomineralic biotite-bearing rocks (glimmerite) are represented in this study by specimen C 4034a from Kakunyu crater, Bunyaruguru. This rock is composed essentially of biotite γ = 1.631, accompanied by no more than traces of augite (Combe and Holmes, 1945, p. 377). Biotite is present in anhedral reddish brown crystals which frequently show distortion, as in the case of other glimmerites described by Holmes from other craters (Holmes and Harwood, 1932, p. 406; 1937, p. 31; and Combe and Holmes, 1945, p. 376).

The commonest type of pyroxene occurring in the pyroxenites is a pale green, slightly pleochroic variety of augite /

augite with $Z \wedge c = 44°$ and 2V about 60°. Its normative composition in the Kakunyu pyroxenite, C 4035, considered in this study is approximately: diopside 90 per cent; aegirine, 4; hypersthene, 2; Al_2O_3 and Fe_2O_3, 4 (Combe and Holmes, 1945, p. 375). Many other varieties of augite, some richer in hedenbergite, some in aegirine and some more titaniferous are also found in the pyroxene-bearing types.

Other rocks of the sub-volcanic series are the peridotites (C 1963 and C 4034b) and the biotite-pyroxenites (C 2786, G 20 and K 4), the latter being by far the commonest.

C 1963 is a biotite-bearing augite-peridotite from an ejected block near Mabungo crater (Bufumbira). Olivine, almost perfectly fresh, forms roughly a quarter of this rock. Augite is more abundant and occurs as prismatic greenish crystals displaying faint pleochroism with X = Z = pale green; Y = yellowish green. Biotite makes up about 8 per cent of the rock, as flakes between the individual crystals of olivine and pyroxene. Its pleochroism is X = green yellow; Y = light brown; Z = brown (Holmes and Harwood, 1937, pp. 21-22). The other peridotite (C 4034b) from Kakunyu crater (Bunyaruguru) is richer in biotite and very much poorer in augite. The augite is greyish-green in colour; its biotite is reddish brown with X = very pale yellow; Y = yellowish brown; Z = reddish brown, and is partially corroded around its edges. Olivine is found in /

in relatively small fresh grains.

C 2786 is part of an ejected block of biotite-pyroxenite from Lutale crater (Bufumbira). It is a holocrystalline aggregate of copper-coloured plates of biotite, blue-black tarnished-looking prisms of augite and black garnet, with accessory black ores and rare olivine. Biotite of this type is present in two distinct varieties; a dominant type displaying the pleochroism X = green yellow, Y = light red brown; Z = copper brown. The smaller crystals of this variety exhibit alternations of colour parallel to the cleavage and show marked pleochroism with X = metallic grey; Y = purple grey; Z = deep chestnut brown. The other variety of biotite is less common and invades the dominant type along strips between the cleavage cracks. Its basal sections resemble malanite and can only be readily distinguished from it by the biaxial interference figure. The garnet of this biotite-pyroxenite is a titaniferous melanite found in elongated lobes and aggregates of rounded grains with dominant deep chestnut brown colour (Holmes and Harwood, 1937, p. 26). Specimen G 20 is a biotite-pyroxenite from Katwe crater. Its minerals are similar to those found in other biotite-pyroxenites from Katwe, and already fully described by Holmes (Holmes and Harwood, 1932, pp. 408-409). The chief constituents of these rocks are pleochroic diopside- /

diopside-hedenbergite and deep brown biotite. The accessories are sphene, ilmenite or titaniferous magnetite, melanite and perovskite, with traces of nepheline. In places, sphene may be present in such conspicuous amounts as to justify naming the rock "sphene-rich biotite-pyroxenite". Specimen K 4 is a representative of this variety. Holmes points out that in mineralogy and structure the biotite-pyroxenites of South-west Uganda (Holmes and Harwood, 1932, p. 409) closely resemble the corresponding rocks found in situ in the Libby stock (Montana) described by Larsen and Pardee (1929).

Leucite-kentallenite is an interesting variety of the cognate sub-volcanic rocks, so far found only in Birunga, where it is associated with kivite. These rocks differ from the previously mentioned types in possessing feldspars among their constituents. C 3033 is part of an ejected block of leucite-kentallenite from the caldera of Nyamuragira, a vigorously active volcano situated in the western part of Birunga. The rock is composed of phenocrysts of augite and smaller rounded grains of clear brown-green olivine, embedded in a white feldspathic matrix. Augite is purple in colour and displays strong pleochroism with X = fawn, sometimes with a greenish tinge; Y = purple; Z = brownish purple. Zoning is noticeable in some crystals. Leucite and a dominantly feldspathic matrix occupy /

occupy the interstitial spaces. The matrix is composed of fine-grained plagioclase laths, most of which are zoned (An_{30}-An_{85}), together with smaller amounts of alkali-feldspar flecked with yellowish ferruginous staining, biotite in minute flakes, apatite needles and small grains of olivine (Holmes and Harwood, 1937, pp. 113-114).

The specimens of sub-volcanic rocks studied in this investigation are listed in the following Table.

No. of specimen	Name	Locality	Reference
K 9	Ejected block of partially fused granodiorite-gneiss	Katwe crater, Katwe-Kikorongo	Holmes & Harwood 1932, pp. 411-412
G 20	Ejected block of biotite-pyroxenite	"	*ibid.*, p. 408
K 4	Ejected block of sphene-rich biotite-pyroxenite	"	*ibid.*, p. 409
C 4034a	Xenolith of glimmerite from olivine-rich ugandite	Kakunyu crater Bunyaruguru	Combe & Holmes, 1945, p. 377
C 4035	Xenolith of pyroxenite from olivine-rich ugandite	"	*ibid.*, p. 375
C 4034b	Xenolith of biotite-peridotite from olivine-rich ugandite	"	*ibid.*, p. 377
C 2786	Ejected block of biotite-pyroxenite	Lutale crater Bufumbira	Holmes & Harwood 1937, p. 26
C 1963	Ejected block of biotite-bearing augite-peridotite	Mabungo crater Bufumbira	*ibid.*, pp. 21-22
C 3033	Ejected block of leucite-kentallenite	Caldera of Nyamuragira, Birunga	*ibid.*, pp. 113-

(C) /

(C). Volcanic rocks from the Toro-Ankole fields

The mineralogical classification of the chief volcanic rocks adopted in this study is that introduced by Holmes (1950, Fig. 2, p. 776), shown graphically in Fig. 1. The principal rock varieties are katungite, ugandite and mafurite. Katungite is rich in melilite, but free from augite; its potash is mainly in glass. Ugandite and mafurite contain augite, but their dominant feldspathoids are leucite and kalsilite respectively. Olivine is present in these three types, but there is an important variety of katungite which is free from this mineral and has been given the name proto-katungite (Holmes, 1942, p. 199; 1950, p. 784). The investigated rocks also include members of the potash-ankaratrite-melaleucitite series from the Katwe-Kikorongo field. This series differs mineralogically from the ugandite-mafurite series in being conspicuously rich in augite and relatively poor in olivine (Holmes, 1950. p. 776). Xenocrysts derived from the "O.B.P." series differ in the various volcanic rocks. They are mainly, but not exclusively, biotite and augite in the case of katungite; olivine in ugandite; and augite in ankaratrite. Mafurite carries variable amounts of all the three minerals, often with a conspicuous abundance of biotite (Holmes, 1950, p. 777).

(i) Katungite /

(i) Katungite

Katungite is the most widely distributed of all the volcanic types. As defined by Holmes (1937, p. 210), who proposed the term, katungite is "an alkali ultrabasic rock with morepotash than soda, the essential minerals being melilite and olivine; the potash may be present in glass, zeolites, potash-rich nepheline, kaliophilite [later recognised as a new mineral kalsilite; Holmes, 1942, p. 210], leucite, or biotite; special varieties may be distinguished by appropriate mineralogical prefixes, e.g. leucite-katungite, biotite-katungite, leucite-biotite-katungite". Its significant characters and relationships to olivine-melilites and related rocks from other regions are discussed in detail by Holmes (1937). The seven katungites investigated include specimens from the Katunga, Bunyaruguru and Katwe volcanic areas. With one exception (Katunga) they are lapilli or blocks. A list of these specimens is given in the adjoining Table.

No. /

No.	Name	Locality	Reference
C 4407	Katungite	W. lava flow, Katunga	Holmes, 1937, p. 205
G 21	Katungite	Lapilli, Katwe crater	<u>ibid.</u>, p. 207
G 56	Biotite-katungite[*]	Ejected block Katwe crater	<u>ibid.</u>,
C 3509	Katungite	Ejected block Chamakumba crater Bunyaruguru	Holmes, 1942, p. 212; and Combe and Holmes, 1945, p. 367
C 5945	Katungite	Lapilli, N.W. edge of Bunyaruguru	Combe and Holmes, 1945, p. 367
C 4012	Kalsilite-katungite	Lapilli, Changabe crater, Bunyaruguru	Holmes, 1942, p. 210; and Combe and Holmes, 1945, p. 367
C 6065	Proto-katungite	Ejected block, Lugazi ridge, Bunyaruguru	Holmes, 1950, p. 784

[*] This is an augite-bearing biotite-katungite and has been referred to under the more familiar name alnöite (Holmes, 1950, p. 780).

(ii) <u>Ouachitite</u>

The examined specimen (C 5844) is an olivine-rich ouachitite from Katwe crater. It is fine-grained porphyritic rock with phenocrysts of olivine and diopsidic augite. Its groundmass is composed mainly of shreds of reddish-brown biotit

and /

and of aggregards of diopsidic augite. Associated with these constituents, are small olivine crystals and minute grains of perovskite and black ore. Calcite patches and zeolite infillings of vesicles are scattered here and there in the matrix. Rare leucite grains and a few glass-clear crystals of potash-nepheline occur interstitially.

Katungite (G 21), augite-bearing biotite-katungite or alnöite (G 56) and ouachitite (C 5844) are all from Katwe crater. They form a series in which there appears to be a complementary relationship between melilite and pyroxene. The katungite is rich in melilite and free from augite whereas the other end-member of the series (ouachitite) has preponderant augite and no melilite. The volume percentages of melilite in these rocks are estimated by Holmes (1950, p. 781) as 37 in katungite, 18 in alnoite, and none in ouachitite.

(iii) Ugandite

Ugandite is the term proposed by Holmes (Holmes and Harwood, 1937, p. 11) for melanocratic types of olivine-leucitites. Such volcanic rocks are found in the Katwe-Kikorongo, Bunyaruguru and Bufumbira volcanic fields. Varieties exceptionally rich in olivine are locally common and are referred to as olivine-rich ugandite.

The /

The ugandite here investigated (C 3052) is an olivine-rich variety from Kichwamba, adjoining Kachuba crater, Bunyaruguru. A detailed petrographic description is given by Holmes (Holmes and Harwood, 1932, pp. 414-415). The rock contains conspicuous phenocrysts of olivine, clino-enstatite and augite. Olivine is sporadically rimmed by biotite. Augite is most generally straw-green in colour. Apart from a few small crystals (0.1 to 0.2 mm.) of olivine, augite, and mica, the groundmass is composed of augite microlites, leucite, perovskite, opaque ores, apatite needles, and little patches of calcite and cloudy analcite.

For descriptions of other interesting varieties of ugandite, reference should be made to Holmes (Combe and Holmes, 1945, pp. 371-372) who records nosean in the kalsilite- and the kalsilite-melilite-ugandite lavas of Kabirenge and Lyakauli, Bunyaruguru; and to his earlier investigations of the Bufumbira ugandites and their relationships to similar volcanic rocks in other provinces (Holmes and Harwood, 1937, p. 60).

(iv) Mafurite

The term mafurite has been proposed by Holmes (1942, p. 199) for olivine-melakalsilitites, composed of olivine, pyroxene, kalsilite, perovskite, and black ore, found in and around the Mafuru craters, Bunyaruguru. The specimen here investigated /

investigated (C 6073) is porphyritic with phenocrysts of deeply corroded olivine and of diopsidic augite. The volume percentages of these and of the constituents of the groundmass are given by Holmes (1942, p. 203) as follows:

	Groundmass	Phenocrysts
Diopside	26.0	20.6
Kalsilite	23.7	
Perovskite	6.2	
Black ore	5.7	
Olivine	4.4	6.3
Biotite	2.3	
Glass	4.1	
Totals	72.4	26.9

Some varieties of mafurite contain melilite, melilite-mafurite being transitional towards katungite. Leucite-mafurite and kalsilite-ugandite are intermediate varieties in the series mafurite — ugandite. The microscopical features of examples of these types, as well as of the variety biotite-mafurite, from various craters in Bunyaruguru, are given and illustrated by Holmes (1942, pp. 207-210; and plate VI, p. 216).

(v) Leucite-ankaratrite and Leucite-melilite-ankaratrite

In general, the ankaratritic series can be distinguishe from the mafurite-ugandite series by its relative abundance of pyroxenes compared with olivine, which may, indeed by absent from some members (Holmes, 1950, p. 776; 1952). The mineralogical constitution of the Katwe-Kikorongo ankaratrites is closely similar /

similar to that of the melanocratic nephelinites of Madagascar, the type ankaratrites described by Lacroix (1923, p. 59). But, on account of their higher potash content and K_2O/Na_2O value, Holmes (Holmes and Harwood, 1932, p. 388) has distinguished the Uganda examples by the name "potash-ankaratrite". By increase of leucite at the expense of potash-nepheline these types pass through leucite-ankaratrite to melaleucitite or olivine-melaleucitite, the latter being like olivine-poor ugandite. Melilite-bearing varieties are also known.

The ankaratritic rocks here investigated are leucite-ankaratrite (C 5635), from a lava exposed in the wall of Lake Mbuga crater (Holmes, 1952, p. 204), and leucite-melilite-ankaratrite (C 5692), part of an ejected block from the south rim of Nyaluzigati crater; both localities are in the Katwe-Kikorongo field.

C 5635 is a coarse-grained porphyritic variety. The phenocrysts are mainly augite together with less abundant olivine and some black ores and perovskite. Augite occurs in elongated hypidiomorphic prismatic and bladed forms, up to 8 mm. long, showing notable sub-parallelism. It is yellowish-green in colour exhibiting distincly purplish outer margins. The cores of some of the crystals are very pale in colour. The rims are heavily sprinkled with minute grains of black ore, together /

together with occasional crystals of perovskite. The terminations are frayed and show no sign of variation in composition towards aegirine-augite. Most of the olivine grains are smaller in size than those of augite and are irregularly rounded. Their borders are commonly rimmed with brown ferruginous matter and reddish-brown biotite.

The groundmass is composed of very clear patches of potash-nepheline, mainly occupying parts of the interstitial spaces between adjacent augite phenocrysts, where it is associated with numerous round crystals of leucite. Aggregates of augite and black ores; shreds of biotite; calcite; and minute crystals of perovskite are also found in the groundmass. Apatite in rounded grains is present as sporadic inclusions in biotite and in the black ores.

Potash ankaratrites and leucite-ankaratrites from Mbuga and Nabugando craters in the Katwe-Kikorongo field, have recently been described in detail by Holmes (1952). In an earlier paper he gave the modal composition of several rocks belonging to this series (Holmes and Harwood, 1932, pp. 387-390 and pp. 392-394). The feldspathoidal members in these rocks are potash-nepheline with subsidiary leucite, as in the specimen (C 5635) here investigated. Moreover, the mode of C 5635 approximates to that of leucite-ankaratrite (C 1000) which is as /

as follows (Holmes and Harwood, 1932, p. 387):

Phenocrysts:

Pyroxenes	50 per cent
Olivine	4
Opaque ores	11

Groundmass:

Pyroxenes	10
Biotite	4
Ores,&c.	7
Feldspathoids	14

The other investigated ankaratritic rock (C 5692) is a leucite-melilite variety. It is porphyritic, with small phenocrysts of augite and sparse olivine. Augite occurs as yellowish-green prismatic crystals arranged in a sub-parallel manner; purplish margins are lacking and the rims are not strewn with black ores and perovskite as in the augite phenocrysts of C 5635. Olivine occurs as clear transparent crystals without reaction borders. The groundmass is composed of minute laths of augite, prisms of melilite, cloudy in patches, rounded grains of leucite, occasionally carrying black inclusions, transparent crystals of olivine, black ores and perovskite, the latter being more abundant than in C 5635. These constituents are set in a greenish glassy background.

(vi) Mela-potash-nephelinite and mela-leucitite.

The mela-potash-nephelinite (C 5566, from an ejected block /

block, north of the Lake in South Nymununka crater, Katwe-Kikorongo volcanic area) and the mela-leucitite (C 5545, from an ejected block, western rim of South Nymununka crater) are olivine-free types.

C 5566 is very fine-grained, but C 5545 is slightly coarser and porphyritic. They are composed essentially of augite and feldspathoid, as indicated respectively in the names adopted. C 5545 also contains occasional crystals of nosean or hauyne. Together with these constituents abundant aggregates of black ores and perovskite occur in both rocks. Apatite, occurring as needles, is a minor accessory.

(D) Volcanic rocks from the Birunga field

The specimens investigated of the volcanic rocks from the Birunga field comprise: (i) types with feldspathoids and no feldspars, such as olivine-melilitite (C 7360) and potash-nepheline-milililitite (C 3022); (ii) feldspar-and-leucite-bearing varieties represented by kivite or leucite-basanite (C 9780, C 9892) and leucitic trachybasalt (C 9878); and (iii) limburgite (C 7347).

(i) Olivine-melilitite (C 7360) comes from Lwabikari crater, north of Lake Kivu, Belgian Congo. It is porphyritic with /

with abundant phenocrysts of augite and occasional olivine. Augite is grey to buff with a purplish tinge and more distinctly purple margins. Some of the larger grains are deeply embayed by the groundmass. Olivine crystals, some of which are corroded, are generally smaller than those of augite. The groundmass is cryptocrystalline and consists mainly of aggregates of black ore and augite, accompanied by small prisms of melilite, olivine grains, glass-clear tabular crystals of potash nepheline, occasional rounded grains of leucite and small needles of apatite. The mode of this rock approaches that of the melilite-leucite-ankaratrite (C 5692) described on page 21 except that it contains less melilite and is free from perovskite.

Potash nepheline-melilitite (C 3022) is a typical specimen of a flow from Ninagongo volcano. It has been already described by Holmes (Holmes and Harwood, 1937, p. 84), who mentions that melilite-nepheline lavas are not uncommon in the southern part of Birunga, between Ninagongo and Lake Kivu, e.g. from the Bushwaga and Goma Volcanoes. C 3022 is fine-grained and consists essentially of melilite laths exhibiting a somewhat trachytic texture, together with clear crystals of potash nepheline and aggregates of black ore, in an interstitial matrix of greenish material which may be chlorophaeite. Perovskite is absent. This rock cannot be matched mineralogically with any of the volcanic /

volcanic types of the Toro-Ankole volcanic areas mentioned above, but it may be akin to the original lavas (now highly carbonated) of the Fort Portal field (Holmes and Harwood, 1932, p. 380).

(ii) C 3030 represents a kivite lava, from the northern slopes of Nyamuragira at 9500 feet, which has been petrographically described by Holmes (Holmes and Harwood, 1937, p. 116). It is a vesicular porphyritic rock with phenocrysts of purple augite, clusters of plagioclase, and olivine. The groundmass is composed of abundant grains of augite, minute laths of plagioclase, leucite, mainly in clear patches, and black ores. Inclusions are present, consisting of the leucite-kentallenite described on p. 11. For detailed descriptions of other kivites from Birunga reference should be made to Holmes (Holmes and Harwood, 1937, pp. 102-136); and to Verhoogen (1948, p. 160) who gives the petrographical characters of the lavas of the 1938 Nyamuragira eruption.

C 9780 is a representative of the 1948 eruption of Kituru (a new volcanic cone on the flanks of Nyamuragira). This typs is a scoracious and finer grained variety of kivite but has essentially the same mineralogical constitution as C 3030.

C 9892 represents the 1948 eruption of Muhubuli (a new cone on the same line of fissure as Kituru). The rock is also a kivite, with microscopical features very similar to those of C 9780.

The /

The leucitic trachybasalt C 9878 is from a lava flow erupted in 1948 from a fissure north-west of Kituru. The phenocrysts of this rock are similar to those of the kivites just mentioned, but the groundmass is hyaline except for very minute laths of plagioclase and a few more or less rounded grains of leucite.

(iii) C 7347 is a characteristic specimen of the limburgite erupted in 1904 from Nahimbi volcano (formerly called Adolf Friedrich Kegel) situated in the south-western portion of the Birunga field (Holmes and Harwood, 1937, p. 214). Finckh (1912, p. 20) described the lava as a porphyritic rock with abundant phenocrysts of titanaugite (up to 10 mm.) and olivine in a groundmass composed essentially of augite and black ore, together with a little olivine and interstitial brownish glass. The specimen here investigated corresponds, except that the augite is only very faintly purple and the groundmass is mainly brownish glass.

III. /

III. ANALYTICAL METHODS AND DATA OBTAINED

Samples of the powders originally prepared for chemical analysis of all the above mentioned sub-volcanic and volcanic rocks were kindly provided by Professor Arthur Holmes, for their spectrographical investigation. The chemical compositions of most of the types investigated have already been published by holmes in his various papers to which reference has already been made. Professor Holmes has kindly given me permission to make use of hitherto unpublished chemical analyses of some of the specimens from the Katwe-Kikorongo and Birunga fields.

The trace elements of these rocks, as well as those of four carbonatites (from the Premier Diamond mine, South Africa; Spitzkop alkaline complex, Bushveld, Transvaal; Marongwe Hill, Chilwa Island, Nyasaland; and Hartung, Alnö Island, Sweden), and two limestones (from the Transvaal System, South Africa; and Mansjö, Sweden), also provided by Professor Holmes, were spectrographically determined by the author at the Macaulay Institute for Soil Research at Aberdeen, Scotland. The semi-quantitative method adopted in this study is that described in detail by Mitchell (1948). The determined elements and the wave lengths of their diagnostic lines have already been given by the writer (Higazy, 1952a).

IV. GEOCHEMISTRY OF THE SUB-VOLCANIC ROCKS (O.B.P.) SERIES

(i) Major constituents

The chemical composition and the trace-element contents of the sub-volcanic suite of rocks are recorded in Table 1a and 1b respectively. Three of the chief members of the "O.B.P." series — peridotite, pyroxenite and glimmerite — are represented by specimens from Kakunyu crater, Bunyaruguru (Nos. 4034b, 4035 and 4034a respectively). The distribution of the major constituents of these rocks will now be discussed in order to illustrate their main geochemical features.

Of all the major constituents, the iron oxides have the most uniform distribution, with $FeO > Fe_2O_3$. The range of FeO is from 2.55 per cent in the peridotite to 2.90 in the glimmerite; and that of Fe_2O_3 is confined to the narrow limits of 4.96 per cent in the peridotite to 5.42 in the pyroxenite.

Na_2O is relatively very low and roughly uniform, ranging from 0.26 per cent in the peridotite to 0.56 in the pyroxenite and glimmerite.

The other major constituents, however, show marked variations in the different types. As would be expected, Al_2O_3 is low in pyroxenite and peridotite and much higher in glimmerite.

MgO /

Mgo reaches 33.84 per cent in the peridotite and amounts to 19.32 in the glimmerite and 13.14 in the pyroxenite. The difference in the CaO contents of these rocks is still more pronounced. The pyroxenite has 22.57 per cent of CaO, whereas the peridotite and the glimmerite have only 2.84 and 1.16 respectively. The biotite-augite-peridotite, C 1963, from Bufumbira, however, possesses lower Mgo (19.31 per cent) and considerably higher CaO (16.99) than the Bunyaruguru peridotite C 4034b. These differences are due to the relative abundance of augite in the Bufumbira peridotite and of olivine in the Bunyaruguru variety.

It is not surprising to find 9.01 per cent K_2O in the glimmerite, since it is composed almost entirely of biotite, which is responsible also for its relatively high TiO_2 (5.18 per cent). The peridotite and the pyroxenite, however, possess considerably lower K_2O contents, being 2.58 and 0.08 per cent respectively. The glimmerite and the peridotite have $K_2O > Na_2O$, whereas the pyroxenite has $Na_2O > K_2O$, corresponding to its complete lack of biotite. All three rock types have $Al_2O_3 > K_2O$.

The analysed biotite-pyroxenites, G 20 from Katwe and C 2786 from Bufumbira, have $K_2O > Na_2O$ and $Fe_2O_3 > FeO$, the reverse of what is found in the pyroxenite C 4035, The sphene-rich biotite-pyroxenite K 4 of Katwe, is remarkable for its very abundant /

abundant TiO_2 (8.65 per cent) and P_2O_5 (2.80). Its total FeO and Fe_2O_3 (17.89 per cent) is considerably higher than that of the biotite-pyroxenites of Katwe (9.97) and Bufumbira (7.91).

Chemical analysis of the leucite-kentallenite (C 3033a) from Bufumbira reveals a marked excess of FeO (12.00 per cent) over Fe_2O_3 (1.15). Since the rock contains plagioclase Al_2O_3 (12.20) and Na_2O (1.60) are higher than in the "O.B.P." series (apart from the high Al_2O_3 of glimmerite).

In summary, it is found that the sub-volcanic rocks discussed above show variations in the amounts of their major oxides consistent with their mineralogical constitution. The peridotites (average of C 4034b and C 1963) have $MgO > CaO > (Al_2O_3+K_2O+Na_2O)$ whereas the pyroxenites (average of G 20, K 4, C 4035 and C 2786) have $CaO > MgO > (Al_2O_3+K_2O+Na_2O)$; the glimmerite (C 4034a) has $(Al_2O_3+K_2O+Na_2O) > MgO > CaO$; and the leucite-kentallenite (C 3033a) has $(Al_2O_3+ K_2O+Na_2O) > CaO > MgO$.

(ii) Trace Elements

(a) Rubidium and barium

The distribution of Rb and Ba in the different O.B.P. sun-volcanic types is primarily related to that of biotite. The peridotites and the pyroxenite in which biotite is negligible or absent contain undetectable contents of Rb (less than 1 ppm.) and /

and are relatively poor in Ba (15-50 ppm.). The biotite-pyroxenites, however, contain appreciable and almost uniform amounts of Rb (150-170 ppm.). Their Ba contents are relatively high, ranging from 1200 to 2000 ppm. The glimmerite (biotite-rich rock), possesses still higher contents of both Rb (1000 ppm.) and Ba (3200 ppm.). This clearly indicates that, of the ferromagnesian minerals, biotite is the richest depository of these two elements.

The leucite-kentallenite is a biotite-free rock, but it contains feldspars, mainly plagioclase, and leucite. The presence of appreciable amounts of Rb (75 ppm.) and Ba (1000 ppm.) in this rock is therefore, understandable.

The (Rb+Ba) and K_2O contents of the above rocks vary sympathetically, as indicated in the following list:

Type	(Rb+Ba) in ppm.	K_2O in wt. per cent.
Pyroxenite	20	0.08
Peridotite (2 analyses)	33	1.73
Leucite-kentallenite	1075	2.02
Sphene-rich biotite-pyroxenite	1370	2.38
Biotite-pyroxenite (2 analyses)	1905	3.55
Glimmerite	4200	9.01

(b) Gallium

Ga is present in relatively low amounts ($<$ 1-10 ppm.) in the peridotites and pyroxenites. The distribution of this element /

element in the other types, namely, biotite-pyroxenites, glimmerite and leucite-kentallenite is almost uniform (20-30 ppm.). It is noticed that the total (Al_2O_3+Fe_2O_3) in the relatively Ga-poor varieties (5.65 - 6.86 per cent) is lower than that in the Ga-rich types (11.48 - 19.42).

(c) Strontium, lanthanum and yttrium

Sr varies from 40 ppm. in the peridotite (C 4034b) to 1000 in the sphene-rich biotite pyroxenite. The pyroxenite and biotite-pyroxenites, which contain little or no sphene, have much less (340-600 ppm.) than the sphene-rich type, indicating that sphene is responsible for the relatively high Sr content of the latter.

The biotite-pyroxenites and the glimmerite (relatively rich in biotite) all have Ba $>$ Sr, but the peridotites and the pyroxenite (relatively poor in biotite) have the reverse relationship. It is interesting to notice that the values of Ba/Sr in the biotite-pyroxenite (G 20) from Katwe and that from Bufumbira (C 2786) are similar, being 3.3 and 3.0 respectively. Moreover, the values of the same ratio in the peridotite from Bunyaruguru (C 4034b) and that from Bufumbira (C 1963) are also much the same - 0.4 and 0.5 respectively. The pyroxenite

(C 4035) shows considerably greater enrichment in Sr relative to Ba, its Sr/Ba value being 16.6. This corresponds to the greater enrichment of Ca relative to K in this rock than in the other types, the CaO/K_2O value being 280 in the pyroxenite (C 4035) and ranging from 1.1 to 19.3 in the biotite pyroxenites and peridotites.

La is present in a detectable amount ($<$ 30 ppm.) only in the sphene-rich biotite-pyroxenite, which also contains a similar amount of Y. Two of the other rocks also contain Y, the biotite-pyroxenite from Katwe ($<$ 30 ppm.) and the leucite-kentallenite (35 ppm.), although they are free from detectable quantities of La (i.e. $<$ 30 ppm.).

(d) Lithium

Li is present in very low amounts in the different types of the sub-volcanic series ($<$ 1-8 ppm.). This feature is also noticeable in all the volcanic rocks investigated. The variation of the Li content is so narrow that no significance can be attached to it. Moreover, although Li is liable to be enriched in the micas, it is remarkable that even the glimmerite has $<$ 1 ppm. This indicates that the parental materials from which these rocks developed were deficient in this element. This is confirmed by the analyses of Uganda granites listed in King /

King (1939, Table 3, p. 138); Li_2O is recorded as "none" in seven out of eight analyses and as 'trace' in the remaining one.

(e) Chromium, Nickel and Cobalt

The peridotites are characterised by normally high Cr and Ni contents. The peridotite from Bufumbira has 4000 ppm. Cr and 350 ppm. Ni, and that from Bunyaruguru 2400 ppm. Cr and 1900 ppm. Ni. It is noticeable that the former (relatively rich in pyroxene) has higher Cr and lower Ni contents than the latter (relatively rich in olivine). This adds further support to the writer's statement - in connection with the distribution of these elements in ferromagnesian minerals (Higazy, 1952b) - that the Cr content of the olivines seems to be lower than that of the pyroxenes and that Ni shows the reverse distribution in these two groups.

Cr and Ni are more concentrated in the glimmerite (1500 and 320 ppm. respectively) than in the different varieties of biotite-pyroxenite (average: Cr, 775; Ni 190 ppm.) and the pyroxenite has still less (100 and 85 ppm. respectively). The sphene-rich biotite-pyroxenite is remarkable in containing negligible amounts of both Cr ($<$ 1 ppm.) and Ni (2 ppm.). This rock contains abundant sphene which forms roughly 40 per cent of its modal composition, while yellowish green pyroxene, biotite /

biotite and black ores constitute approximately 60 per cent. The deficiency of this rock in both Cr and Ni is therefore, very striking.

The contents of Cr and Ni in the leucite-kentallenite are 350 and 120 ppm. respectively, being similar to the corresponding averages for gabbros (Cr, 340; Ni, 158 ppm.), as given by Goldschmidt (1937).

The total (Cr+Ni) and the MgO contents of the different types vary rather sympathetically:

Type	(Cr+Ni) in ppm.	MgO in wt. per cent
Peridotite (2 analyses)	4325	26.58
Glimmerite	1820	19.32
Biotite-pyroxenite (2 analyses)	965	14.72
Pyroxenite	185	13.14
Sphene-rich biotite-pyroxenite	2	7.53

The distribution of Co is much less variable than that of Cr and Ni, the average contents of the various types all falling within the range 55 to 75 ppm.

All the varieties except the sphene-rich biotite-pyroxenite are characterised by Cr > Ni > Co, as in ordinary ultrabasic rocks (Lundegårdh, 1949; Higazy, 1952b). The sphene-rich biotite-pyroxenite, however, has Co > Ni > Cr.

(f) /

(f) Vanadium and Copper

On the whole, the pyroxenites contain more V than the other members of the "O.B.P." series. The sphene-rich biotite-pyroxenite has the highest content of this element (550 ppm.); the biotite-pyroxenites (345 ppm.) and the glimmerite (200 ppm.) coming next, followed by pyroxenite (150 ppm.) and the peridotites (120 ppm.). V can be present in pyroxenes, sphene and biotite. V^3 (ionic radius, 0.65 Å) replaces Fe^3 (0.67) in the pyroxene structure. But in the sphene and biotite lattices, V is most likely to be present in its tetravalent state replacing Ti^4, since V^4 and Ti^4 have similar ionic radii, 0.61 and 0.64 Å respectively. The concentration of V in the leucite-kentallenite (380 ppm.) is approximately the same as that of the average content in the pyroxenites (350 ppm.).

The total (Co+V) in the different types increases with increase in the total ($FeO+Fe_2O_3$) as assembled below:

Type	(Co+V) in ppm.	($FeO+Fe_2O_3$) in wt. per cent.
Peridotite (2 analyses)	188	6.57
Pyroxenite	205	8.03
Glimmerite	255	8.14
Biotite-pyroxenite (2 analyses)	408	8.94
Leucite-kentallenite	455	13.15
Sphene-rich biotite-pyroxenite	610	17.89

The Cu content of the biotite-pyroxenites (average 75 ppm.) is higher than that of the peridotites (average 45 ppm.).

But /

But the glimmerite and pyroxenite both contain only 3 ppm. of this element. The distribution of Cu is obviously very erratic in these rocks.

The total (Cr+Ni+Co+V+Cu) increases with the total ($MgO+FeO+Fe_2O_3$) as shown below:

Type	(Cr+Ni+Co+V+Cu) in ppm.	($MgO+FeO+Fe_2O_3$) in wt. per cent
Pyroxenite	393	21.17
Leucite-kentallenite	960	23.41
Biotite-pyroxenite (2 analyses)	1448	23.91
Glimmerite	2078	27.46
Peridotite (2 analyses)	4558	33.15

These trace elements are known to replace Mg, Fe^2 and Fe^3 in the different appropriate crystal lattices.

(g) Other trace elements

Zr is much more abundant in the sphene-rich biotite-pyroxenite (1200 ppm.) than in the other types ($<$ 10-250 ppm.). This indicates that the sphene in this rock is relatively rich in Zr.

Sc is found in detectable amounts (15-40 ppm.) only in the pyroxene-rich rocks, its content in augite-poor peridotite, glimmerite and leucite-kentallenite being below the limit of sensitivity ($<$ 10 ppm.).

Ag is detectable except in leucite-kentallenite, the members /

members of the "O.B.P." series having variable amounts of this element ranging from 1 to 20 ppm.

The variation in the distribution of Pb cannot be determined. Most of the examined types have $<$10 ppm. of this element.

Mo is detectable only in the peridotites (average, 2 ppm.) while Be and In are determinable only in the glimmerite (5 and $<$ 10 ppm. respectively). Tl and Ge if present are found in amounts below the limits of sensitivity throughout this suite.

Summary of the trace-element distribution in the sub-volcanic rocks

Generally the outstanding features of the distribution of the trace elements in the analysed members of the "O.B.P." series are as follows:

(1) Cr and Ni are relatively abundant in the peridotite; Rb and Ba in the glimmerite; and Sr and (Co+V) in the biotite-pyroxenites.

(2) Li is very sparse in all the members.

(3) All the types have $Cr > Ni > Co$ as in normal ultrabasic rocks.

(4) It has been shown that the average peridotite has $MgO > CaO > (Al_2O_3+K\,O+Na\,O)$ while the glimmerite has $(Al_2O_3+K_2O+Na_2O) > MgO > CaO$. Correspondingly, the former shows $(Cr+Ni) > (Sr+La+Y) > (Ga+Rb+Ba)$, and the latter has $(Ga+Rb+Ba) > (Cr+Ni) > (Sr+La+Y)$. The /

The pyroxenite has $CaO > MgO > (Al_2O_3+K_2O+Na_2O)$ and accordingly shows $(Ga+Rb+Ba) > (Sr+La+Y)$ $(Cr + Ni)$.

(5) The biotite-pyroxenites have $MgO > CaO > (Al_2O_3+K_2O+Na_2O)$ and $(Ga+Rb+Ba) > (Cr+Ni) > (Sr+La+Y)$; and the sphene-rich biotite-pyroxenite has CaO $(Al_2O_3+K_2O+Na_2O) > MgO$ and $(Ga+Rb+Ba) > (Sr+La+Y) > (Cr+Ni)$.

(6) The leucite-kentallenite is characterised by relatively moderate amounts of Rb, Ba; Sr; and Cr and Ni. It has $Cr > Ni > Co$; and $(Ga+Rb+Ba) > (Sr+La+Y) > (Cr+Ni)$ corresponding to the relation $(Al_2O_3+K_2O+Na_2O) > CaO > MgO$.

V. GEOCHEMISTRY OF THE VOLCANIC ROCKS

A. Katungite, ugandite and mafurite

(i) Major constituents.

The chemical compositions of the investigated katungites, ugandite and mafurite are recorded in Table 2a. It is noticeable that the katungites of the different volcanic areas do not vary in the contents of their major oxides, and consequently no individual katungite differs significantly from the average composition here adopted for discussion. There are certain characters shared by allthree types. All are relatively rich /

rich in K_2O (3.46-6.98 per cent) and TiO_2 (3.52-4.86), and have $K_2O > Na_2O$, their chief feldspathoids being leucite and/or kalsilite. They also have $Al_2O_3 > (K_2O+Na_2O)$, thus differing from the leucite-bearing rocks of West Kimberley, Western Australia which have $K_2O > Al_2O_3$ (Wade and Prider, 1940).

The chief mineralogical differences are naturally reflected chemically. Katungite, being melilite-rich, possesses the highest CaO content (16.06 per cent). Ugandite, being the richest in olivine, has the highest MgO (24.84 per cent). Mafurite, being kalsilite-rich, contains the highest Al_2O_3 (8.18) and K_2O (6.98).

The average katungite possesses higher CO_2 (1.53 per cent) and P_2O_5 (0.97) than mafurite (trace and 0.61 respectively) and ugandite (0.36 and 0.29 respectively).

Amongst the members of the "O.B.P." series, the average composition of biotite-pyroxenite has features in common with average katungite, just as the peridotites have with olivine-rich ugandite. Glimmerite similarly shares certain chemical features with mafurite.

(ii) Trace elements

The trace-element contents of the three volcanic types are given in Table 2b. The variations in the katungites from the /

the different volcanic areas are insignificant. Proto-katungite however, has notably more abundant Ba, Sr, La and Cu, and less abundant Cr, Ni and V than average katungite. The distribution of the different trace elements in the main types will now be discussed.

(a) Rubidium and barium

Generally, the three main volcanic types have abundant Rb, which is most likely replacing K in leucite and/or kalsilite, or accompanying it in the potash-rich groundmass. Both ugandite (relatively rich in leucite) and mafurite (relatively rich in kalsilite) have 450 ppm. of Rb, whereas the average katungite (containing potash-rich glass and generally poor in leucite and/or kalsilite) has 220 ppm. Kalsilite-katungite from Bunyaruguru has more Rb (380 ppm.) than three other kalsilite-free katungites from the same field (150-240 ppm.).

The volcanic rocks of South-West Uganda are highly enriched in Ba, as was first reported by Holmes and Harwood (1932, p. 420). Ba reaches 7500 ppm. in the K_2O-rich mafurite, compared with 3370 ppm. in katungite and 2000 ppm. in ugandite. In mafurite and ugandite, Ba appears to be chiefly present replacing K in their potash feldspathoids. The relatively high Ba content of katungite suggests that this element may in part be present replacing Ca in melilite. This view is strengthened by /

by the fact that uncompahgrite (a coarse-grained melilite-pyroxene rock occurring at Iron Hill, Gunnison County, Colorado) has 2685 ppm. of Ba, whereas ijolite (melilite-free) from the same locality has only 895 ppm. (Larsen, 1942, p. 36). The possibility, however, that Ba chiefly exists among the constituents of the potash-rich groundmass of katungite cannot be overlooked.

(b) Strontium

The volcanic rocks of South-Western Uganda are also remarkable for their abundant Sr. Katungite and mafurite have similar amounts, 6685 and 7000 ppm. respectively, but ugandite, corresponding to its relatively low Ca has a much lower content (1800 ppm.).

The Sr contents of both mafurite and ugandite are slightly lower than those of Ba; whereas katungite has considerably more Sr than Ba. This is understandable, since katungite is rich in melilite, the mineral in which most of the Sr, replacing Ca, is likely to exist. That Sr is more easily accommodated into the melilite lattice than into that of pyroxene, becomes very obvious when we consider that pyroxenite (C 4035, Table la; pyroxene-rich and melilite-free) has 22.57 per cent CaO and possesses only 340 ppm. Sr; whereas katungite (C 4012 /

(C 4012, Table 2a; pyroxene-free and melilite-rich) has only 16.79 per cent CaO and possesses as much as 9500 ppm. Sr.

(c) Lanthanum and yttrium

The volcanic types contain both La and Y in detectable amounts, with La $>$ Y. The variation of La in the different katungite samples is from 30 to 70 ppm., but proto-katungite has more abundant La (100 ppm.) in accordance with the corresponding relative abundance of Sr. Mafurite and ugandite have 80 and 35 ppm. of La respectively. The Y content of the three types appears to be similar ($<$ 30 ppm.), but there may be undetectable differences in the concentration of this element since its sensitivity is 30 ppm.

Compared with the sub-volcanic rocks (as in the case of Sr) the volcanic types are richer in both La and Y.

(d) Gallium

The Ga contents of katungites from the different volcanic areas (Katwe-Kikorongo, Bunyaruguru and Katunga) are almost uniform (20-30 ppm.) with an average of 25 ppm. Mafurite and ugandite have 15 and 5 ppm. of this element respectively. The increase of Ga with (Al_2O_3+Fe_2O_3) which characterises the sub-volcanic series, is again found in the chief volcanic types:

Type	Ga in ppm.	(Al_2O_3+Fe_2O_3) in wt. per cent
Ugandite	5	9.41
Mafurite	15	12.79
Katungite	25	14.83

(e) Lithium

Li is present in uniform and relatively low amounts in the three types (5 to 8 ppm.).

(f) Chromium, Nickel and Cobalt

Cr and Ni are relatively high in the three volcanic types, all of which are rich in olivine. Ugandite and mafurite have 1200 and 900, and 1300 and 300 ppm. respectively, while katungite averages only 720 and 185 ppm., and proto-katungite has even less: 290 and 100 ppm.

The increase of (Cr+Ni) with MgO that characterises the sub-volcanic series is again found in the volcanic rocks as recorded below:

Type	(Cr+Ni) in ppm.	MgO in wt. per cent
Proto-katungite	390	10.93
Katungite	905	12.40
Mafurite	1600	17.66
Ugandite	2100	24.84

The contents of Co in katungite, mafurite and ugandite are /

are 73, 70 and 110 ppm. respectively. Similarly, the FeO contents of both katungite and mafurite are almost alike (5.06 and 4.98 per cent respectively) but that of ugandite is higher (6.47 per cent).

All the types have Cr > Ni > Co, as in the sub-volcanic series.

(g) Vanadium

V appears to increase with (Fe_2O_3+TiO_2) as shown below:

Type	V in ppm.	(Fe_2O_3+TiO_2) in wt. per cent
Ugandite	110	7.55
Mafurite	220	8.97
Katungite	275	11.99

The total of the trace elements which are known to replace Mg, Fe^2 and Fe^3 in the crystal lattices, namely, Cr, Ni, Co, V and Cu, increases with the total of these major elements;

Type	(Cr+Ni+Co+V+Cu) in ppm.	(MgO+FeO+Fe_2O_3) in wt. per cent
Katungite	1238	23.59
Mafurite	1915	27.25
Ugandite	2380	35.34

Comparison of these constituents with those of the sub-volcanic rocks (p. 36) shows that the corresponding totals for katungite and mafurite are closely similar to those for biotite-pyroxenite and glimmerite respectively. Furthermore, for both ugandite and /

and peridotite these totals are higher. But ugandite has slightly higher ($MgO+FeO+Fe_2O_3$) and lower (Cr+Ni+Co+V+Cu) totals (35.34 per cent and 2380 ppm.) than those of peridotite (33.15 per cent and 4558 ppm.).

(h) Zirconium

The distribution of Zr is very interesting. While both katungite and mafurite have relatively high contents of this element (1000 and 900 ppm. respectively), ugandite possesses only 300 ppm. It may be recalled that amongst the members of the "O.B.P." series, the sphene-rich biotite-pyroxenite has an enormous quantity of Zr (1200 ppm.), most of which is present in sphene. Neither katungite nor mafurite carries sphene but they have appreciable amounts of perovskite. It is quite likely, therefore, that most of the Zr in these rocks is present in this mineral, replacing Ti^4.

It is highly significant that in all three types Zr is extraordinarily abundant as compared with normal ultrabasic rocks. Rankama and Sahama (1950, p. 566) report 60 ppm. as the average Zr contents of peridotites. Moreover, three ultrabasic rocks from Garabal Hill-Glen Fyne Complex, Scotland, namely dunite, augite-peridotite and pyroxenite have < 10 ppm. of this element (Nockolds and Mitchell, 1948, Table II, analyses 1, 2 and 3, p. 538).

(i) Other Trace-elements

Pb is present in amounts less than 10 ppm. in all three types; and differences are therefore undetectable, since the sensitivity is 10 ppm.

Tl, Sn, Sc, Mo, Ge, Be, Ag and In, if present, occur in amounts below their respective limits of sensitivity in these volcanic rocks.

Summary of the distribution of the trace elements in katungite, mafurite and ugandite

The outstanding features of katungite, mafurite and ugandite are as follows:

(1) Elements uncommon in ultrabasic rocks, namely, Sr, Ba, Rb and Zr, are very abundant.

(2) Elements common in ultrabasic rocks, namely, Cr and Ni, are normally abundant.

(3) (Sr+La+Y) increases with Ca; (Rb+Ba) with K_2O; and (Cr+Ni) with Mg.

(4) All three rocks have Cr $>$ Ni $>$ Co. Mafurite and ugandite have Ba $\geqslant$ Sr, whereas katungite has Sr $>$ Ba.

(5) Sr and Ba are notably more abundant than in the members of the "O.B.P." series. But otherwise, the trace-element abundances are generally similar for katungite and biotite-pyroxenite; mafurite and glimmerite; and ugandite and peridotite.

B. /

B. Ouachitite

The chemical composition of ouachitite (Table 2a) has much in common with katungite (Table 2a) and biotite-pyroxenite (Table 1a).

The noteworthy features of the trace-element abundances of ouachitite (Table 2b) are the following:

(1) Ba and Sr are both lower than in katungite, but the relation Sr > Ba remains the same, whereas biotite-pyroxenite has Ba > Sr.

(2) Both Sr and Zr are conspicuously abundant compared with the corresponding amounts in biotite-pyroxenite. Zr is also somewhat higher than in katungite.

It is noticeable that the Sr content decreases from proto-katungite (> 10,000 ppm.), through katungite (6685), alnöite (3800), ouachitite (2500) to biotite-pyroxenite (556). Ba and Rb show also a decrease from proto-katungite to ouachitite. As shown in the following table, the average trace-element contents of the end members of the series (proto-katungite and biotite-pyroxenite) are not very different from the corresponding averages for katungite, alnöite and ouachitite.

Element /

Element	A	B	C	D	E	Average A & E	Average B, C & D
Rb	240	200	150	100	155	198	150
Ba	7000	2800	2600	1700	1725	4360	2100
Sr	10,000	7500	3800	2500	550	5300	4600
Cr	290	700	800	550	775	533	683
Co	60	85	70	60	62	61	72
Ni	100	230	140	250	190	145	207
Zr	1100	800	1100	1200	60	580	1030
La	100	30	30	30	*	50	30
Y	30	30	30	30	30	30	30
Cu	200	80	60	65	75	138	68
V	170	320	350	320	345	260	330
Ga	25	25	30	25	23	24	27

A Proto-katungite C 6065, Bunyaruguru
B Katungite G 21, Katwe
C Alnöite (biotite-augite-katungite) G 56, Katwe
D Ouachitite C 5844, Katwe
E Average of biotite-pyroxenites G 20, Katwe and C 2786, Bufumbira
* Considerably less than 30 ppm.

C. Other volcanic rocks from the Toro-Ankole volcanic province

The remaining rocks investigated from the Toro-Ankole volcanic province all come from the Katwe-Kikorongo field. They comprise potassic ankaratritic types, mela-potash nephelinite and mela-leucitite. The chemical composition and the trace-element contents of these rocks are given in Tables 3A and 3b respectively.

(i) /

(i) Potassic ankaratritic types

In general, the analysed leucite-ankaratrite and leucite-melilite-ankaratrite have many chemical characteristics in common with katungite, mafurite and ugandite (K.M.U.): e.g. relatively high K_2O and TiO_2, with $K_2O > Na_2O$ and $Al_2O_3 > (K_2O + Na_2O)$. The ankaratritic types, however, have certain systematic geochemical differences corresponding to their greater abundance of augite relative to olivine: notably lower MgO; higher Al_2O_3 and Na_2O; and $(FeO + Fe_2O_3) > MgO$, the latter being the reverse of what has been found in the "K.M.U." series. These differences justify the recognition of the ankaratritic types as a distinctive group.

Comparison of the trace-element contents of the leucite-ankaratrite with those of the leucite-melilite-ankaratrite (Table 3a, columns A and B) reveals the following interesting features:

(1) Cr and Ni are very similar in both varieties, corresponding to their similar MgO contents.

(2) V is noticeably higher in the leucite-melilite-ankaratrite, where perovskite and TiO_2 are more abundant.

(3) The leucite-ankaratrite has more CaO (16.59 per cent) than the leucite-melilite-ankaratrite (14.34). Yet, Sr is notably lower in the melilite-free variety (4000 ppm.) than in the melilite-rich type (9800 ppm.). This is another example illustrating the relative enrichment of melilite-bearing rocks in Sr.

(4) /

(4) Rb and Ba are more abundant in the leucite-melilite-ankaratrite, corresponding to its higher K_2O content.

The average value of (Cr+Ni) is lower than that for any of the "K.M.U." series, corresponding to the lower MgO of the ankaratritic rocks. On the other hand, (V+Co) and Ga are higher, corresponding to the higher values of ($FeO+Fe_2O_3+TiO_2$) and ($Al_2O_3+Fe_2O_3$) respectively. The potassic ankaratritic rocks have Sr $>$ Ba, like katungite.

The outstanding features of the trace-element abundances for the potassic ankaratritic rocks are the same as those found for the "K.M.U." series: relatively high Sr, Ba, Zr and Rb; low Li; Cr $>$ Ni $>$ Co and La $>$ Y.

(ii) Mela-potash nephelinite and mela-leucitite

Important features in the chemical composition of the mela-potash nephelinite and the mela-leucitite are their low MgO and abundant Na_2O and Al_2O_3, relative to the other volcanic types already discussed. This is in accord with their less mafic character. Otherwise, however, they share the main chemical characters of the other volcanic rocks, viz: relatively high K_2O, TiO_2 and P_2O_5, with $K_2O > Na_2O$ and $Al_2O_3 > (K_2O+Na_2O)$. Furthermore, like the ankaratritic rocks, they have CaO $>$ MgO, and ($FeO+Fe_2O_3$) $>$ MgO.

The /

The mela-potash nephelinite and the mela-leucitite (Table 3a, Columns C and D) have trace-element contents that are strikingly similar. Both have (1) relatively high Sr, Ba and Rb contents of the same order as those of the other volcanic types; (2) relatively high Zr content, like all the others except ugandite; and (3) Sr $>$ Ba as in katungite, ankaratritic rocks and ouachitite.

However, they differ conspicuously from all the other types by their extreme impoverishment in Cr, Co and Ni and by having Co $>$ Ni $>$ Cr instead of Cr $>$ Ni $>$ Co.

D. Volcanic rocks from Birunga volcanic field

(i) Feldspar-free types

The chemical composition and the trace-element contents of these types are given in Tables 4a and 4b respectively. Olivine-melilitite and potash nepheline-melilitite resemble the volcanic rocks from the Toro-ankole field in having relatively high K_2O, TiO_2 and P_2O_5, with $Al_2O_3 > (K_2O+Na_2O)$. However, they differ in the following respects:

(1) Na_2O is slightly more abundant than K_2O. This is related to the preponderance of potash nepheline over leucite in the Birunga types; the ratio Na_2O/K_2O also rises in some of the potash ankaratrites of the Katwe-Kikorongo field.

(2) TiO_2 is relatively low and perovskite is sparse.

(3) /

(3) H_2O in these rocks is also lower than in the Toro-Ankole types.

(4) FeO is higher than Fe_2O_3, a feature shared only by ugandite in the Toro-Ankole fields.

It is noticeable that Al_2O_3 is relatively high in the olivine-melilitite and potash-nepheline-melilitite of Birunga as in the mela-potash nephelinite and mela-leucitite of Toro-Ankole. Moreover, these types have $(FeO+Fe_2O_3) > MgO$, like the ankaratritic rocks.

The outstanding features in the trace-element constitution of the olivine-melilitite and the potash nepheline-melilitite are:

(1) Great abundance of Ba and Sr. The olivine-melilitite has 2200 ppm. of Ba and 8000 ppm. of Sr while the potash nepheline-melilitite possesses as much as $>$10,000 ppm. of each of these elements.

(2) Moderate contents of Cr and Ni in the olivine-bearing melilitite (450 and 100 ppm. respectively) and paucity of these elements in the potash nepheline-bearing melilitite ($<$ 1 and 30 ppm. respectively).

On the whole, the trace-element constitution of the Birunga types under consideration shows the characteristic features of that of the Toro-Ankole, i.e. high Sr, Ba, Zr and Rb contents and low Li content. Cr and Ni are also relatively low corresponding to the low MgO. It must be mentioned, however, that these types have Y $>$ La, the reverse of the relationship /

relationship prevailing in the related Toro-Ankole volcanic types.

(ii) Feldspar-bearing types

The kivites and leucitic trachybasalt (Table 4a) differ from the olivine-melilitite and potash nepheline-melilitite in having higher SiO_2 (average, 44.99 per cent) and Al_2O_3 (18.00); and lower MgO (4.69) and CaO (9.42). Like most of the volcanic rocks of Birunga and Toro-Ankole they are rich in K_2O, TiO_2 and P_2O_5, and have $Al_2O_3 > (K_2O+Na_2O)$. K_2O is not invariably higher than Na_2O, but the relationship $K_2O > Na_2O$, which prevails in the volcanic provinces concerned, holds for the average composition.

The kivitic rocks have $(Al_2O_3+K_2O+Na_2O) > CaO > MgO$; $FeO > Fe_2O_3$; and $(FeO+Fe_2O_3) > MgO$, like their xenolithic sub-volcanic rock, the leucite-kentallenite (p. 29).

The trace-element contents of the four rocks studied are all much alike (Table 4b) and share most of the peculiar features characteristic of the two provinces. Sr, Ba, Rb and Zr are high and Li is low. It is significant that the average Rb, Ba, Sr, and Zr contents of these kivitic rocks are as high as 158, 2600, 4700 and 750 ppm. respectively, and basic types are known to carry negligible or small amounts of each of these elements /

elements. Moreover, the average Cr, Co and Ni contents are relatively low, being only 41, 50 and 35 ppm. respectively. The abundance of V, on the other hand is normally high (322 ppm.) exceeding the total Cr+Co+Ni (126 ppm.). As in the Birunga feldspar-free feldspathoidal types, the kivites have Y > La. But the average Ga content (45 ppm.) is relatively high, corresponding to the high average total Al_2O_3+Fe_2O_3 (20.20 per cent).

Comparison of the respective trace-element constitution reveals that kivite (Table 4b) has more abundant Rb, Ba, Sr, and Zr, and less Cr and Ni than leucite-kentallenite (Table 1b).

(iii) Limburgite

Limburgite (Table 4a) is similar to kivite in having relatively high SiO_2 (44.22 per cent), but the former contains lower Al_2O_3, K_2O and Na_2O; and higher MgO and CaO than the latter. Moreover, limburgite has $CaO > MgO > (Al_2O_3+K_2O+Na_2O)$ whereas the relationship between these oxides in kivite is $(Al_2O_3+K_2O+Na_2O) > CaO > MgO$.

The trace-element constitutions of these types (Table 4b) differ significantly. Limburgite has higher Cr and Ni and lower Ba and Sr than kivite. Moreover, in limburgite, V is much less abundant than (Cr+Ni), whereas in kivite V > (Cr+Ni). It should /

should also be mentioned that limburgite has higher Cr, Ni and Zr than leucite-kentallenite (Table 1a); the Ba and Sr contents of these two types, however, are almost alike. Otherwise, limburgite shares in one of the main geochemical features which characterises the volcanic rocks of the Birunga field, viz: relatively high Rb, Ba, Sr and Zr with Y > La.

Table 5 shows the relative distribution of the different trace elements in all the investigated volcanic types.

VI. TRACE-ELEMENT DISTRIBUTION IN CARBONATITES AND LIMESTONES

Carbonatites and related rocks as well as limestones are usually involved in discussions of the genetic problems of alkaline rocks. Four carbonatites, and two samples of limestones have, therefore, been spectrographically analysed (Table 6). The carbonatites come from different alkaline complexes which have been studied in detail by well-known petrologists. The samples represent a carbonate dyke, Premier Diamond mine, S. Africa (Daly, 1925); a carbonatite from Spitzkop Complex, Bushveld, Transvaal (Shand, 1921); another from Marongwe Hill /

Hill, Chilwa Island, Nyasaland (Dixey, Campbell Smith and Bisset, 1937); and a sövite from Hartung, Alnö Island, Sweden (Eckermann, 1948). The limestones are from the Transvaal System, S. Africa, and Mansjo, Sweden.

Reference to Table 6 shows that the carbonatites as well as the limestones lack Rb and Ga, and that they have inappreciable amounts of Li, Cu or V. Cr, Co and Ni are relatively low in the carbonatites (averages, 11, 14 and 50 ppm. respectively) but negligible in the limestones (2, $<$ 1 and $<$ 1 ppm. respectively). There are, however, far more outstanding differences. The carbonatites are conspicuously rich in Ba, Sr, La and Y, and have Sr $>$ Ba and La $>$ Y; whereas the limestones have relatively very low Sr content and negligible amounts of Ba, La and Y. The following contrast is particularly instructive:

Rock	Ba	Sr	La	Y	
Spitzkop carbonatite	650	10,000	400	120	ppm.
Transvaal limestone	5	5	x	x	ppm.

x below the limit of sensitivity (30 ppm.).

For carbonate rocks (limestones and dolomites) from Southern Lapland, Sahama (1945) reports Ba, 270 ppm.; Sr, 850; La and Y, nil. Noll (1934) gives the range of Sr in limestones as 425-765 ppm.

That limestones are impoverished in Sr, La and Y clearly indicates /

indicates that the susceptibility of these elements to replace Ca decreases remarkably at the relatively low temperatures of formation of such rocks. This corresponds well with the fact that Sr-minerals are exceedingly rare in igneous rocks which form at relatively high temperatures but are not uncommon in hydrothermal and sedimentary deposits. In igneous rocks Sr can easily be accommodated into Ca-minerals and so it has no tendency tobecome concentrated as it has, for example, in low temperature deposits of celestite and strontianite. The poverty of limestones in Ba can be similarly accounted for. However, according to Rankama and Sahama (1950), p. 483), Ba and K are more easily adsorbed by clays than Sr and Na respectively, because they have correspondingly lower ionic potentials. Most of the Ba in limestones is therefore likely to be present in argillacious impurities. The extremely low contents of limestones in Cr, Ni and Co can be explained by (1) the paucity of these elements in sea water and (2) their low capacity for replacing Mg (in dolomitic admixtures) at low temperatures.

VII. /

VII. PETROGENESIS

The origin of alkaline rocks in general continues to be debatable, Daly's well known "limestone assimilation" hypothesis being still under active discussion.

Bowen (1945) in his study of the equilibrium relations in portions of the quaternary system, $Na_2O-CaO-Al_2O_3-SiO_2$, suggested that crystallisation differentiation of an initial melilite-nephelinite (or melilite-nepheline-basalt) magma produced by limestone desilication of normal mafic magma(or perhaps, in some instances by other means, such as selective resorption of hornblende) might give rise to a series of differentiates such as melilite-nephelinite, tephrite and phonolite. Shand has particularly developed the hypothesis of the desilication of a feldspathic magma by reaction with limestone to explain the genesis of the nepheline-rocks of Sekukuniland, South Africa (1921) and those of the Franspoort Line, Pretoria District (1922), and indeed of alkaline rocks in general (1945). The main petrogenetic process suggested by Larsen (1942) - rather diffidently - to account for the derivation of the alkaline rocks of Iron Hill, Gunnison County, Colorado was the assimilation of marble by a basaltic magma. Pulfrey (1950), however, considers that the ijolitic rocks near Homa Bay, Western Kenya were developed chiefly by metasomatic-replacement processes.

Melilite- /

Melilite-bearing rocks from Scawt Hill, Co. Antrim were shown by Tilley to be the products of assimilative reactions between chalk and basaltic magma (Tilley and Harwood, 1931). Taljaard (1936), however, rejected the limestone assimilation hypothesis in his study of the melilite-basalts of South Africa. He (Taljaard, 1936, p. 309) assumed that these rocks were crystallisation products of an original magma rich in CaO and MgO, poor in SiO_2, Al_2O_3 and alkalies, and that resorption of primary olivine into biotite and of primary pyroxene into magnetite, perovskite and melilite has taken place prior to complete consolidation.

Leucite-rocks from Java have been considered to be the result of assimilation of limestone by an andesitic lava (Brouwer 1928). Rittmann (1933) in discussing the evolution of the potassic lavas from the Somma-Vesuvius volcano, assumed that a parental trachytic magma became undersilicated by assimilation of dolomitic limestones. Rittmann suggested that sinking of ferromagnesian minerals, concentration of potash at higher levels and removal of soda by gases into the wall rock accompanied the assimilation process and so led to the development of the leucite-bearing lavas of that volcano. His mechanism, however, does not account for the abundance of potash in the parental trachyte, which is after all, the main problem. Wade and /

and Prider (1940) believe that the various leucite-bearing rocks of West Kimberley, West Australia were derived from the differentiation of a potassic mica-peridotite magma by the early crystallisation and removal of olivine. Here again the essential feature is assumed in the "explanation". They thought (Wade and Prider, 1940) that this mode of origin was also applicable to the case of the leucitic rocks of Leucite Hill, Wyoming. More important, they concluded that the limestone-assimilation hypothesis could not explain the peculiar chemical features of their rocks. Holmes in his account of the petrogenesis of the ultrabasic potassic rocks of the Bufumbira volcanic field has commented adversely on the limestone-assimilation hypothesis. He writes (Holmes and Harwood, 1937, p. 248): "One cannot remain satisfied with a hypothesis that appeals to carbonate-assimilation in the Roman Province, when it is found that similar suites of leucitic rocks, and even of melilite-rich rocks, occur in other areas (e.g., South-west Uganda) where there is little or no limestone or dolomite to be assimilated". In his recent treatment of the petrogenesis of katungite and its associates from South-western Uganda, Holmes (1950) postulates that such rocks are products of reaction between sialic crustal rocks (considered to be the souree of Al_2O_3, SiO_2 and above all of K_2O) and carbonatitic magma rich in MgO, CaO, iron oxides, TiO_2 and P_2O_5. /

P_2O_5. Magmatic carbonatites are also regarded as having been involved in the production of the alkaline rocks of the Fen district, Norway (Brogger, 1921); the Chilwa series, Nyasaland (Dixey, Campbell Smith and Bisset, 1937); and those of the Alnö district, Sweden (Eckermann, 1948; 1950a; and 1950b).

On the whole, the hypotheses postulated by the different authors to account for the origin of alkaline rocks may be summarised as follows:

(1) Crystallisation differentiation of a basic magma accompanied by resorptive reactions of the primary constituents.

(2) Assimilation of carbonate rocks by basaltic or felsic (e.g. trachytic or granitic) magmas.

(3) Reactions of magmatic carbonatites and the sialic country rocks.

In the case of the rocks studied from Toro-Ankole and Birunga any working hypothesis should - to remain tenable - provide an adequate explanation for their peculiar assemblage of geochemical characters, already discussed in detail. Here, we are dealing with rock types which possess the outstanding feature of being ultrabasic and potassic, and enriched not only in Cr and Ni, but also in Rb, Ba, Sr and Zr. Moreover, some of the rocks, e.g. katungite and mafurite, have a relatively high Ga content.

Neither the crystallisation-differentiation nor the limestone /

limestone assimilation hypotheses can furnish adequate reasons for the above-mentioned geochemical peculiarities. This follows from the results of recent investigations concerning the differential concentrations of various trace elements during the progress of crystallisation-differentiation of basic magma (Wager and Mitchell, 1951; and Higazy, 1952b) - results which distinctly show that the Rb, Ba, Sr and Zr contents of basaltic rocks and their differentiates are conspicuously less than those of the volcanic types here under discussion. This very striking contrast indicates that a basaltic parentage for these rocks is so unlikely as to be practically impossible. This inference is independent of the further very significant fact that true basalts have not been encountered in the Toro-Ankole and Birunga volcanic fields (Holmes and Harwood, 1937). Moreover, it is difficult to believe that basaltic magma, which normally differentiates into residues with increasing SiO_2 as crystallisation proceeds, could in some cases give rise to silica-poor differentiates such as the feldspathoid-bearing rocks, unless certain processes responsible for their desilication, such as assimilation of limestone were operating. But this would not solve our problem, since basaltic rocks and limestones (see Table 6 for analyses of limestones) lack those very trace elements - Rb, Ba, Sr and Zr - which are present in such surprising abundance in the volcanic /

volcanic rocks under consideration. Differentiation of basaltic magma, with or without assimilation of limestone, cannot, therefore, be held responsible for their derivation.

Perhaps, then, these rocks originiated as a result of assimilation either (1) of limestone by a felsic magma or (2) of granitic rocks by an olivine-basalt magma. On either assumption it is difficult to account for the fundamental character of Sr abundance, since none of the materials involved can be regarded as an adequate source for this element. Moreover, the high Cr and Ni contents are left without a source in case (1), and the very low SiO_2 becomes still more difficult to account for in case (2).

That the various volcanic and sub-volcanic types of Toro-Ankole are genetically related is quite obvious since the variations in their major elements are accompanied by similar behaviour on the part of their corresponding replaceable trace elements. The recent hypothesis advanced by Holmes (1950) for the explanation of the origin of katungite and its associates advocates that they are products of reaction between magmatic carbonatites and sialic rocks such as granite. The carbonatitic magma is thought to have contributed the cafemic constituents while the granitic types are regarded as the source of the alkaluminous materials. This mode of origin also adequately accounts for /

for the peculiar geochemical features of the rocks concerned. In striking contrast to limestones (Table 6), the analysed carbonatites contain abundant Sr, La, Y and Ba; on the other hand, granites are well known to be enriched in Rb, Ba, Zr and Ga.

On this hypothesis, the high Cr and Ni of some of the studied volcanic types would also be supplied by the carbonatites, since granitic rocks are known to have negligible amounts of these elements. The carbonatites actually analysed, however, do not possess appreciable amounts of either Cr or Ni. This apparent discrepancy disappears, however, when it is realised that the carbonatites met with in the field can represent no more than the relatively Ca-rich portion of the original carbonatitic magma. The latter must also have contained considerable amounts of Mg and Fe (Holmes, 1950, p. 786; 1952, p. 211). During the progress of the complex reactions between carbonatitic magma and granitic rocks, most of the Cr and Ni available would be naturally present in the products developed from the selective silication of the Mg-rich portion of the carbonatitic magma. The residual portion of the carbonatite magma would thus become Ca-rich and would be deficient in Cr and Ni, while, if further reactions with granitic rocks occurred the resulting products would also be poor in Cr and Ni. The Fe-portion /

Fe-portion of the carbonatite magma was apparently involved during the silication of both the Mg- and Ca-rich portions of this magma since all the rock types generated are rich in iron oxides.

From the facts (a) that members of the "O.B.P." series occur ubiquitously as xenolithic materials in the volcanic types, and (b) that the "O.B.P." material is invariably present in the tuffs and agglomerates, a close genetic relationship between the sub-volcanic series and the volcanic types can be regarded as established. In particular, Holmes (1950, p. 783) infers that at the time of eruptivity, the katungite and proto-katungite magmas existed in an "O.B.P." environment consisting largely of biotite-pyroxenite. If the hypothesis of reactions between granite (G) and carbonatitic magma (C) is true, one probable set of complementary products would have been different members of the "O.B.P." series and proto-katungite (P.K.), as indicated by the following qualitative equation:

$$G + C \longrightarrow \text{"O.B.P."} + \text{P.K.}$$

It is important to keep in mind that there are a great many variables involved in the above equation - compositions, proportions and physical conditions - and that discussions of particular combinations of these are no more than illustrations of some of the possibilities that can reasonably be envisaged.

The /

The members of the "O.B.P." series were presumably formed under sub-volcanic conditions (at relatively low crustal levels) where the Mg-rich portion of the carbonatitic magma, with abundant Cr and Ni, reacted with sialic (e.g. granitic) material. The former supplied mainly Mg with Cr and Ni, whereas the latter contributed Si, Al and K with Ga, Rb and Ba. The different members of the series, namely peridotite, glimmerite and pyroxenite, appear to have been formed from correspondingly different proportions of the reactants. The peridotite seems to have developed from reactions between considerable amounts of Mg-rich carbonatitic magma and relatively little granitic material, whereas the formation of glimmerite required reverse quantities of these materials. In the case of pyroxenite the reactants included much of the Ca-rich portion of the carbonatitic magma, while the production of such a variety as the sphene-rich biotite-pyroxenite would require still more. The share of the granitic material in the formation of biotite-pyroxenite seems to have been greater than that required for pyroxenite and sphene-rich biotite-pyroxenite.

Other types such as mela-potash nephelinite, mela-leucititite and potash nepheline-melilitite, and possibly kivite, all of which possess relatively low Cr and Ni contents, can also be considered to develop from essentially similar reactions between /

between Ca-rich carbonatitic magma and granite. It should be mentioned, however, that the proportions of the main reactants would differ in the various cases. Potash nepheline-melilitite, for instance, may have had a relatively high supply of the Ca-rich carbonatitic magma, whereas kivite would require a greater share of sialic reactants and perhaps some basaltic material.

The production of the chief volcanic types, namely, katungite, mafurite and ugandite, may be attributed to either (1) reactions between the different members of the "O.B.P." series and the proto-katungite magma or (2) reactions of a residual Ca-rich portion of the carbonatitic magma with "O.B.P." and granitic material. Combinations of these two processes are also possibilities.

(1) Fig. 2 shows the relative proportions of Sr+La+Y (supplied by the Ca-rich portion of the carbonatitic magma), Rb+Ba+Ga (contributed, like K and Al, by the granitic material) and Cr+Ni (supplied by the Mg-rich portion of the carbonatitic magma) in the chief volcanic types and the different members of the "O.B.P." series. It can be seen from this diagram that, at least arithmetically, reactions between material of glimmerite composition with proto-kagungite could give rise to types with mafuritic constitution. Moreover, katungite could similarly result from reactions with pyroxenite; and ugandite from reactions with material /

material of composition U (approximately 1/3 peridotite and 2/3 biotite-pyroxenite).

The other volcanic types such as ouachitite and potash and leucite-ankaratrites could also develop by similar reactions with but various proportions of the reactants.

(2) It is also possible that reactions between the Ca-rich portion of the carbonatitic magma, granitic material and the different members of the "O.B.P." series could give rise to the various volcanic types. This mode of origin is arithmetically similar to that discussed above, since proto-katungite itself is regarded as the result of the reactions between Ca-rich carbonatitic magma and granite. On this alternative assumption, the different reactants would differ in proportion in the various cases. Ugandite (relatively high Mg with abundant ferromagnesian species) would need a higher amount of the olivine-rich types of the "O.B.P." series than that required for mafurite or katungite. The proportion of granite would need to be greater for mafurite (relatively high K and Al with abundant kalsilite); while the proportion of the Ca-rich carbonatitic magma would need to be greater for katungite.

It may also be inferred that, as compared with the requirements for mafurite, transitional forms such as (a) leucite-mafurite (between mafurite and ugandite) would require higher proportions /

proportions of olivine in the "O.B.P." part of the reactants; while (b) melilite-mafurite (between mafurite and katungite) would require higher proportions of the Ca-rich carbonatitic magma. Moreover, kalsilite-katungite would require a higher proportion of the reacting granitic material than that needed for the production of katungite.

It should be emphasised that all the reactions discussed above are merely representatives of the great variety which may have taken place during the genesis of the various volcanic and sub-volcanic rocks of the Toro-Ankole fields. Fundamentally, however, the reactants appear to be essentially similar for all the rocks involved - carbonatite magma and sialic material of approximately granitic composition in every case. These reactants are the most promising sources for the peculiar chemical composition and trace-element constitution of the rocks under consideration.

The leading geochemical features of the studied volcanic types from Birunga, especially kivite, olivine- and potash nepheline-melilites, are essentially similar to those from Toro-Ankole, and therefore their genesis can be explained in a similar manner. However, they differ mainly in the following respects: K is not invariably higher than Na in the Birunga /

Birunga rocks; the latter also possess Y > La, whereas a reverse relationship prevails in the Toro-Ankole rocks. These differences can be attributed either to (a) local variations in the reacting sialic crustal material or (b) incorporation of basaltic material in the different reactions, since basaltic rocks have relatively high Na_2O content and are known to possess the relationship Y > La. Such influence of basic rocks is most marked in the case of limburgite.

It is not pretended to suggest that alkaline rocks of other districts have necessarily originated in a similar way. It is highly desirable to fill in the lacunae in our knowledge concerning the trace-element contents of such rocks, with a view to testing to what extent Holmes' recent hypothesis may prove to be applicable in explaining their genesis.

VIII. CONCLUSIONS

The chief volcanic rocks of Toro-Ankole fields (South-west Uganda) are: katungite (olivine, melilite and potash-rich glass), Ugandite (olivine, augite and leucite) and mafurite (olivine, augite and kalsilite). Ouachitite (olivine, augite, biotite /

biotite and feldspathoids); and members of the potash ankaratrite-melaleucitite series (different from the mafurite-ugandite series in being conspicuously rich in augite and relatively poor in olivine) also occur. All these types contain invariable amounts of perovskite and black ores. Sub-volcanic rocks, represented by peridotite, pyroxenites and glimmerite, are ubiquitously present as xenolithic materials in the lava types and fragmental materials in the pyroclasts.

The studied types from the Birunga field (North of Lake Kivu) are: (a) feldspathoid-bearing feldspar-free rocks such as olivine-melilitite and potash-nepheline-melilitite, (b) feldspar-bearing varieties comprising kivite (leucite-basanite) and leucitic trachybasalt, and (c) limburgite.

The volcanic rocks of Toro-Ankole are ultrabasic types, relatively rich in K_2O, TiO_2 and P_2O_5 and characterised by having $K_2O > Na_2O$ and $Al_2O_3 > (K_2O+Na_2O)$. The outstanding features concerning their trace-element contents are (1) relative abundance of elements uncommon in ultrabasic rocks, namely, Sr, Ba, Rb and Zr; (2) normally high contents of Cr and Ni in all types except those which are relatively poor in Mg, namely, mela-leucitite and mela-potash nephelinite; (3) low Li content; and (4) relatively high La and Y with $La > Y$.

The /

The studied types from Birunga are also relatively rich in K_2O, TiO_2 and P_2O_5, but in these rocks K_2O is not invariably higher than Na_2O. They also have $Al_2O_3 > (K_2O+Na_2O)$, and share with the Toro-Ankole types the peculiar geochemical character of being relatively rich in Sr, Ba, Rb and Zr. The Birunga rocks, however, possess $Y > La$, i.e. the reverse of the relationship prevailing in Toro-Ankole.

The geochemical characters of the rocks investigated cannot be explained by fractionation of either basaltic or felsic magma with or without assimilation by limestones, since these sources lack adequate amounts of Sr, Ba, Rb and Zr. The most promising hypothesis for explaining the genesis of the Toro-Ankole rocks and their geochemical peculiarities is that introduced by Holmes (1950). The volcanic and sub-volcanic products are regarded as derivatives of reactions between

(a) magmatic carbonatite, which contributed Ca with Sr, La and Y; Mg with Cr and Ni; Fe with V and Ti; and P; and

(b) sialic crustal rocks of approximately granitic composition, which provided Si; Al with Ga; and K with Rb and Ba.

The differences in composition of the various products are attributed to respective variations in the proportions of the reacting materials, and in the physical conditions under which the reactions took place.

The /

The Birunga rocks originated in essentially the same manner as that of the Toro-Ankole types, but in addition to the sialic reactants basaltic materials may have played a significant part in their production.

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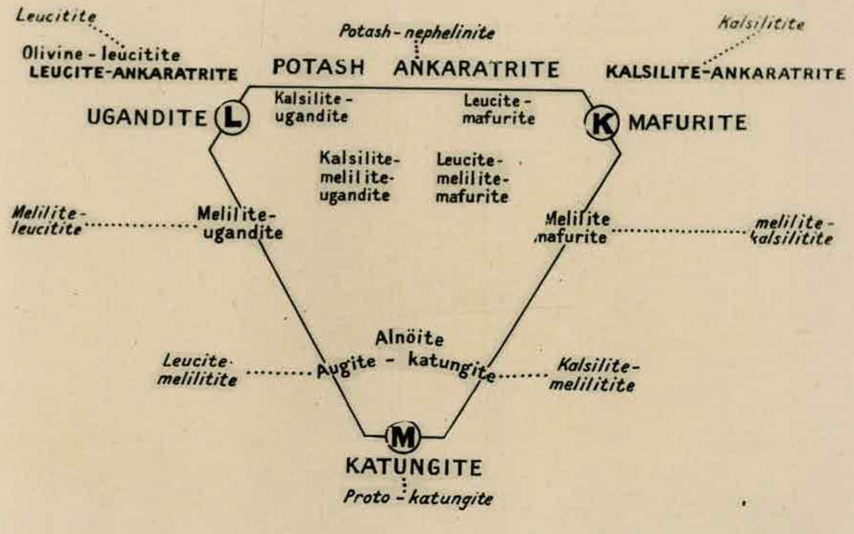

Fig. 1

Triangular classification of the rock-types occurring in the volcanic fields near Ruwenzori. L=Leucite and augite; K=Kalsilite and augite; M=Melilite and potash-rich glass, occasionally with kalsilite or leucite. All the types contain olivine, except those named in italics. Biotite varieties (including heteromorphs such as olivine-ouachitite) of some of the types are known, but are not named except in the case of alnöite. The ankaratrite series differs from the mafurite-ugandite series in being conspicuously rich in augite and relatively poor in olivine. After Holmes (1950, Fig. 2, p. 776).

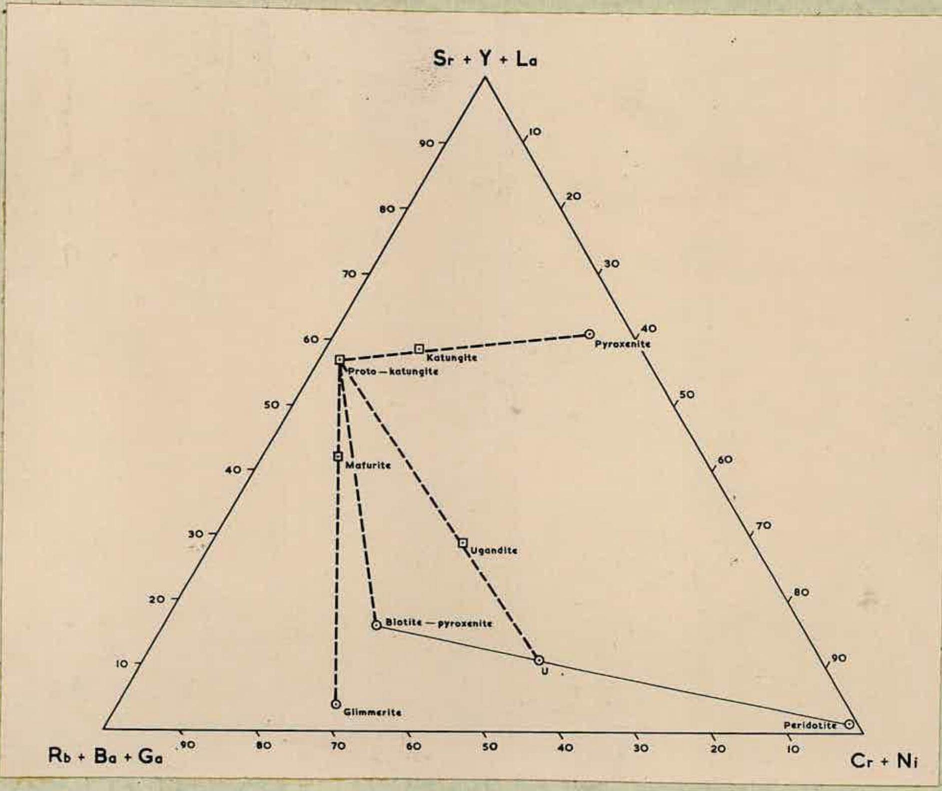

Fig. 2

Relative proportions of Sr+Y+La, Rb+Ba+Ga and Cr+Ni in the different volcanic types and members of the "O.B.P." series.
Pyroxenite:C 4035, Peridotite=average of C 1963 and C 4034b, Biotite-pyroxenite=average of G 20 and C 2786, Glimmerite=C 4034a, and U=1/3 peridotite and 2/3 biotite-pyroxenite.
Katungite=average of all analysed katungites given in Table 1b, Mafurite:C 6073, and Ugandite=C 3052.

TABLE 1a

Chemical composition of members of the sub-volcanic series

	A	B	C	D	E	F	G	H
	C4034b	C1963	C4035	K4	G20	C2786	C4034a	C3033a
SiO_2	42.59	47.33	50.39	33.99	44.39	43.35	38.18	42.91
Al_2O_3	3.82	6.84	3.04	5.86	6.37	9.67	16.52	12.20
Fe_2O_3	2.55	0.02	2.61	9.35	5.11	5.26	2.90	1.15
FeO	4.96	5.62	5.42	8.54	4.86	2.65	5.24	12.00
MnO	0.10	0.12	0.05	0.15	0.10	0.09	tr.	0.19
MgO	33.84	19.31	13.14	7.53	14.20	15.74	19.32	10.26
CaO	2.84	16.99	22.57	18.23	17.02	12.20	1.16	13.65
Na_2O	0.26	0.41	0.56	0.69	0.50	0.44	0.56	1.60
K_2O	2.58	0.88	0.08	2.38	2.35	4.74	9.01	2.02
H_2O+	2.96	0.55	0.14	0.96	0.35	0.59	1.22	0.20
H_2O-	0.63	0.21	none	0.18	0.05	0.07	0.58	0.02
CO_2	0.25	0.02	none	0.30	0.04	0.04	None	0.06
TiO_2	1.60	1.26	1.96	8.65	3.91	4.38	5.18	3.37
P_2O_5	0.22	0.21	tr.	2.80	0.26	tr.	-	0.36
Cl	0.05	tr.	-	0.02	0.04	tr.	-	0.08
F	0.12	0.01	-	0.09	0.04	0.11	-	0.06
S	0.18	0.01	-	0.03	0.02	tr.	-	0.05
Cr_2O_3	0.23	0.32	-	none	0.03	0.05	0.14	0.02
V_2O_3	0.01	-	-	0.07	0.05	0.04	-	0.06
NiO	0.21	0.04	-	none	0.01	0.04	-	0.01
BaO	0.13	0.03	tr.	0.13	0.16	0.30	0.16	0.05
SrO	0.02	none	0.12	0.05	0.03	none	0.22	0.05
Li_2O	tr.	tr.	-	none	tr.	tr.	-	-
CuO	-	-	-	-	-	0.03	-	0.05
Total	100.15	100.22	100.08	100.00	99.89	99.79	100.17	100.42
Less O	0.11	0.01	-	0.05	0.03	0.04	-	0.04
	100.04	100.21	100.08	99.95	99.86	99.75	100.17	100.38

Table 1a (Contd.)

A. = Biotite peridotite. Xenolith from ejected block of olivine-rich ugandite, C 4034b, Kakunyu crater, Bunyaruguru (Combe and Holmes, 1945, p. 377). Analyst: H.F. Harwood.

B. = Biotite-bearing augite-peridotite. Ejected block, C 1963, Mabungo crater, Bufumbira (Holmes and Harwood, 1937, p. 23). Analyst: H.F. Harwood.

C. = Pyroxenite. Xenolith from ejected block of olivine-rich ugandite, C 4035, Kakunyu crater, Bunyaruguru (Combe and Holmes, 1945, p. 377). Analyst: W.H. Herdsman.

D. = Sphene-rich biotite-pyroxenite. Ejected block, K 4, Katwe crater (Holmes and Harwood, 1937, p. 30). Analyst: H.F. Harwood.

E. = Biotite-pyroxenite. Ejected block, G 20, Katwe crater (Holmes and Harwood, 1937, p. 30). Analyst: H.F. Harwood.

F. = Biotite-pyroxenite. Ejected block, C 2786, vent on S.S.W. end of Lutale Ridge, Bufumbira (Holmes and Harwood, 1937, p. 29). Analyst: H.F. Harwood.

G. = Glimmerite. Xenolith from ejected block of olivine-rich ugandite, C 4034a, Kakunyu crater, Bunyaruguru (Combe and Holmes, 1945, p. 377). Analyst: W.H. Herdsman.

H. = Leucite-kentallenite. Ejected block, C 3033a, Nyamuragira, Belgian Congo. New analysis by Imperial Chemical Industries Limited, Research Department, Billingham, Co. Durham.

TABLE 1b

Trace-element contents in ppm. of members of the sub-volcanic series.

Element	Sensitivity	A	B	C	D	E	F	G	H
Rb	1	*	*	*	170	160	150	1000	75
Li	1	2	4	6	3	1	1	*	8
Ba	5	15	50	20	1200	2000	1500	3200	1000
Sr	5	40	100	340	1000	600	500	240	1000
Cr	1	2400	4000	100	*	900	650	1500	350
CO	2	45	90	55	60	75	50	55	75
Ni	2	1900	350	85	2	150	230	320	120
Zr	10	40	90	200	1200	50	70	*	250
La	30	*	*	*	<30	*	*	*	*
Y	30	*	*	*	<30	<30	*	*	35
Cu	3	40	50	3	50	90	60	3	35
V	5	110	130	150	550	400	290	200	380
Ga	1	*	5	10	30	25	20	25	20
Tl	30	*	*	*	*	*	*	*	*
Sn	5	5	10?	*	*	*	*	<5	*
Pb	10	<10	<10	<10	<10	<10	<10	10	<10
Sc	10	*	20?	40	*	20	15	*	*
Mo	1	3	1	*	*	*	*	*	*
Ge	10	*	*	*	*	*	*	*	*
Be	5	*	*	*	*	*	*	5	*
Ag	1	2	3	15	5	20	1	1	*
In	10	*	*	*	*	*	*	<10?	*

Analyst: R.A. Higazy

* = less than the respective limits of sensitivity

A - H as in Table 1a

TABLE 3a

Chemical composition of ankaratrite, mela-potash nephelinite, and mela-leucitite

	Ankaratrites		Average ankaratrite	Mela-potash nephelinite	Mela-leucitite
	A	B		C	D
SiO_2	39.86	35.28	35.27	34.77	37.09
Al_2O_3	8.64	9.84	9.24	10.62	13.03
Fe_2O_3	7.68	6.62	7.15	7.24	7.50
FeO	6.57	6.21	6.39	6.37	5.83
MnO	0.29	0.36	0.33	0.27	0.23
MgO	10.64	9.08	9.86	6.32	5.48
CaO	16.59	14.34	15.47	15.34	14.02
Na_2O	1.30	3.07	2.19	3.58	3.14
K_2O	2.27	5.33	3.80	3.88	4.13
H_2O+	0.88	2.02	1.45	1.77	2.02
H_2O-	0.09	0.44	0.27	1.44	0.88
CO_2	none	none	none	2.01	0.90
TiO_2	4.37	6.37	5.37	5.03	4.98
P_2O_5	0.37	0.92	0.65	1.23	1.09
Cl	0.05	-	-	-	-
F	0.06	-	-	-	-
S	-	-	-	-	-
Other constituents	0.40	-	-	-	-
Total	100.06	99.88	99.74	99.87	100.32
Less O	0.04	-	-	-	-
	100.02	99.88	99.74	99.87	100.32

TABLE 8a (Contd.)

A = Leucite-ankaratrite C 5635. Lava occurrence, Lake Mbuga crater, Katwe-Kikorongo (Holmes, 1952). Analyst: W.H. Herdsman. Other constituents include SO_3 0.17; BaO 0.05; and SrO 0.18.

B = Leucite-melilite ankaratrite C 5692. Ejected block from S. rim of Nyaluzigati crater, Katwe-Kikorongo. New analysis by W.H. Herdsman.

C = Mela-potash-nephelinite C 5566. Ejected block N.N.W. of crater floor S. Nyamununka crater, Katwe-Kikorongo. New analysis by W.H. Herdsman.

D = Mela-leucitite C 5545. Loose ejected block from three feet W. rim of South Nyamununka crater, Katwe-Kikorongo. New analysis by W.H. Herdsman.

Grateful acknowledgment is due to Professor Arthur Holmes for his kind permission for publishing analyses B, C and D.

TABLE 3b

Trace-element contents in ppm. of ankaratrite, mela-potash nephelinite and mela-leucitite

	Ankaratrites		Average ankaratrite	Mela-potash nephelinite	Mela-leucitite
	A	B		C	D
Rb	70	270	170	120	180
Li	6	10	8	20	25
Ba	1800	4000	2900	5900	6000
Sr	4000	9800	6900	> 1%	> 1%
Cr	400	400	400	< 1	5
CO	70	80	75	50	40
Ni	100	85	93	15	15
Zr	300	800	550	500	700
La	< 30	35	30	< 30	< 30
Y	< 30	30	< 30	< 30	< 30
Cu	90	45	68	250	100
V	250	450	350	350	400
Ga	25	35	30	30	30
Tl	*	*	*	*	*
Sn	*	*	*	*	*
Pb	*	< 10	*	*	*
Sc	10?	*	*	*	*
Mo	*	*	*	*	*
Ge	*	*	*	*	*
Be	*	*	*	*	*
Ag	*	*	*	*	*
In	*	*	*	*	*

Analyst: R.A. Higazy

* = Element if present is below its limit of sensitivity given in Table 1b.

A - D as in Table 3a

TABLE 4a

Chemical composition of volcanic rocks from Birunga field.

	Feldspar-free types		Feldspar-bearing types				Average feldspar-bearing types	Limburgite G
	A	B	C	D	E	F		
SiO_2	38.45	36.86	45.66	44.74	44.73	44.86	44.99	44.22
Al_2O_3	13.42	14.97	16.90	18.68	18.18	18.24	18.00	11.56
Fe_2O_3	3.97	3.93	2.20	2.42	1.98	2.20	2.20	2.16
FeO	7.86	7.04	10.35	9.27	9.79	9.53	9.74	8.41
MnO	0.38	0.32	0.21	0.27	0.25	0.24	0.24	0.25
MgO	9.54	4.86	3.98	4.62	4.96	5.19	4.69	13.86
CaO	17.03	15.31	8.97	9.77	9.64	9.29	9.42	13.60
Na_2O	2.52	6.09	3.23	3.05	3.13	2.77	3.06	1.73
K_2O	2.46	5.47	4.23	2.94	3.16	3.16	3.37	1.05
H_2O+	0.42	0.26	0.25	0.26	0.52	0.46	0.37	0.26
H_2O-	0.03	0.21	0.06	0.10	0.05	0.22	0.10	0.24
CO_2	none	tr.	0.09	none	none	none	0.02	none
TiO_2	1.94	2.60	3.09	3.02	2.96	3.02	3.02	2.03
P_2O_5	1.33	1.32	0.68	0.53	0.54	0.43	0.54	0.21
Cl	0.06	0.17	0.08	0.09	0.09	0.08	0.09	0.06
F	tr.	0.12	0.15	none	0.01	none	0.04	none
S	-	-	0.07	0.08	0.10	0.10	0.09	0.03
SO_3	0.17	0.14	-	-	-	-	-	-
Cr_2O_3	-	-	0.01	-	-	-	-	-
V_2O_3	-	-	0.06	-	-	-	-	-
NiO	-	-	0.01	-	-	-	-	-
BaO	0.08	0.15	0.09	0.13	0.11	0.11	0.11	0.10
SrO	0.43	0.22	0.08	0.16	0.18	0.15	0.14	0.18
CuO	-	-	0.04	-	-	-	-	-
Total	100.09	100.04	100.49	100.13	100.38	100.05	100.23	99.95
Less O	0.01	0.09	0.08	0.04	0.05	0.04	0.05	0.02
	100.08	99.95	100.41	100.09	100.33	100.01	100.18	99.93

TABLE 4a (Contd.)

A = Olivine-melilitite, C 7360, Livabikari crater, N. of Lake Kivu. New analysis by W.H. Herdsman

B = Potash-nepheline-melilitite, C 3022. Ninagongo crater. New analysis by Imperial Chemical Industries Limited, Research Department, Billingham, Co. Durham.

C = Kivite, C 3030. Lava northern slope of Nyamuragira at 9500 feet. New analysis by Imperial Chemical Industries, Limited, Research Department, Billingham, Co. Durham.

D = Leucite-basanite (kivite), C 9780. Kituru, new Volcano 1948 SSW of Nyamuragira. New analysis by W.H. Herdsman.

E = Leucite-basanite (kivite) C 9892. Muhubuli 1948. New analysis by W.H. Herdsman.

F = Leucite trachybasalt, C 9878. Fissure NW of Kituru 1948. New analysis by W.H. Herdsman.

G = Limburgite, C 7347. Nahimbi 1904 between Nyamuragira and Lake Kivu. New analysis by W.H. Herdsman.

Grateful acknowledgment is due to Professor Arthur Holmes for his kind permission to publish these analyses.

TABLE 4b

Trace-element contents in ppm. of volcanic rocks from Birunga field

Element	Feldspar-free types		Feldspar-bearing types				Average feldspar-bearing types	Limburgite
	A	B	C	D	E	F		G
Rb	85	300	150	160	180	140	158	50
Li	5	10	9	9	8	18	11	8
Ba	2200	>1%	2800	2600	2000	3000	2600	900
Sr	8000	>1%	4500	5500	4500	5000	4700	1200
Cr	450	<1	10	50	75	70	41	1200
CO	85	70	60	50	40	50	50	75
Ni	100	30	35	30	35	40	35	270
Zr	1000	1100	900	700	650	750	750	400
La	<30	80	<30	<30	<30	<30	<30	<30
Y	60	100	45	40	40	40	41	40
Cu	60	45	35	12	15	15	19	40
V	650	340	320	300	320	350	322	300
Ga	45	35	40	50	50	40	45	8
Tl	*	*	*	*	*	*	*	*-
Sn	*	*	*	*	*	*	*	*
Pb	<10	<10	<10	<10	<10	<10	<10	<10
Sc	10	*	*	*	*	*	*	15
Mo	*	2	*	<1?	<1?	<1?	*	1
Ge	*	*	*-	*	*	*	*	*
Be	*	*	*	*	*	*	*	*
Ag	<1	<1	*	<1	*	*	*	*
In	*	*	*	*	*	*	*	*

Analyst: R.A. Higazy

* = Element if present is below its limit of sensitivity given in Table 1b.

A - G as in Table 4a.

TABLE 5

Trace-element constitution of volcanic types from Toto-Ankole and Birunga

Rock	Rb	Ba	Sr	Cr	Co	Ni	Zr	V	Ga
Ugandite	XXX	X	X	XXX	XXX	XXX	X	X	X
Mafurite	XXX	XXX	XX	XXX	XX	XX	XX	XX	XX
Katungite	XX	XX	XX	XX	XX	XX	XX	XX	XX
Ouachitite	X	X	X	XX	XX	XX	XX	XX	XX
Ankaratrite	XX	XX	XX	XX	XX	XX	XX	XX	XX
Mela-leucitite	XX	XX	XXX	X	XX	X	XX	XX	XX
Mela-potash nephelinite	XX	XX	XXX	X	XX	X	XX	XX	XX
Olivine-melilitite	X	XX	XX	XX	XX	XX	XX	XXX	XXX
Potash nepheline-melilitite	XX	XXX	XXX	X	XX	X	XX	XX	XX
Kivite	XX	XX	XX	X	XX	X	XX	XX	XXX
Limburgite	X	X	X	XXX	XX	XX	XX	XX	XX
Average contents in all types in ppm.	210	4100	6250	535	70	200	765	330	28
XXX	>315	>6150	>9375	>802	>105	>300	>1147	>495	>42
XX	105-315	2050-6150	3125-9375	267-802	35-105	100-300	382p 1147	165-495	14-42
X	<105	<2050	<3125	<267	<35	<100	<382	<165	<14

TABLE 6

Trace-element contents of carbonatites and limestones

	Carbonatites					Limestones		
	A	B	C	D	Average carbonatite	E	F	Average limestone
Rb	*	*	*	*	*	*	*	*
Li	20	<1	<1	*	5	1	1	1
Ba	290	650	4000	3000	1985	<5	<5	<5
Sr	1000	>1%	1%	>1%	>7750	<5	300	150
Cr	45	*	*	*	11	3	*	2
CO	50	<5	<5	<5	14	*	*	*
Ni	200	*	*	*	50	*	*	*
Zr	90	70	80	*	60	10	40?	25
La	140	400	700	500	435	*	*	*
Y	45	120	300	100	140	*	*	*
Cu	45	4	7	3	15	4	6	5
V	16	16	30	30	18	6	10	8
Ga	4	*	*	*	1	*	*	*
Tl	*	*	*	*	*	*	*	*
Sn	<5	*	*	<5	*	*	10	5
Pb	<10	<10	10	*	<10	*	*	*
Sc	*	*	*	*	*	*	*	*
Mo	12	1?	1?	3	4	*	2?	1
Ge	*	*	*	*	*	*	*	*
Be	10	*	*	*	*	*	*	*
Ag	8	4	10	2	6	4	1	3
In	*	*	*	*	*	*	*	*

Analyst: R.A. Higazy

* = Element if present is in amounts below its limit of sensititivy given in Table 1b.

TABLE 6 (Contd.)

A = Carbonate dyke, Premier Diamond Mine, S. Africa.

B = Carbonatite, Spitzkop alkaline Complex, Bushveld, Transvaal.

C = Carbonatite, Maronzge Hill, Chilwa Island, Nyasaland.

D = Sövite, Hartung, Alnö Island, Sweden.

E = Limestone, Transvaal System.

F = Limestone, M-1, Mansjo, Sweden.

PART VIII

SIGNIFICANCE OF THE ORTHOCLASE-ALBITE-ANORTHITE, AND THE $NaAlSiO_4$-$KAlSiO_4$-SiO_2 EQUILIBRIUM DIAGRAMS IN IGNEOUS PETROGENY

BY

RIAD A. HIGAZY

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SIGNIFICANCE OF THE ORTHOCLASE-ALBITE-ANORTHITE, AND THE $NaAlSiO_4$-$KAlSiO_4$-SiO_2 EQUILIBRIUM DIAGRAMS IN IGNEOUS PETROGENY

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Abstract

High temperature studies of silicate systems indicate that rocks which form at the latest stages of the differentiation of a basaltic magma should have salic normative proportions which lie in the low temperature region of the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilbrium diagram. Their normative feldspar content should lie approximately on the cotectic curve of the Or-Ab-An equilibrium diagram. The chemical compositions of some potash- and soda-rich acidic rocks do not harmonize with these requirements. It is suggested, therefore, that such rocks are sometimes enriched in potash or soda through metasomatic processes, in other cases they are derived from the crystallization of potash-rich granitic or soda-rich spilitic magmas respectively, which form by differential remelting of the crust.

Introduction

The potash-rich rocks have normative feldspar contents corresponding to points in the orthoclase field of the Or-Ab-An equilibrium diagram (Bowen, 1928, p. 231). The salic normative constituents other than anorthite of most of these rocks exceed 80 per cent. The plot of the proportions of the salic normative constituents exclusive of anorthite of such potash-rich acidic rocks lies outside the region of low temperature representing the residual magma in the system $NaAlSiO_4$-$KAlSiO_4$-SiO_2 (Schairer & Bowen, 1935; and Bowen, 1937, p. 12). High temperature studies, on the other hand, indicate that rocks formed as products of the latest stages of primary crystallization of a basaltic magma should not have normative feldspar contents which lie in the orthoclase field, and they should have salic normative constituents placing them in the low temperature "valley" in the system $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagram.

The discrepancy between the results of the above-mentioned equilibrium diagrams and the composition of the potash-rich acidic rocks with regard to their magmatic mode of origin needs discussion.

Some Examples of Potash-Rich Rocks

Noble (1948) gave chemical analyses of some potash-rich rhyolites from the Homestake Mine, Lead, South Dakota. He classified these rhyolites into two divisions; namely, high potash and low potash types. Soda and potash of the high potash type ranges from 0.23 to 0.59 per

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[*] On a study leave at Stanford University.

cent and 9.17 to 13.16 per cent, respectively. The potash: soda ratio in these rocks ranges from 15.5:1 to 48.8:1. He mentions that Washington (1917, p. 107) has listed ten other rocks which have chemical compositions similar to those of Lead, South Dakota. They are rhyolites, granites, and quartz prophyries. The normative feldspar contents of the rocks studied by Noble (1948, p. 933) as well as those given by the author (Higazy, 1949, Fig. 4) lie in the orthoclase field of the Or-Ab-An equilibrium diagram. In addition to these rocks, there are two rocks (Washington, 1917, p. 79), namely, a porphyry and a pitchstone which have identical chemical character to the high-potash rhyolites studied

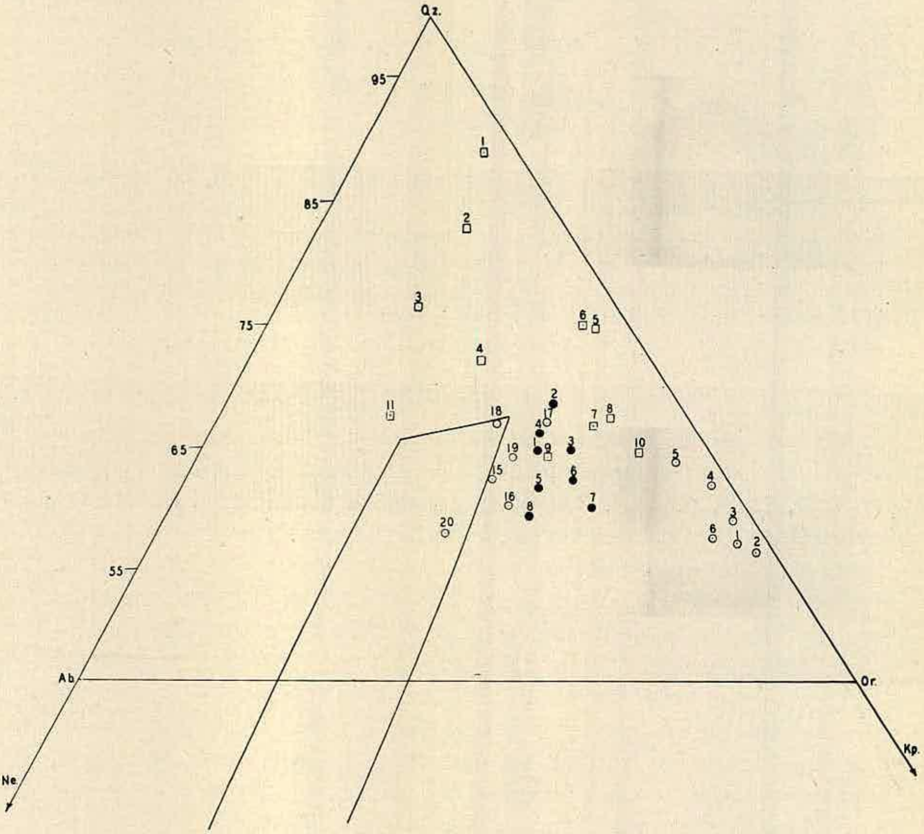

FIG. 1. Squares 1 to 11 = 1 to 11 (Terzaghi, 1948, p. 21). Circles 1 to 6 = 1 to 6 (Noble, 1948, p. 932, high-potash type). Circles 15 to 20 = 15 to 20 (Noble, 1948, p. 932, low-potash type). Solid circles 1 to 8 = averages of rhyolite, rhyolite family 116, sodaclase rhyolite, leuco-rhyolite, all aplites, alkali aplite, runite, and sodaclase granite respectively (Johannsen, 1931, pp. 509–513).

by Noble. The porphyry has a potash:soda ratio of 28.5:1 and the pitchstone has a higher ratio since it possesses 6.75 per cent of K_2O and traces of Na_2O.

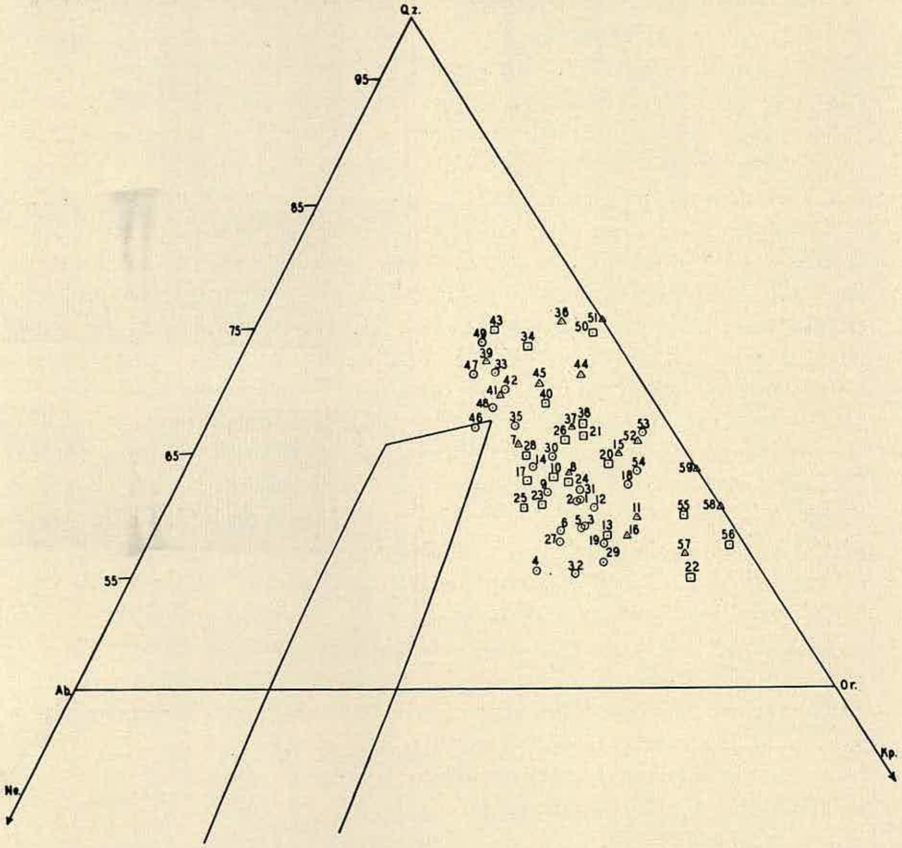

FIG. 2. Circle = deep-seated rocks, triangle = volcanic rocks, square = hypabyssal rocks. 1 to 5 and 6 to 32 = 1 to 5 and 7 to 33. Order quardofelic britannare. Subrang dopotassic omeose (Washington, 1917, p. 109), 33 to 45 = 1, 2, 3, 11, 12, 13, 15, 18, 22, 25, 27, 30, and 31. Order quarfelic columbare. Subrang dopotassic magdeburgose (Washington, 1917, p. 57), 46 to 49 = 10, 31, 32, and 60. Order quarfelic columbare. Subrang sodipotassic alaskose (Washington, 1917, p. 61), 50 and 51 = 1 and 2. Order quarfelic columbare. Subrang perpotassic (Washington, 1917, p. 79), 52 to 59 = 4, 5, 7, 8, 9, 10, 11, and 12. Order quardofelic britannare. Subrang perpotassic lebachose (Washington, 1917, p. 107).

The low-potash rhyolites of the Homestake Mine have soda and potash ranging from 1.84 to 4.48 per cent and 5.11 to 7.50 per cent, respectively. The potash:soda ratio in this type varies from 1.2:1 to 3.3:1. Examples of such rocks given by the author (Higazy, 1949, Fig. 4) are more abundant than those of the high-potash type. They are granites, aplites, and pegmatites; quartz and granite porphyries; rhyolites, pitchstones, obsidians, and comendites—that is, rocks which are supposed to crystallize at the latest stages of the differentiation of the basaltic magma. The normative feldspar contents of the low-potash rhyolites of Lead, South Dakota (Noble, 1948, Fig. 1B), as well as those of the above mentioned examples (Higazy, 1949, Fig. 4), also lie in the orthoclase field. The salic normative proportions, excluding anorthite, of all the cited rocks lie outside the low temperature region of the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagram, close to its Or point as illustrated in Figs. 1 and 2.

Terzaghi (1948) gave chemical analyses of some potash-rich rhyolites from the Esterel region, France. In these rocks soda and potash ranges from 0.54 to 3.95 per cent and 2.45 to 8.71 per cent, respectively. The potash:soda ratio ranges from 0.8:1 to 11.6:1. It is 0.8:1 in a vitric rhyolite and 0.9:1 in a spherulitic rhyolite. Both of these rocks have normative feldspar content lying outside the orthoclase field of the Or-Ab-An diagram (Terzaghi, 1948, Fig. 1). The potash:soda ratio in the other nine rhyolites studied by Terzaghi ranges from 1.9:1 to 11.6:1. In four rocks the ratio lies within the range of the low-potash type of Noble. The plot of the salic normative constituents excluding anorthite of the Esterel region rocks falls outside the low temperature "valley" of the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagram, closer to its Q (SiO_2) point as shown in Fig. 1.

Johannsen (1931) gave average chemical compositions of rhyolites, sodaclase rhyolites, leuco-rhyolites, all aplites, alkali aplites, runite, and sodaclase granites. The normative salic constituents of these averages excluding anorthite form more than 80 per cent of the rock composition. The proportions of these constituents are plotted on the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagram (Fig. 1). They lie outside the "valley" of the residual liquids.

ORIGIN OF THE POTASH-RICH ROCKS

The potash-rich rocks may be explained as originating in two ways; namely, (a) crystallization differentiation and (b) metasomatic alterations.

Crystallization differentiation

The formation of a potash-rich liquor at the latest stages of magmatic crystallization has first been shown to be possible by Bowen (1928, p. 231). He postulated a reaction relation between anorthite and orthoclase enabling liquids to cross the cotectic curve of the Or-Ab-An system during the end of the magmatic crystallization history. This supposition was considered by Noble (1948) to be true and accordingly he favored the differentiation theory to account for the genesis of the rhyolites he studied. However, the reaction relation has recently been found by Schairer and Bowen (1947) to be non-existent so that this hypothesis can no longer hold. Terzaghi (1935) thought that the presence of the normative feldspar content of the potash-rich rocks in the orthoclase field might be due to pressure. However, pressure should have but a negligible effect in the case of the rhyolites since they are extrusive types. Moreover, the author (Higazy, 1949) has shown that pressure does not seen to be responsible for the presence in the orthoclase field of the normative feldspar content of the deep-seated potash-rich rocks of granitic compositions derived from the differential crystallization of a purely basaltic magma. It might be argued that the volatiles affect the course of the crystallization, but the presence of other rocks supposed to form at the latest stages of crystallization whose normative feldspar contents do not lie in the orthoclase field and whose salic normative constituents lie in the low temperature region of the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 diagram leads to the belief that the influence of the fugitive components cannot be the reason that compositions of the potash-rich rocks fail to conform to the crystallization differentiation theory as expressed by the feldspar and the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagrams. Nockolds (1946) studied some granitic rocks and found that their normative feldspar contents lie approximately on the cotectic curve of the Or-Ab-An equilibrium diagram. These rocks studied by Nockolds could be the result of the latest stages of crystallization of the basaltic magma. This, of course, would only be true in the case that the cotectic curve of the Or-Ab-An diagram is accepted to represent compositions which form at the latest stages of magmatic differentiation.

It may be true that the potash-rich rhyolites of the Lead region (Noble, 1948) are of a truly magmatic origin and have been derived from the differential crystallization of a basaltic magma, but neither the Or-Ab-An nor the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagram can satisfactorily account for their compositions. If such were the case, it would not be reasonable for petrologists to use the presence of the normative compositions of the different rocks types in certain portions of the equilibrium diagrams as proof or disproof of their derivation from the differentiation of a basaltic magma. If, however, we assume these diagrams to be valid in every case we must seek some other explanation for the origin of these rocks that do not conform to them.

One possible mode of origin of the potash-rich rhyolites is their formation from a primordial rhyolitic magma. Fenner (1948) believes in the presence of two immiscible liquids at high temperature, a rhyolitic one and a basaltic one; these two liquids re-unite to form a single liquid before crystallization starts unless the two liquids have become separated from each others influence. The potash-rich rhyolites might on this assumption be the result of the crystallization of a rhyolitic magma originally rich in potash. The rhyolites of the Gardiner River area in Yellowstone Park impregnating the basalts of an earlier flow have been shown by Fenner (1948) to support his view. If this were true, one would not expect to find that the compositions of the rhyolites formed in this way follow the rules expressed by both the feldspar and the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagrams since these apply only in the case of crystallization differentiation of a purely basaltic magma. Under this assumption we can have two types of rhyolites. One type forms as the latest product of the differentiation of a purely basaltic magma, or a re-united mixture of both basaltic and rhyolitic magmas, the rhyolite magma being subordinate in amount. The other type is the product of the crystallization of a purely rhyolitic magma or a re-united mixture of both rhyolitic and basaltic magmas, the basaltic magma being subordinate in amount. The former category of rhyolites would have normative compositions which are in harmony with the phase equilibrium diagrams; examples of these rocks may be those selected by Bowen from the Eastern African lavas (Bowen, 1937). The rhyolites of the latter category would not necessarily have normative compositions which conform to the demands of the differentiation theory because they form substantially from an originally rhyolitic magma.

There are also soda-rich rhyolites. The normative salic constituents of this type also lie outside the field of the low temperature in the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagram close to its Ab point. Examples of this type are some aplites, microgranite, albite pegmatite, granite porphyry, granophyre, felsite, quartz keratophyre, and soda rhyolites (Washington, 1917, p. 77). Potash in these rocks varies from 0.00 to 0.99 per cent, while soda ranges from 4.53 to 6.89 per cent; the normative orthoclase and albite range from 0.00 to 6.12 and 37.73 to 58.16 per cent, respectively. Hatch (1889, p. 72) gives the chemical composition of a soda felsite from Brittas Bridge, Co. Wicklow, Ireland, which has 0.16 per cent potash and 7.60 per cent of soda. Thomas (1911), in his study of the Skomer volcanic rocks (Pembrokeshire) among which a soda rhyolite possessing 0.38 per cent of potash and 6.40 per cent of soda and whose orthoclase and albite normative percentages are 2.22 and 53.97 respectively, considered the chief mineralogical and chemical peculiarities of the Skomer rocks to be primary and he regarded the series in part as being rich in original soda and as having pantellerian affinities (Thomas, 1911, p. 210). Bowen (1945) in his studies of the equilibrium relations in portions of the quaternary system, Na_2O-CaO-Al_2O_3-SiO_2, shows that fractional crystallization in these compositions could give rise to differentiates analogous to tephrites, phonolites, and alkali rhyolites (soda-rich). The system studied by Bowen (1945) does not contain any potash. It seems probable that if K_2O were added to this system instead of Na_2O, similar differentiates could develop; namely, leucitites, leucite basalts, leucite bearing phonolites, and alkali rhyolites (potash-rich). There are no studies concerning the presence of both Na_2O and K_2O in a system containing CaO, Al_2O_3, and SiO_2 and the prediction of the actual situation in such a quintuple system would indeed be difficult. The studies of the system $NaAlSiO_4$-$KAlSiO_4$-SiO_2 where potash and soda are equally represented indicate, however, that the latest products of differentiation will be restricted to those which have normative salic constituents which lie in the low temperature region of that system. Compositions which are relatively rich in either potash or soda cannot be explained. It seems, therefore, on the basis of what we know from the dry equilibrium phase diagrams, that the soda-rich and the potash-rich rhyolites could develop as the latest differentiates of two separate magmas, a soda-rich and a potash-rich liquor, respectively. This assumption cannot hold if we consider a primordial basaltic magma as the original material since there is no evident way at present of separating potassium- and sodium- alumino silicates in the differential crystallization of a basaltic magma.

In the pegmatite phase, we may get replacing solutions composed essentially of albitic materials with negligible amounts of potash. In other cases, however, the replacing hydrothermal solutions may be composed substantially of microclinic materials with no or negligible amounts of soda. The question now is; are the albitic or soda-rich material and the microclinic or potash-rich material derived from the same original source? If they came from one source, then it can be assumed that there had been immiscibility between the sodium and the potassium alumino silicates in the hydrothermal stages and this immiscibility might have been assisted by the enrichment in water in the hydrothermal stage. If immiscibility between the sodium and the potassium alumino silicates is effective in the hydrothermal stage, has it also any influence at higher temperatures at which the rhyolites form? Experiments supporting the immiscibility between the alkali alumino silicates at relatively high temperatures are not available. In the absence of such experiments, it is doubtful that this process occurs; it is more reasonable to assume that the albitic soda-rich and the microclinic potash-rich materials have been derived from two different sources.

Wahl (1949) states that during geosynclinal orogenies at least four different kinds of parental magmas are formed by differential remelting of the crust; (1) spilitic and picrospilitic magmas, (2) granodioritic and dacitic-andesitic magmas, (3) basaltic magma, and (4) granitic magma. Furthermore, under cratogenic conditions other magmas are obtained. One of these magmas is a granitic one which differentiates into potash granite and gabbro-norite-anorthosite. The occurrence of such a granitic magma which is analogous in composition to rhyolitic compositions would solve the problem of the potash-rich acidic rocks. The soda-rich rocks, however, seem to be related to the spilitic and picrospilitic magmas, whereas the normal subalkalic rocks are apparently the differentiates of either a dacitic-andesitic magma or a basaltic magma or both.

Metasomatic alterations

Potash enrichment has been ascribed by some authors to secondary processes. Fenner (1936) has shown that thermal waters containing alkali halides and bicarbonates are still in the process of altering the rhyolite of the Yellowstone Park region. Terzaghi (1948) attributed the enrichment in potash of the rhyolites of the Esterel region, France, to alteration processes. Terzaghi arrived at that conclusion after some field evidences and the investigation of the textures of the studied rhyolites. The presence of the normative feldspar proportions of these rocks in the orthoclase field of the Or-Ab-An equilibrium diagram and the existence of the salic proportions outside the region of low temperature in the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagram is believed due to the secondary enrichment in potash. The vitric rhyolite studied by Terzaghi possesses a normative feldspar content which lies outside the orthoclase field and close to the cotectic curve of the feldspar equilibrium diagram. This might indicate that the rhyolite before devitrification and alteration was formed as an end stage of the differentiation of a basaltic magma. The formation of some potash-rich pegmatites of the Black Hills, South Dakota, has been shown by the author (Higazy, 1949) to be due to metasomatic processes. This conclusion has been drawn from the study of the chemical compositions and the textural features of the investigated rocks. Examples of secondary soda enrichment are numerous in the literature and need not be cited here. It may then be true that the other potash- and soda-rich rocks are altered by metasomatic processes but this conclusion cannot be arrived at except from field evidences and through investigation of the textural features of every individual occurrence of these rocks. Until we have such studies and more information about every individual case of the potash- and soda-rich rocks it should be stated that it is possible for these rocks to form directly by magmatic crystallization with no alteration. However, the possibility of these rocks forming from the differentiation of a basaltic magma is very remote, if not altogether non-existent, unless the equilibrium systems which are discussed in this paper are changed in one way or the other in order to harmonize with the extreme compositions which we get in the case of the potash- and soda-rich rocks. The complications and the changes in these systems which are supposed to be due to pressure, water, volatile components, or even the combination of all these factors do not seem to affect the principal results derived from these equilibrium systems. It might possibly be proved that by means of some mechanism or relationship between the different components unknown at the present, that these factors have a significant influence in modifying the principles of crystallization in the studied equilibrium diagrams. Available data and experiments, on the other hand, do not point in that direction. The assumption of the presence of potash- and soda-rich magmas seems to solve the problem of the magmatic derivation of the potash- and soda-rich rocks respectively. Metasomatic processes by flowing pore solutions or diffusion of individual particles (Ramberg, 1944) may also be significant.

CONCLUSIONS

The Or-Ab-An and the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 equilibrium diagrams fail at present to account for the derivation of the potash- and the soda-rich rocks from the differentiation of a basaltic magma. Until a reasonable mechanism for their formation from such a magma is known it is assumed that they are in some cases the differentiates of potash-rich rhyolitic and soda-rich spilitic magmas respectively. In other cases, they are probably metasomatic rocks formed from the alteration of other subalkalic rocks. The field and textural features for every individual occurrence must be known to establish their metasomatic derivation.

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PART IX

With the authors' Compliments

JOURNAL OF SEDIMENTARY PETROLOGY, VOL. 14, NO. 2, PP. 43–69
FIGS 1–20, TABLES 1–2, AUGUST, 1944

MECHANICAL ANALYSIS OF SOME BOTTOM DEPOSITS OF THE NORTHERN RED SEA

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ABSTRACT

The following account is an investigation of the mechanical composition of some sixty bottom samples from the Northern Part of the Red Sea, in particular from the three differently constituted areas, the Gulf of Suez, the Gulf of Aqaba and the Red Sea proper. The statistical constants were correlated with each other and with the contents of calcium carbonate, nitrogen and organic matter and these properties were correlated with the environmental conditions of deposition. Though sufficient work has not been done on the Red Sea deposits to enable general conclusions to be drawn, still conclusions relating to the effect of depth and the configuration of the sea-bottom seem to be well established. The irregular bottom topography gives rise to variety in the deposits. Contrasts appear between the deposits of the shallow and smooth Gulf of Suez, of the deeper Gulf of Aqaba, and the very irregular Red Sea proper.

INTRODUCTION

The following paper is an investigation of the mechanical analysis of some bottom samples collected during the Egyptian Preliminary Expedition to the Northern Red Sea in the R.RS. "Mabahith" in 1934–1935, when the senior author accompanied the expedition (2, 3 and 10). The mineralogy of the sediments is given in the succeeding article of this *Journal.* Sixty four samples were examined, of which fourteen are cores and fifty are grab samples. The localities of the different sampling stations are given in a previous publication (3, table p. 77), and their distribution is also shown in figure 1 (see also track chart and position of various sections in 3, figure 1, p. 6 and 10, figure 1, p. 308).[a] In table 1, the number of samples and the corresponding sections examined are given.

Core samples were collected by a Bigelow sounding rod whereas the grab samples were collected by a modified type of a Petersen grab.

To the author's knowledge, samples collected during previous expeditions to the Red Sea, such as the "Pola," the Magnaghi and the John Murray Expeditions[b] (15, 16 and 17), were not subjected

TABLE 1

Section examined	No. of samples
Gulf of Suez	3 core samples.
Gulf of Aqaba	7 grab samples.
Ghardaqa-Shadwan-Senafir	3 core samples and 31 grab samples.
Yuba-Mersa Daba	1 core sample and 2 grab samples.
Safaga-Mowila	3 core samples and 3 grab samples.
Qoseir-Brothers-No'man	4 core samples and 2 grab samples.
Daedalus-Hanạk	5 grab samples.

[a] Also 20 charts and 5 sheets with echo sections published in connection with an article on bottom topography (1). Unfortunately these charts though published were never issued but could be obtained from the Librarian—Faculty of Science—Cairo.

[b] The observations of the John Murray Expedition as well as of the Dutch Snellius Expedition were restricted to but a few stations scattered over the southern part of the Red Sea.

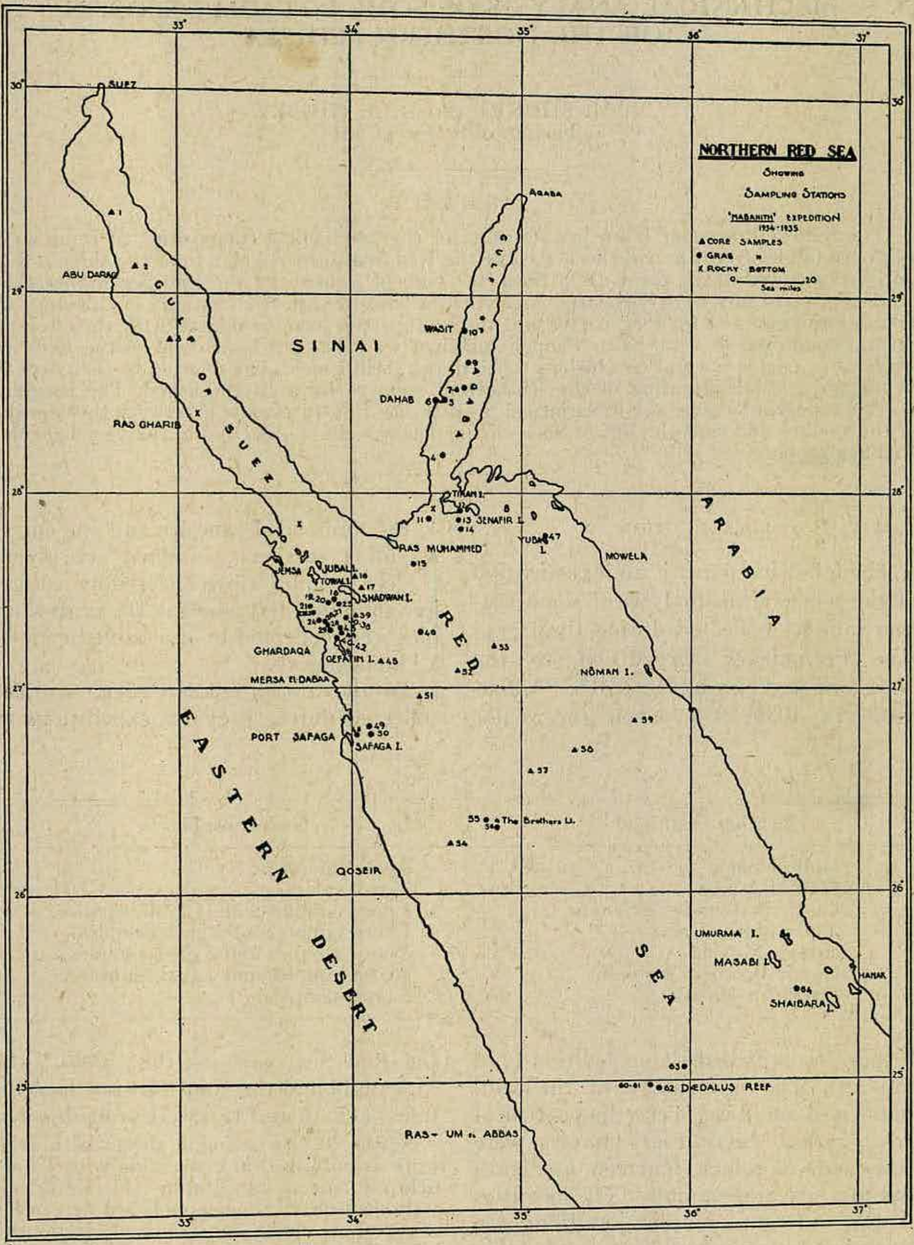

FIG. 1.—Northern Red Sea showing sampling stations.

TABLE 2. *Statistical constants of bottom sediments of Red Sea Northern Part.*

Section 1. Gulf of Suez.

No. of sample	University No.[1]	Station No.	Type of sample	Position		Depth in mts. (Echo)	Q_1 (mm)	Md (mm)	Q_3 (mm)	So	log So	Sk	log Sk	CaCO$_3$[2] %	Nitrogen %	Organic C %	Remarks
				Latitude N.	Longitude E.												
1	8503	1	Core—Top	29° 23′ 30″	32° 37′ 00″	62	.178	.044	.011	4.02	.604	1.01	.004	60.77	.050	.35	Marked increase of temp. and transparency.
			“ —Bottom	“	“	“	.063	.017	.007	2.92	.465	1.61	.207				
2	8504	2	Core—Top	29 08 15	32 45 30	59	.072	.020	.006	3.42	.534	1.12	.049				Decrease of salinity in passing down Gulf of Suez.
			“ —Middle	“	“	“	.043	.015	.004	3.20	.505	0.80	$\bar{1}$.903	57.27	.055	.45	
			“ —Bottom	“	“	“	.074	.023	.008	3.00	.477	1.15	.061				
3	8505	3	Core—Top	28 46 45	32 57 15	64	.180	.064	.015	3.46	.539	0.66	$\bar{1}$.819				
			“ —Middle	“	“	“	.200	.060	.010	4.58	.661	0.53	$\bar{1}$.723	73.02	.049	.38	
			“ —Bottom	“	“	“	.115	.040	.012	3.16	.500	0.83	$\bar{1}$.919				

Section 2. Gulf of Aqaba.

No. of sample	University No.[1]	Station No.	Type of sample	Latitude N.	Longitude E.	Depth in mts. (Echo)	Q_1 (mm)	Md (mm)	Q_3 (mm)	So	log So	Sk	log Sk	CaCO$_3$[2] %	Nitrogen %	Organic C %	Remarks
4	8506	57	Grab	28 11 54	34 32 12	1128	.045	.010	.002	4.33	.637	1.20	.079	71.11	.033	.15	
5	8507	48	“	28 27 42	34 32 00	365	.060	.034	.015	2.00	.301	0.78	$\bar{1}$.892	77.20	.024	.06	Wire soundings excessive over echo as grab fell down slope. Echo (given in table probably too low owing to slope.
6	8508	49	“	28 27 24	34 30 18	265	.460	.200	.082	2.37	.375	0.95	$\bar{1}$.975				
7	8509	52b	“	28 32 00 28 32 18	34 40 12 34 40 06	1113–1143	.067	.018	.004	3.99	.601	0.87	$\bar{1}$.940	42.20	.023	.08	
8	8510	“	“	28 32 00 28 32 18	34 40 12 34 40 06	“	.080	.030	.008	3.14	.497	0.72	$\bar{1}$.857				
9	8511	54	“	28 40 30 28 38 30	34 42 18 34 41 18	1161–1393	.038	.014	.002	3.98	.600	0.47	$\bar{1}$.668	58.62	.024	.11	
10	8512	55	“	28 49 12	34 39 12	442	.014	.005	.002	2.52	.401	1.23	.090	57.65	.025	2.1	

Section 3. Ghardaqa-Shadwan-Senafir.

No. of sample	University No.[1]	Station No.	Type of sample	Latitude N.	Longitude E.	Depth in mts. (Echo)	Q_1 (mm)	Md (mm)	Q_3 (mm)	So	log So	Sk	log Sk	CaCO$_3$[2] %	Nitrogen %	Organic C %	Remarks
11	8513	43	Grab	27 52 00	34 27 24	1147	.048	.018	.003	3.70	.568	.47	1.676	76.52	.041	.21	Near Tiran Island.
12	8514	41a	“	27 54 57	34 37 38	24	.450	.260	.180	1.58	.199	1.20	.079	95.17	.044	.09	
13	8515	58	“	27 51 30 27 52 00	34 38 12 34 38 00	596–616	.057	.022	.007	2.88	.459	.81	1.910	78.47	.055	.20	
14	8516	42	“	27 49 30 27 49 00	34 39 30 34 38 42	741	.042	.015	.007	2.45	.389	1.31	.117	77.13	.032	.12	
15	8517	45a	“	27 29 30 27 38 00	34 23 30 34 22 36	960	.055	.200	.013	2.06	.314	1.79	.253	75.21	.016	.09	Near Ras Mohamed.
16	8518	40	Core—Top	27 34 36	34 00 51	941	.051	.022	.010	2.26	.354	1.03	.013				East of Shadwan Island.
			“ —Middle	“	“		.040	.019	.007	2.39	.378	.77	$\bar{1}$.890	80.32	.086	.22	
			“ —Bottom	“	“		.038	.018	.007	2.35	.371	.81	$\bar{1}$.908				
17	8519	7	Core—Top	27 30 40 27 29 36	34 03 30 34 05 10	731	.066	.029	.009	2.70	.431	.70	$\bar{1}$.848				
			“ —Middle	“	“		.060	.031	.012	2.24	.350	.75	$\bar{1}$.875	81.27	.049	.31	
			“ —Bottom	“	“		.064	.038	.018	1.88	.274	.75	$\bar{1}$.875				

TABLE 2. (*continued*)

Section 3. Ghardaga-Shadwan-Senafir (*continued*)

No. of sample	University No.[1]	Station No.	Type of sample	Position		Depth in mts. (Echo)	Q_1 (mm)	Md (mm)	Q_3 (mm)	So	log So	Sk	log Sk	$CaCO_3$[2] %	Nitrogen %	Organic C %	Remarks
				Latitude N.	Longitude E.												
18	8520	26	Grab	27 27 48	33 54 18	236	.320	.200	.085	1.94	.288	.68	$\bar{1}$.832	83.62	.041	.11	Between Ghardaqa and Shadwan Island.
19	8521	32a	"	Round 27 17	33 52 06	30–102 (wire)	1.400	.640	.220	2.52	.401	.75	$\bar{1}$.878	89.09	.058	.24	
20	8522	32c	"	"	"	"	1.440	.710	.310	2.16	.334	.89	$\bar{1}$.948				
21	8523	21a	"	27 26 42	33 45 33	73	.078	.035	.015	2.28	.358	.95	$\bar{1}$.980	84.70	.091	.35	
22	8524	20j	"	27 21 51	33 46 30	17–21	1.38	.57	.27	2.26	.354	1.14	.059				
23	8525	20c	"	"	"	"	"	"	"	"	"	"	"	96.96	.029	.19	
24	8526	15a	"	27 20 48 27 20 30	33 47 48 33 48 03	20–53 (wire)	1.82	.780	.36	2.25	.352	1.08	.033				
25	8527	27	"	27 27 48	33 54 00	203	.74	.34	.20	1.93	.286	1.28	.107				
26	8528	14a	"	27 19 39 27 19 30	33 48 06 33 48 24	66–70 (wire)	.80	.37	.21	1.95	.290	1.22	.088	92.26	.029	.13	
27	8529	14c	"	"	"	"	1.10	.50	.30	1.91	.282	1.32	.121				
28	8530	18a	"	27 19 18	33 48 48	66–71 (wire)	.132	.035	.021	2.51	.400	2.26	.354	91.28	.042	.15	
29	8531	19	"	27 17 54	33 50 12	102 (wire)	.14	.059	.025	2.36	.373	1.01	.002	88.33	.052	.39	
30	8532	34h	"	27 23 24 27 24 21	33 56 30 33 55 48	80–433	.42	.240	.14	1.73	.238	1.02	.009	92.53	.024	.09	
31	8533	34	Grab 9	"	"	"	.42	.290	.20	1.45	.161	1.00	.000				
32	8534	34c	"	"	"	"	.94	.580	.33	1.69	.227	.92	$\bar{1}$.965				
33	8535	34a	"	"	"	"	.70	.320	.18	1.97	.294	1.23	.090	94.86	.030	.11	
34	8536	34	Grab 12	"	"	"	.56	.320	.21	1.63	.212	1.15	.061				
35	8537	34b	"	"	"	"	.50	.270	.18	1.66	.221	1.23	.092				
36	8538	34L	"	"	"	"	.080	.034	.014	2.39	.378	.97	$\bar{1}$.987	81.66	.072	.30	
37	8539	34	Grab 5	"	"	"	1.00	.550	.30	1.82	.261	.99	$\bar{1}$.996				
38	8540	34	Grab 8	"	"	"	.40	.220	.13	1.75	.244	1.07	.031				
39	8541	37	Core—Top	27 24 48 27 24 42	33 59 15 34 00 00	366	.052	.024	.010	2.30	.362	.89	$\bar{1}$.948	80.52	.039	.19	
			" —Bottom	"	"	"	.041	.018	.005	2.78	.444	.67	$\bar{1}$.826				
40	8542	22b	Grab	27 16 00	33 51 54	89	.065	.031	.011	2.38	.377	.95	$\bar{1}$.978				
41	8543	22c	"	27 16 24	33 51 18	102	.062	.028	.012	2.28	.358	.95	$\bar{1}$.978	88.14	.082	.38	
42	8544	22a	"	27 16 12	33 51 24	102	.056	.025	.015	1.93	.287	1.34	.127				
43	8545	23c	"	27 18 24	33 52 36	93	.55	.300	.195	1.68	.225	1.19	.075	95.43	.025	.11	
44	8546	33	"	Round 27 17	33 52 06	22–51	.18	.085	.03	2.45	.389	.75	1.873				

Section 4. Yuba-Mersa Daba'

No. of sample	University No.[1]	Station No.	Type of sample	Latitude N.	Longitude E.	Depth in mts. (Echo)	Q_1 (mm)	Md (mm)	Q_3 (mm)	So	log So	Sk	log Sk	$CaCO_3$[2] %	Nitrogen %	Organic C %	Remarks
45	8547	67	Core—Top	27 08 42 27 07 00	34 10 00 34 10 45	814	.060	.027	.014	2.07	.316	1.15	.061	75.77	.031	.18	
			" —Middle	"	"	"	.090	.027	.014	2.53	.403	1.73	.238				
			" —Bottom	"	"	"	.070	.025	.010	2.64	.421	2.80	.447				
46	8548	66	Grab	27 19 00 27 17 15	34 26 30 34 21 00	1079– 1225	—	.080	.014	—	—	—	—	—	—	—	Ships' clinkers present.
47	8549	62	"	27 46 30 27 46 42	35 09 00 35 08 00	247– 336	.050	.020	.008	2.53	.403	.92	$\bar{1}$.989				

Section 5. Safaga-Mowila.

48	8550	75	Grab	27 03 18	34 12 24	468–486	.120	.050	.020	2.45	.389	.96	Ī.982				Near Safaga Island.
49	8551	69	"	"	"	92–400	1.440	.380	.160	3.00	.477	1.59	.201				Panorama Reef.
50	8552	74	"	"	"	—	.250	.170	.130	1.39	.143	1.12	.051				
51	8553	76	Core—Top	26 57 36 26 57 12	34 23 36 34 23 30	951	.045	.011	.005	2.94	.468	1.93	.285				
			" —Middle	"	"	"	.060	.014	.006	3.22	.508	1.77	.249	69.45	.030	.15	
			" —Bottom	"	"		.040	.012	.002	4.08	.611	.66	Ī.823				
52	8554	77	" —Top	27 05 24 27 04 54	34 37 00 34 37 09	1274	.015	.005	.002	2.61	.416	1.27	.104				
			" —Middle	"	"		.015	.014	.005	1.77	.248	2.38	.376	78.27	.023	.13	
			" —Bottom	"	"		.046	.025	.007	2.53	.403	.53	Ī.724				
53	8555	78	" —Top	27 13 21 27 12 30	34 50 12 34 50 30	1148	.150	.024	.011	3.69	.567	2.82	.450				
			" —Middle	"	"		.054	.019	.006	3.00	.477	.85	Ī.929	77.52	.019	.11	
			" —Bottom	"	"		.080	.020	.004	4.59	.662	.76	Ī.881				

Section 6. Qoseir-Brothers'-No'man.

54	8556	86	Core—Top	26 13 15	34 36 12	667	.051	.012	.006	2.80	.447	2.30	.362				
			" —Middle	"	"		.048	.013	.003	3.94	.595	.88	Ī.944	78.72	.024	.13	Between Egyptian coast and Brothers'.
			" —Bottom	"	"		.052	.025	.007	2.64	.422	.62	Ī.795				
55	8557	88	Grab	On slopes of Brothers' Islets.		90–940	1.58	.760	.47	1.83	.262	1.29	.111				Grab generally failed to close.
56	8558	87a	"	"		84–198	.95	.51	.37	1.60	.204	1.35	.130				Near Brothers' Island.
57	8559	83	Core—Top	26 34 33 26 33 30	35 03 45 35 03 06	1234	.050	.011	.004	3.63	.560	1.57	.196				
			" —Middle	"	"		.032	.011	.005	2.61	.417	1.24	.095	58.82	.047	.29	
			" —Bottom	"	"		.050	.018	.005	3.10	.491	.80	Ī.906				
58	8560	82a	" —Top	26 38 00	35 21 30	834	.115	.011	.004	5.65	.752	3.42	.534				
			" —Middle	"	"		.050	.012	.004	3.49	.543	1.42	.154	80.87	.018	.11	Between Brothers' and Arabian coast.
			" —Bottom	"	"		.044	.015	.002	4.47	.650	.43	Ī.633				
59	8561	81b	" —Top	26 48 30 26 50 30	35 40 36 35 41 30	873	.048	.017	.007	2.62	.418	1.16	.065				
			" —Middle	"	"		.12	.025	.007	4.00	.602	1.44	1.58	72.49	.028	.15	
			" —Bottom	"	"		.036	.012	.004	3.00	.477	1.00	.000				

Section 7. Daedalus-Hanak

60	8562	102c	Grab	24 55 15	35 51 27	183	1.38	.82	.50	1.66	.220	1.02	.011				
61	8563	102	Grab 3	"	"	466	1.20	.75	.50	1.55	.190	1.07	.029				Near Daedalus Reef.
62	8564	103	"	24 55 20	35 51 00	512	.33	.28	.20	1.28	.107	.842	Ī.925				
63	8565	98	"	25 01 00 25 02 48	36 01 00 36 00 30	1214	.18	.029	.022	2.86	.456	4.71	.673	—	—	—	"Mabahith" Deep.
64	8566	91	"	25 25 00	36 40 00	19–25	.38	.22	.16	1.54	.187	1.26	.100				

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[1] Numbers refer to specimens housed in the Geological Museum, Fouad I. University, Cairo.

[2] After A. F. Mohamed (9).

to mechanical analyses and, with the exception of Sujkowski's work (12) on a few samples collected by S. S. Endeavour from the southern part of the Sea, nothing is known about the mineralogy of the bottom deposits. A. F. Mohamed examined the chemistry of some of the bottom samples collected during the present expedition (10, p. 314 and 9) and he concluded that the environmental conditions of deposition are, on the whole, different in each of the three main regions investigated, namely the Gulf of Suez, the Gulf of Aqaba and the northern part of the Red Sea proper.

The Gulfs of Suez and Aqaba differ greatly, the former having a flat bottom at a depth of 36–72 meters, whereas the latter has a trough 1600–1800 meters (900–1000 fms.) deep over to its eastern side, and its bottom is irregular even at the greatest depth. The Gulf of Aqaba, only about 22 kms. wide, has a depth nearly equal to the greatest depth of the Red Sea, which is about ten times as broad. The Red Sea itself is deeper in proportion to breadth than any other. The maritime plain so characteristic of the Red Sea shores, where it is generally up to 32 kms. wide, is almost absent on the Gulf of Aqaba where the shores are extremely abrupt and the mountains on its sides rise sheer from the water. The descent to the greatest depths in the Red Sea proper is by a series of steps, except in places on the Arabian side, where there are abrupt falls to 720–900 meters. Another character of the topography of the Red Sea bottom is the presence of small isolated reefs rising abruptly from deep water and lying on foundation rocks. The most conspicuous are the Brothers' Islets, rising from 1080 meters (11) and Daedalus Reefs located not far from the middle of the sea. Other ridges do not reach the surface but form submarine hills and mountains giving the bottom a very irregular topography[c] (1 and 2, Figs. 1 & 2) Such variation in topography has a great influence on the mechanical composition of the bottom deposits.

TECHNIQUE USED IN THE LABORATORY

The samples examined were divided into two divisions, those containing 95% or more of material coarser than 84.7μ and a second division containing samples with more than 5% of material finer than 84.7μ. The samples of the first division were analyzed by sieving methods. They were quartered and about 25 to 30 g. were screened through a set of sieves (meshes Nos. 10, 30, 60, 120, and 200 with openings of 2001, 610.2, 271.1, 135.6 and 84.7 microns in diameter as calibrated microscopically), using a mechanical shaker for fifteen minutes. Both sieving and sedimentation methods were used for sediments of the second division. In this case about 40 g. of each sample were thoroughly deflocculated using the technique suggested by Krumbein (7 and 8, pp. 51 ff.). Experiments were made to choose a suitable procedure for effectively dispersing the samples. For this reason 0.5 g. of a representative sample was put into each of a set of test tubes which were subsequently filled with the following peptizers:—N/25, N/50 and N/100 sodium carbonate, dilute ammonia (400 ml. distilled water added to 40 ml. of freshly prepared 33% ammonia solution), N/100 sodium oxalate, sodium silicate (0.5 ml. of N/5 sodium silicate in 500 ml. distilled water), N sodium hydroxide, N ammonium carbonates and boiling N ammonium carbonate plus a few drops of sodium hydroxide solution. The suspensions were subsequently well stirred and left overnight. The same experiments were made after washing the samples free from electrolytes as confirmed by the addition of silver nitrate to the filtrate. None of the unwashed samples were deflocculated. On the other hand, all the samples free from electrolytes were at least partially dispersed. Examining a few drops of each suspension under the microscope, it was concluded that the

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[c] The charts and sections published in connection with this reference were not issued as previously mentioned.

dilute ammonia solution is the most suitable peptizer. A mechanical stirrer was used for ten minutes to complete the dispersion.

After thorough dispersion the pipette method as described by Krumbein (6 and 8, pp. 166 ff.) was used for mechanical analysis. Suspension was sucked by the pipette at intervals corresponding to the following grain sizes in microns: 84.7–31.2, 31.2–15.6, 15.6–7.8, 7.8–3.9, 3.9–1.95, 1.95–0.98. In both coarser and finer sediments the weight percentages of the different fractions (corresponding with the different meshes used or with the different readings of the pipette) were determined. The data obtained were then represented on cumulative logarithmic curves. The median diameter Md, the coefficient of sorting So and its logarithm log So, and the coefficient of skewness Sk and its logarithm log Sk (8, pp. 229 ff.) were calculated from the cumulative curves. The weight percentages of the grain sizes corresponding with the Wenworth scale (8, p. 80) were also calculated from the cumulative curves and the corresponding histograms were drawn.

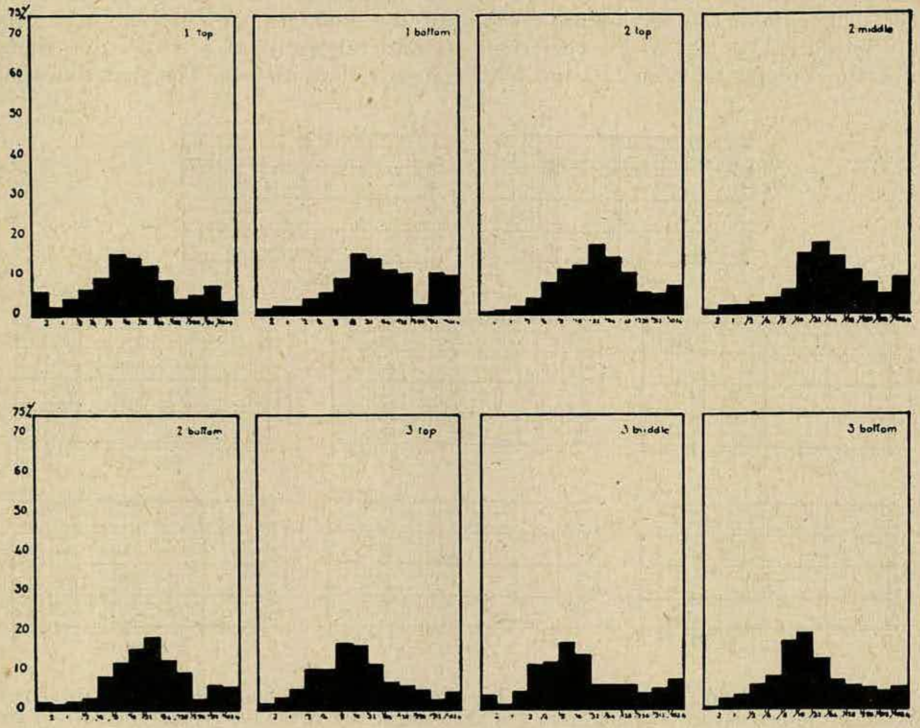


FIG. 2.—Histograms of section 1 of sediments of Gulf of Suez. Vertical components represent percentage from 0 at the bottom to 75 at the top; horizontal components shown at the bottom of each diagram range from 4 mm. at the extreme left to 1/2048 at the extreme right.

DISCUSSION OF RESULTS

1. *Gulf of Suez*

Section 1 of Table No. 2 includes the statistical constants of the three cores collected from the Gulf of Suez, (six, nine and fourteen kms. away from its western shore and from about the same depth, ranging from 59 to 64 meters) and their corresponding histograms and cumulative curves are given in figures 2 and 3. Inspection of table 2 shows that the median diameters of the sediments range between 15 and 64 μ. There is a decrease from top to bottom in cores 1 and 3, a relation which does not hold for core 2. The sediments of this section are normally sorted (13, p. 62), with a coefficient of sorting ranging between 2.92 and 4.02, with the exception of the middle portion of core No. 3 which is a poorly sorted sediment with So = 4.58. The average sorting factor of each of the three cores varies slightly (3.47—3.20—3.73). This might be attributed to their approximate equal depths, to the identity in the configuration of the flat bottom, and to the fact that no samples were collected from the shore[d].

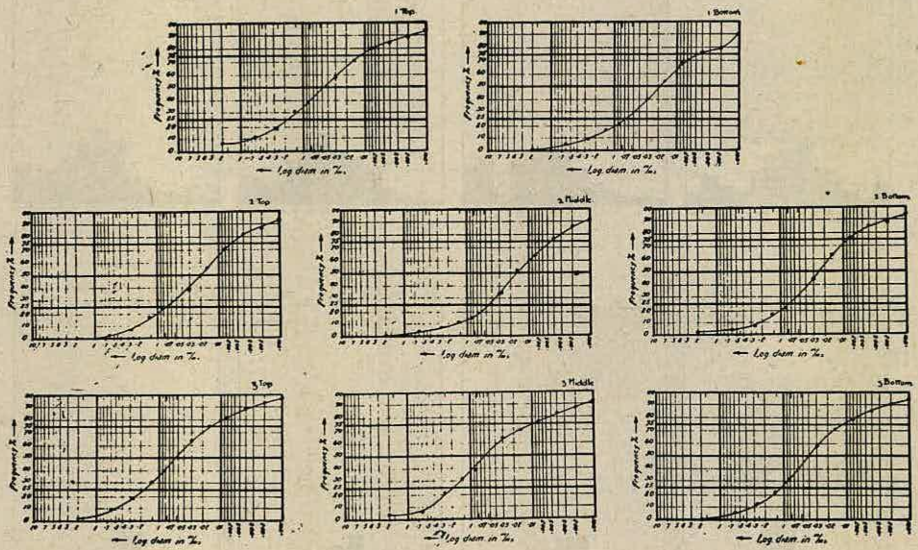


FIG. 3.—Cumulative curves of section 1 sediments of Gulf of Suez. Frequencies are shown on the left in percentages ranging from 0 at the base to 100 at the top. Along the bottom are shown values of the log. diam. in m/ms.

Skewness is very small in some parts of the cores, whereas, in others it tends towards either the finer or the coarser fractions. These data are comparable with those given by other normally sorted sediments from continental shelves; the Gulf of Suez is itself a shallow flat shelf filled with the surface water of the Red Sea and descending at its mouth abruptly to a depth five times greater than its own. The smoothness of the bottom of the gulf explains in part the mild changes in the physical constants of its bottom sediments. Further discussion of the interrelations of the properties of the sediments of the Gulf of Suez and of these properties with environmental conditions of deposition are referred to later.

2. *Gulf of Aqaba*

Section 2 of table 2 gives the statistical constants of the seven grab samples collected from the Gulf of Aqaba. The samples were secured from deeper waters (ranging between 265–1393 meters) than those of the Gulf of Suez. Three grab

[d] Fifteen samples were kindly provided to the authors by Dr. H. A. F. Gohar from the shore between Suez and Ghardaqa. They were found to be well sorted and were comparable with other beach deposits described in the literature.

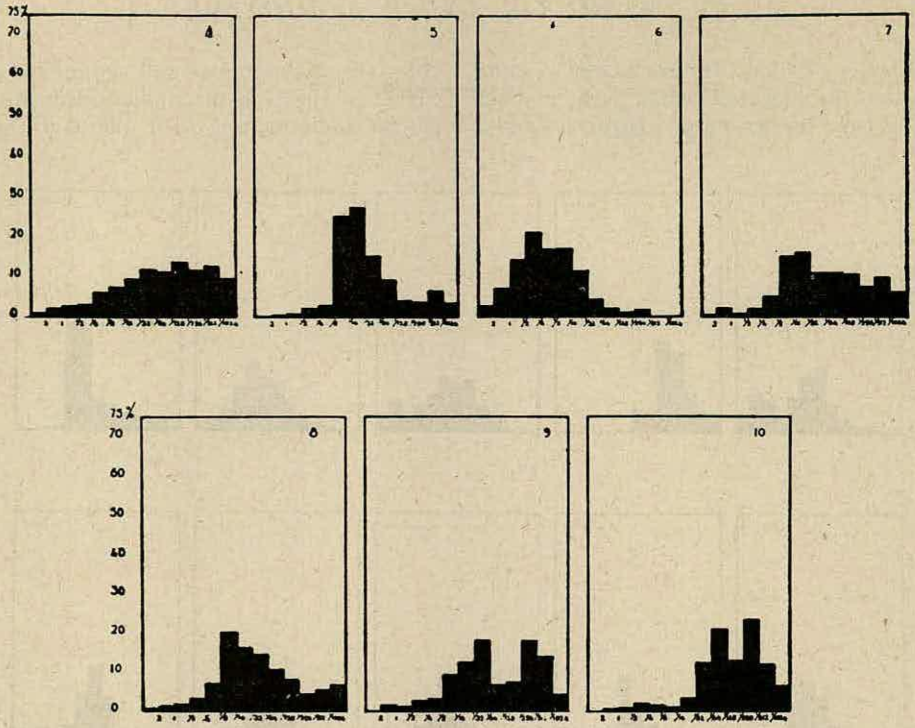


FIG. 4.—Histograms of section 2 sediments of Gulf of Aqaba. Vertical components represent percentage from 0 at the bottom to 75 at the top; horizontal components shown at the bottom of each diagram range from 4 mm. at the extreme left to 1/2048 at the extreme right.

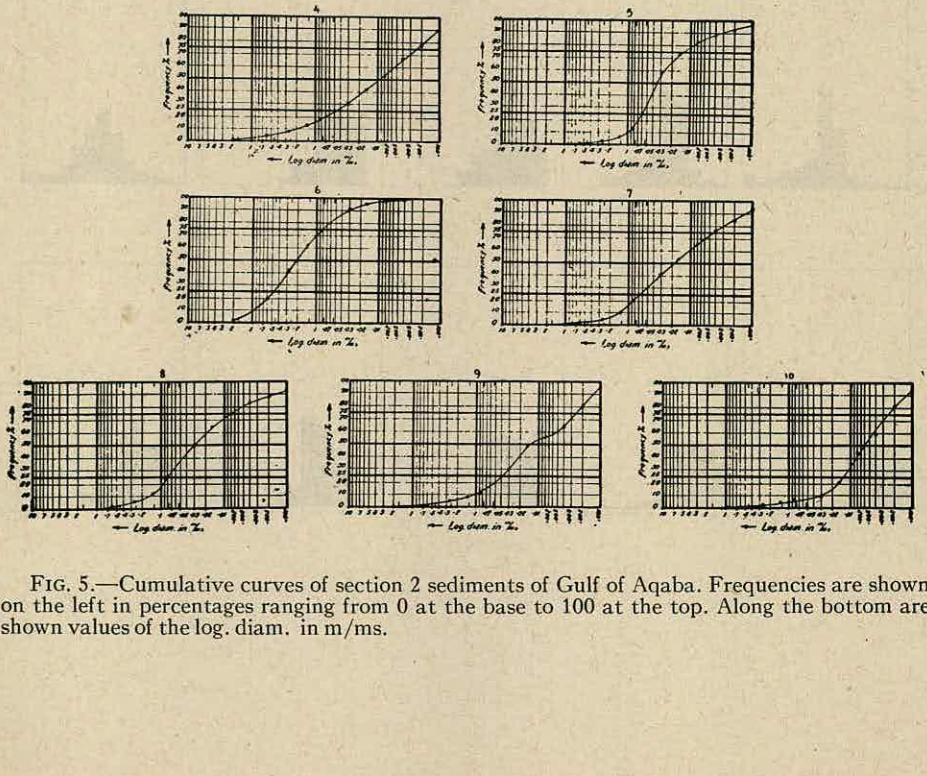


FIG. 5.—Cumulative curves of section 2 sediments of Gulf of Aqaba. Frequencies are shown on the left in percentages ranging from 0 at the base to 100 at the top. Along the bottom are shown values of the log. diam. in m/ms.

samples (5, 6 and 10) are nearer to shore than others located nearer to the mid-sea and from deeper waters. Figures 4 and 5 give the histograms and cumulative curves of the Gulf of Aqaba sediments. In contradistinction with the Gulf of

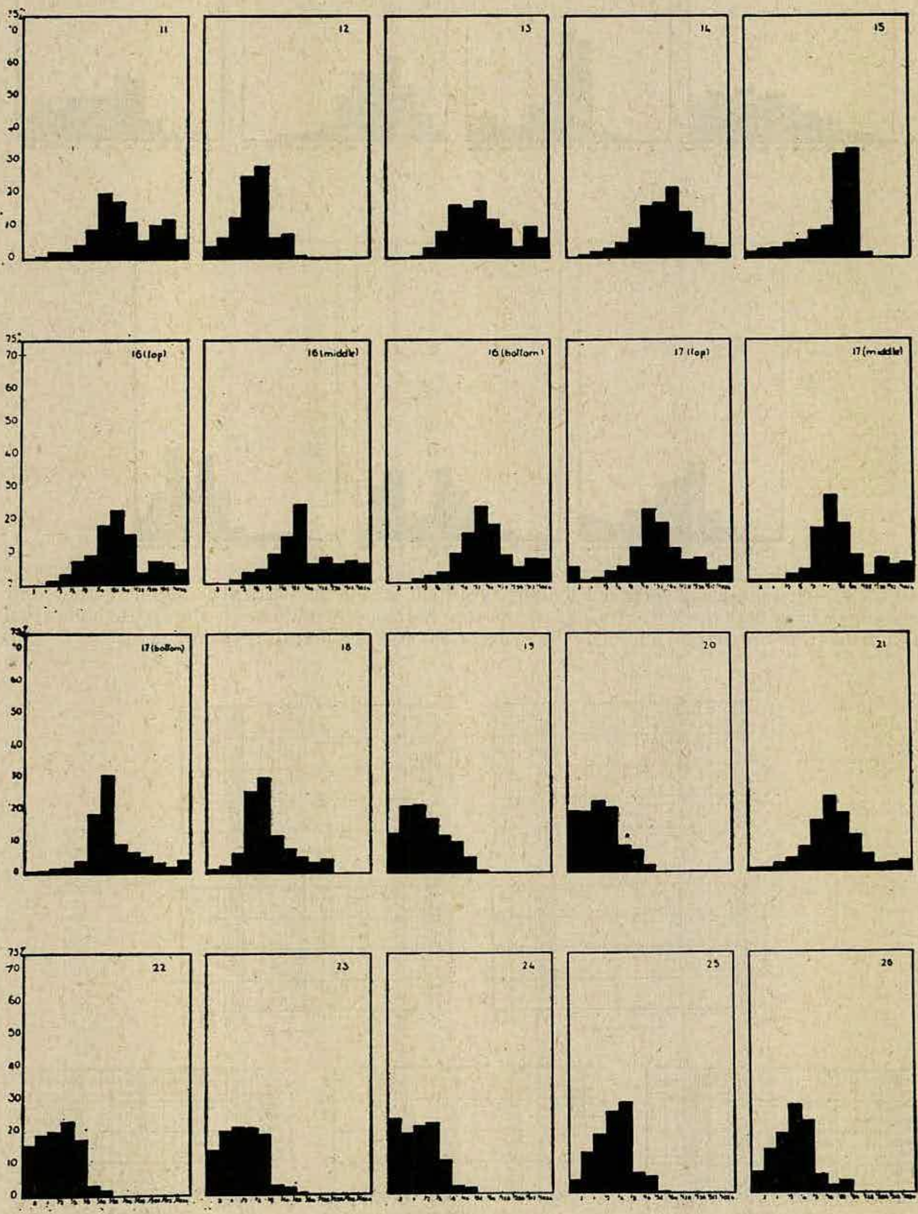


FIG. 6.—(Continued on next page)

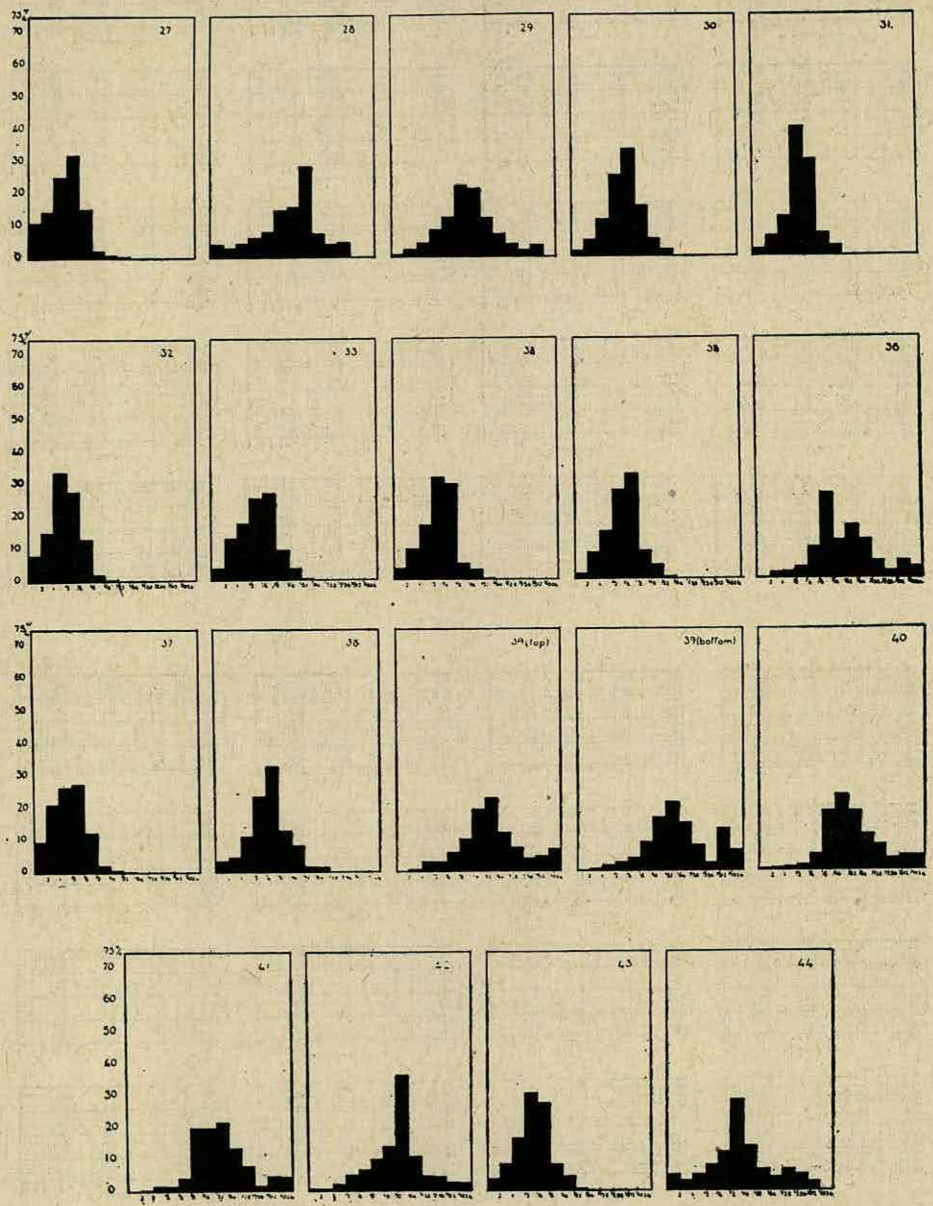


FIG. 6.—Histograms of section 3 sediments of Ghardaqa-Shadwan-Senafir. Vertical components represent percentage from 0 at the bottom to 75 at the top; horizontal components shown at the bottom of each diagram range from 4 mm. at the extreme left to 1/2048 at the extreme right.

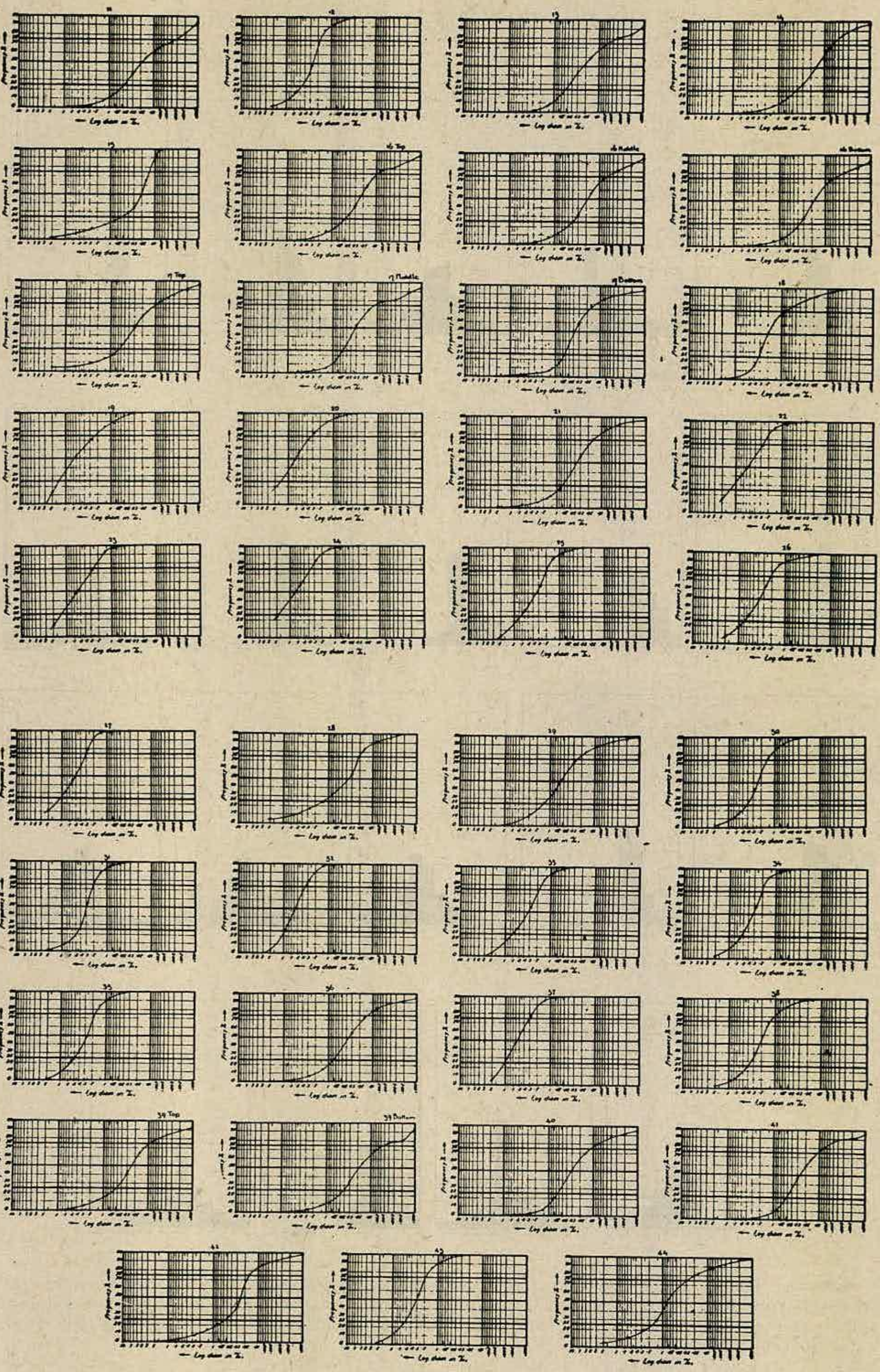


FIG. 7.—Cumulative curves of section 3 sediments of Ghardaqa-Shadwan-Senafir. Frequencies are shown on the left in percentages ranging from 0 at the base to 100 at the top. Along the bottom are shown values of the log. diam. in m/ms.

Suez samples the median diameters of the Gulf of Aqaba samples vary greatly, ranging from .005–.200 mm. The samples are either well sorted or normally sorted, the sorting factor ranging between 2.00 and 4.33. It is to be noted here that the well sorted samples are those collected from the shallower and nearer shore stations, off Dahab and Wasit. It is also of interest to note that two of these well sorted sediments (5 and 6) collected outside Wasit are located on a slope, and have fractions of nearly the same size. Log of skewness of the samples varies between +.090 and −.332.

In contradistinction with the Gulf of Suez, variation of the statistical data of the bottom sediments of the Gulf of Aqaba is in harmony with the roughness and irregular configuration of its bottom.

3. *Ghardaqa—Shadwan—Senafir Section.*

Three core samples and 31 grab samples were examined from this most northern section of the Red Sea, from depths varying from 17–1147 meters. The samples include four, collected near Tiran and Senafir Islands at the entrance of the Gulf of Aqaba (11–14), one south of Ras Mohamed (15), two east of Shadwan Island (16–17) and the majority (18–44) between Shadwan Island and the Marine Biological Station of the Fouad I University at Ghardaqa (Hurghada). Their statistical constants and other properties are given in section 3 of table 2, and the corresponding histograms and cumulative curves are shown in figures 6 and 7.

The median diameters range between .015–.780 mm. Those of the samples collected from the entrance of the Gulf of Aqaba are small (.015–0.22 mm.) and the sediments are normally sorted, except the single sample collected from the shallow waters nearer to the shores of Tiran Island (12) which possesses a greater median (0.260 mm.) and is better sorted than the others (So = 1.58). The samples collected south of Ras Mohamed and east of Shadwan possess small medians (.018–.038 mm.) and are all from relatively deep waters. The median diameter of the remaining sediments between Shadwan and Ghardaqa varies greatly, ranging between .018–.780 mm. and sediments are mostly well sorted with but few possessing a sorting coefficient slightly greater than 2.5, the upper limit of well sorted sediments (sorting coefficient varying between 1.45–2.78). Log of skewness varies from zero to 1.989, all being either symmetrical or asymmetrical in a positive sense.

The fact that the statistical constants depend on the configuration of the sea bottom is beautifully illustrated by the samples collected at station 34, which lies over a submarine hill discovered by the present Expedition west of Shadwan Island. All samples (31–88) lie on the slopes of the hill except one sample (36) located at its foot. The sample from the base possesses the smallest median diameter and is not as well sorted as the other samples. The median diameter varies widely in samples collected between Shadwan Island and Ghardaqa; the irregularity of the bottom, with submarine hills and slopes, in the area is in harmony with this variation in mechanical constitution (see 4, fig. 2, p. 26, showing reefs and shoals of area and 2, fig. 1 showing Section between Shadwan and Ghardaqa).

4. *Yuba—Mersa Daba' Section*

Section 4 of table 2 gives the statistical constants of the single core and two grab samples analyzed, whereas figures 8 and 9 give the corresponding histograms and cumulative curves. The samples were secured from comparatively deep waters ranging between 247 and 1225 meters and far from the mainland, except one (47) which was collected not far from the northern end of Yuba Island. They are fine grained sediments with median diameters varying from .020–.080 mm. One sample is very poorly sorted owing to the presence of ships' clinkers in the coarser fractions; the sample being secured from underneath the main route of ships crossing the Red Sea; the two others are on the border line between well sorted and

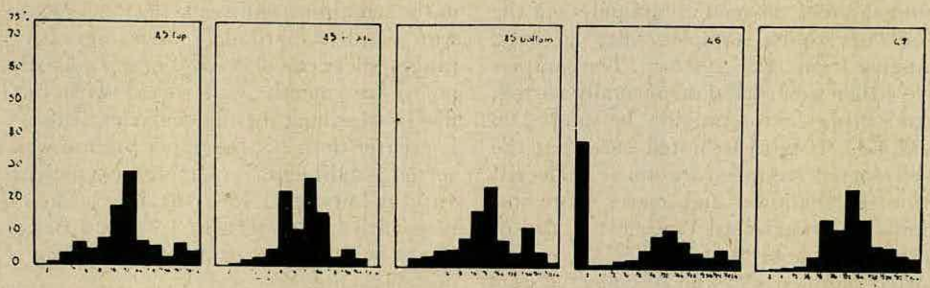


FIG. 8.—Histograms of section 4 sediments of Yuba-Mersa Daba'. Vertical components represent percentage from 0 at the bottom to 75 at the top; horizontal components shown at the bottom of each diagram range from 4 mm. at the extreme left to 1/2048 at the extreme right.

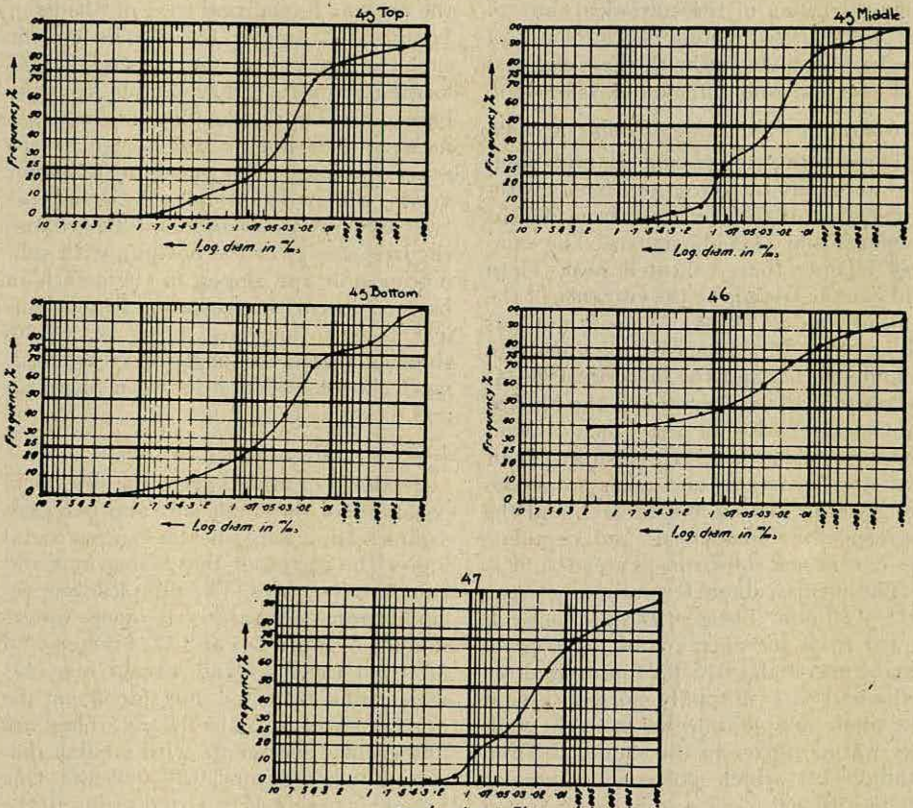


FIG. 9.—Cumulative curves of section 4 sediments of Yuba-Mersa Daba'. Frequencies are shown on the left in percentages ranging from 0 at the base to 100 at the top. Along the bottom are shown values of the log. diam. in m/ms.

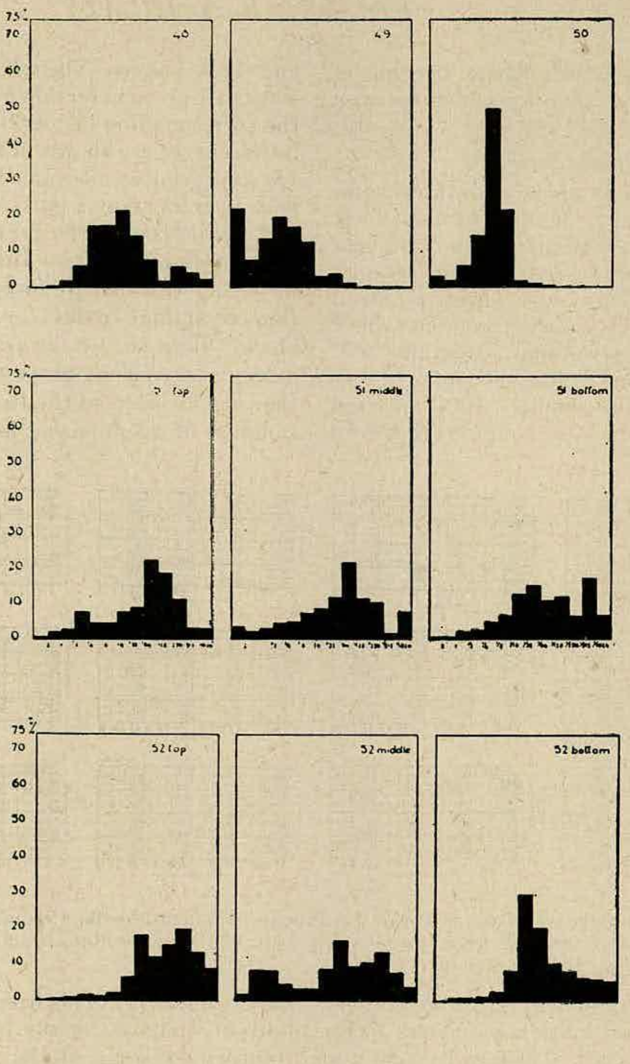


FIG. 10.—Histogram of section 5 sediments of Safaga-Mowila. Vertical components represent percentage from 0 at the bottom to 75 at the top; horizontal components shown at the bottom of each diagram range from 4 mm. at the extreme left to 1/2048 at the extreme right.

normally sorted sediments. The log of skewness of the samples varies between .975 and 2.80.

5. *Safaga—Mowila Section*

Three grab samples and three cores were examined from this section. They spread from east of Safaga Island to near the middle of the sea with no samples from the Arabian side. Their statistical constants are given in section 5 in table 2 and the corresponding histograms and cumulative curves are shown in figures 10 and 11. The samples were collected from relatively deep waters (between 468–1274 meters) and are fine grained sediments with median diameters varying between .005–.050 mm. except for two samples collected from Panorama Reef, which are from shallower water and coarser in nature (with Md =.38 and .17 mm.). The sediments are either well sorted, normally sorted, or poorly sorted with sorting factor varying between 1.39 and 4.59. The asymmetry of the sediments is either towards the coarser or finer fractions.

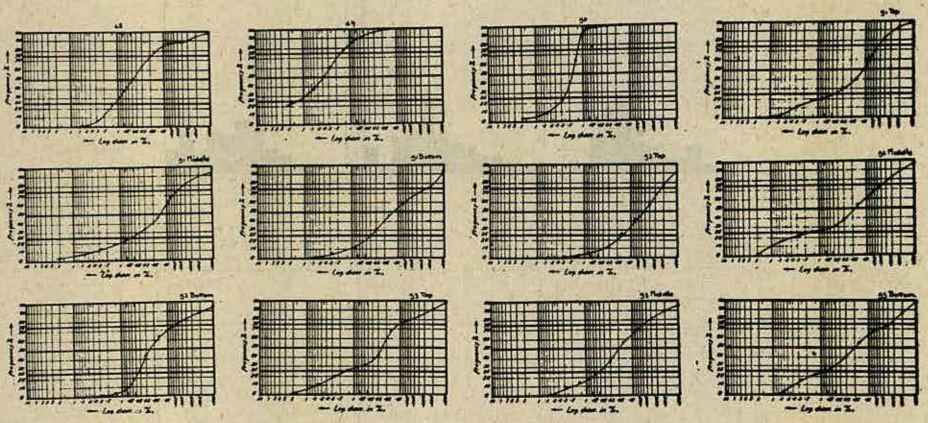
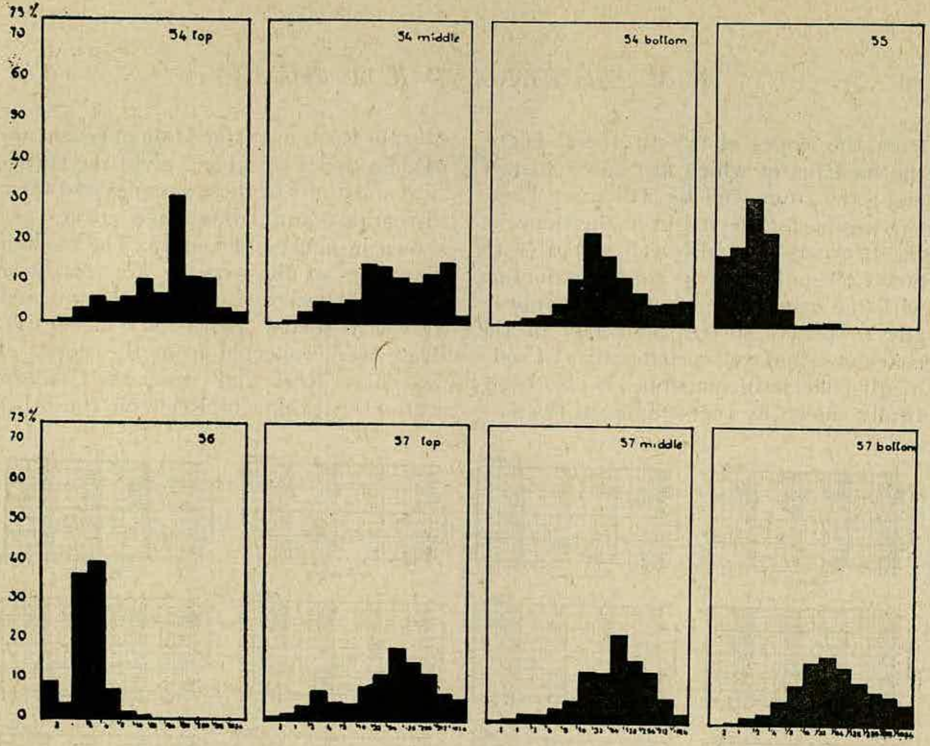


FIG. 11.—Cumulative curves of section 5 sediments of Safaga-Mowila. Frequencies are shown on the left in percentages ranging from 0 at the base to 100 at the top. Along the bottom are shown values of the log. diam. in m/ms.

6. *Qoseir—Brothers'—No'man Section.*

Four cores and two grab samples were analysed from this section, and were collected from depths varying between 84 and 1234 meters. Their statistical constants are given in section 6 of table 2 and the corresponding histograms and cumulative curves are shown in figures 12 and 13. As previously mentioned, the Red Sea floor is in its greater parts very irregular and the bottom of the present section is no exception. The two Brothers' Islets, for instance, which are formed of foundation crystalline rocks (or "continental blocks") and not by the accumulation of volcanic extrusions as is the case with the volcanic islets of the Pacific, form the summits of a submarine hill about 1000 meters high (11). This irregularity of the bottom is shown by the following notes recorded at some of the sampling stations: "irregular bottom, no catch," "grab generally failed to close," "grab closed upon, and damaged its wire, indicating steep irregular bottom." The samples collected from this section are distributed as follows: one sample from the bottom between the Egyptian coast and the Brothers' (no. 54), two from the slopes of the Brothers' (nos. 55–56) and three cores from between the Brothers' and the Arabian coast (nos. 57–59).

The median diameters of the samples of this section vary from .011–.025 mm. for the samples other than those collected



SECTION VI

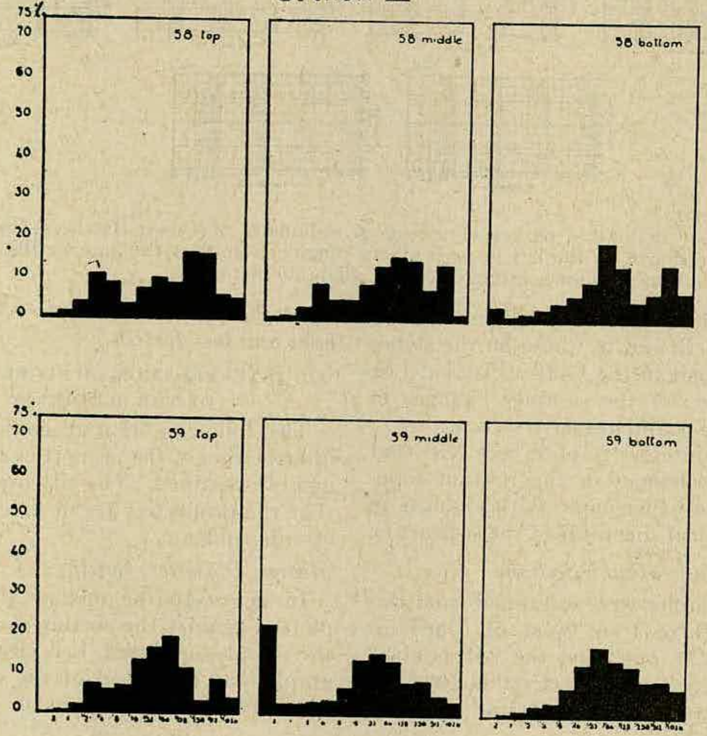


FIG. 12.—Histograms of section 6 sediments of Qoseir-Brothers'-No'man. Vertical components represent percentage from 0 at the bottom to 75 at the top; horizontal components shown at the bottom of each diagram range from 4 mm. at the extreme left to 1/2048 at the extreme right.

from the slopes of the Brothers' Islets, the medians of which are much coarser and vary from .760 to .510 mm. These two samples, collected from the slopes of the Brothers', are also well sorted (with So = 1.60 and 1.83) in contradistinction with the other samples which are normally or poorly sorted. This fact of the coarseness and well sorted nature of sediments collected from slopes is also beautifully shown by the samples of the submarine hill west of Shadwan Island further north and by those on the slopes east of Wasit in the Gulf of Aqaba. Log of skewness of the samples changes in both positive and negative senses.

It is of interest to note here also that the great changes in the bottom topography are in harmony with changes in the statistical constants of the sediments.

7. Daedalus—Hanak Section.

Five samples were examined from this section: three from west of Daedalus (nos. 60–62), one from the "Mabahith" Deep lying between Daedalus Reef and the Arabian coast (no. 63) and one from Masabi Reef, near the Arabian coast (no. 64). Section 7 of table 2 gives the statistical constants of these samples and their histograms and cumulative curves are shown in figures 14 and 15. The median diameters of the samples are relatively coarse and vary from .22–.82 mm. and are well sorted (with So = 1.28–1.66). They were collected from the slopes of Daedalus Reef and from the shallow waters near Masabi Reef, on the other hand the deep sample (no. 63) is much finer and less sorted.

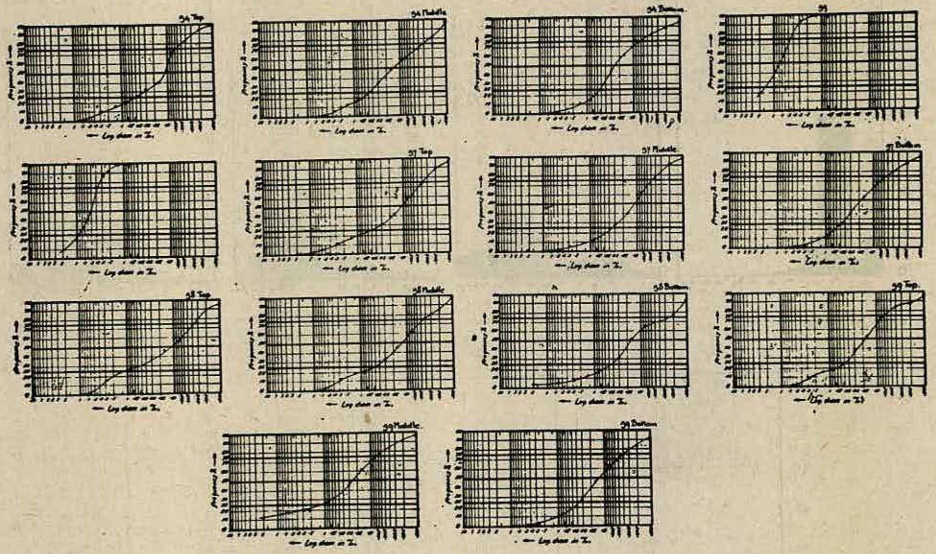


FIG. 13.—Cumulative curves of section 6 sediments of Qoseir-Brothers'-No'man. Frequencies are shown on the left in percentages ranging from 0 at the base to 100 at the top. Along the bottom are shown values of the log. diam. in m/ms.

INTERRELATION OF PROPERTIES OF THE SEDIMENTS

The following is a discussion of the interrelation of the properties of the sediments examined. The discussion shows that the properties are in many respects interdependent.

Median Diameter: Sorting:

In figure 16 the median diameter is plotted against the sorting factor for all the samples analyzed. It is clear from the graph that the trend of the line drawn indicates that the degree of sorting be-

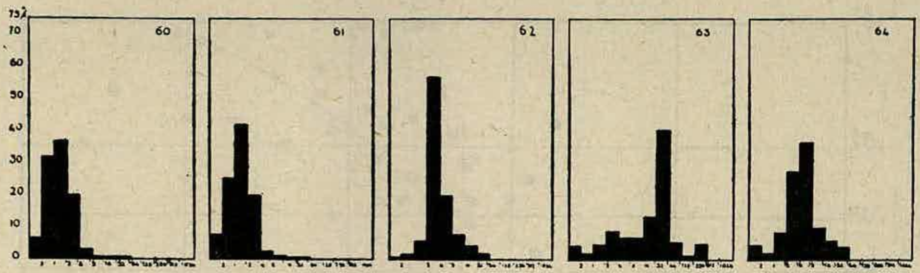


FIG. 14.—Histograms of section 7 sediments of Daedalus-Hanak. Vertical components represent percentage from 0 at the bottom to 75 at the top; horizontal components shown at the bottom of each diagram range from 5 mm. at the extreme right left to 1/2048 at the extreme right.

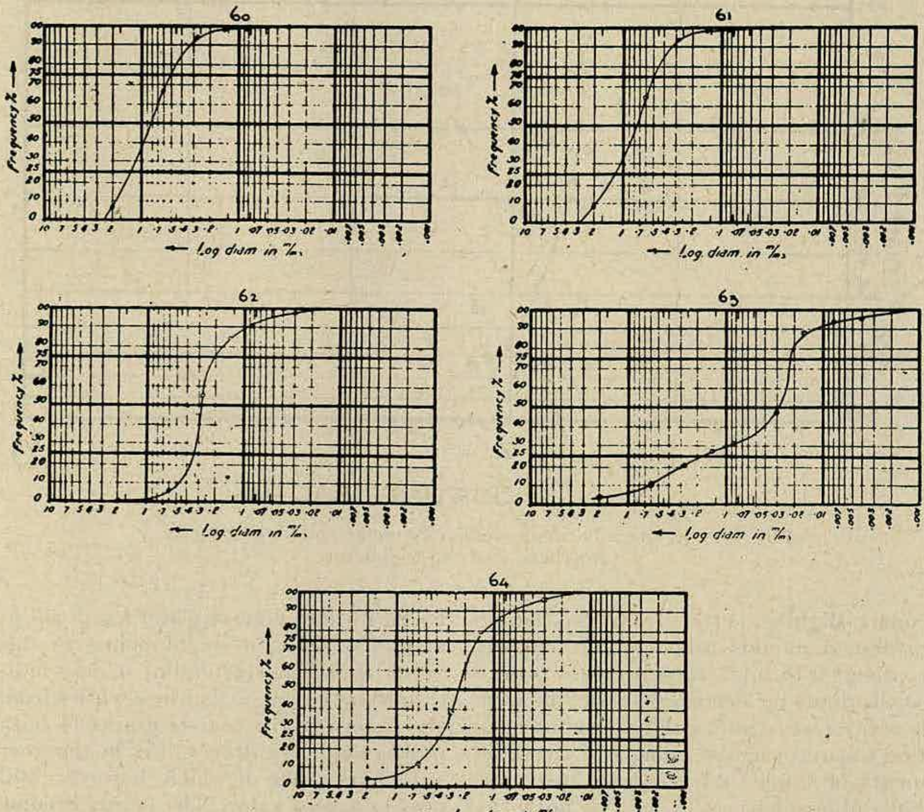


FIG. 15.—Cumulative curves of section 7 sediments of Daedalus-Hanak. Frequencies are shown on the left in percentages ranging from 0 at the base to 100 at the top. Along the bottom are shown values of the log. diam. in m/ms.

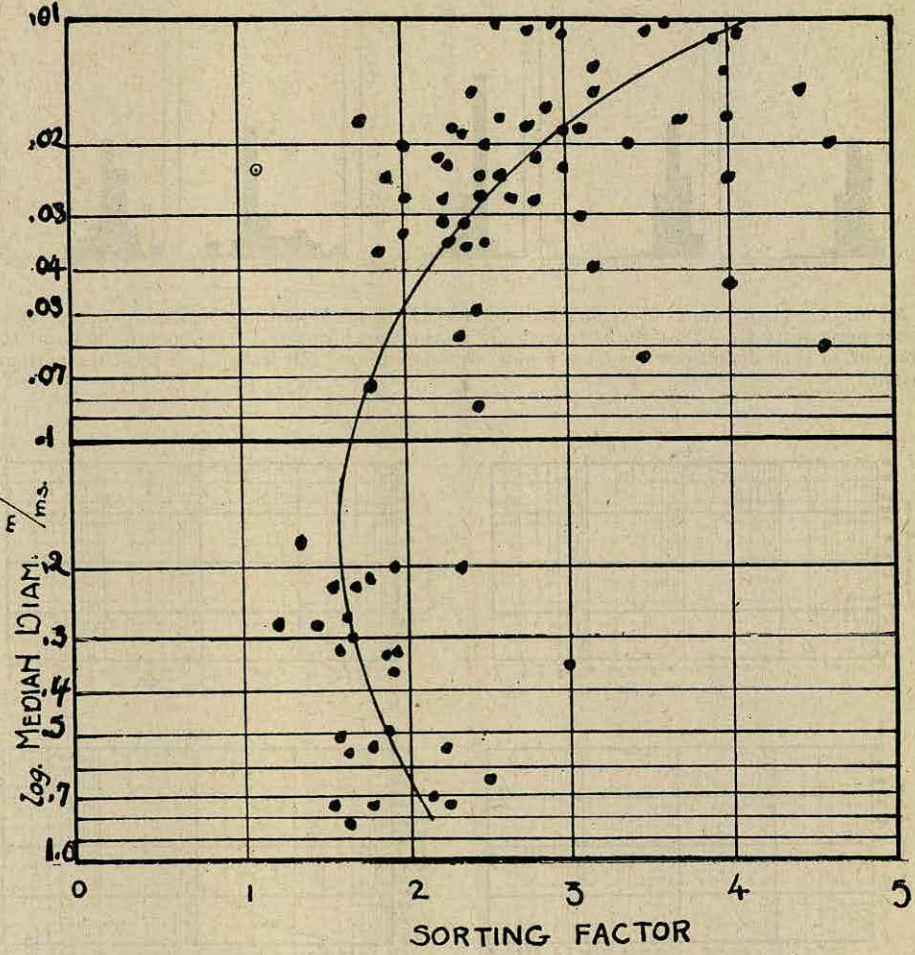


FIG. 16.—Relation between median diameter and sorting factor of Northern Red Sea sediments.

comes slightly better from the larger median diameters (about 1 mm.) down to about 0.15 mm., then becomes poorer as the diameter decreases to .009 mm. It is of interest to notice that a similar relation was recorded by Hough for the sediments of Cape Cod Bay and Buzzards Bay, Massachusetts (5, p. 19), notwithstanding the fact that the Red Sea sediments are of very different environments.

Median Diameter: Skewness:

Figure 17 shows the relationship between median diameter and log of skewness. The distribution of points in this graph is not conclusive but it may indicate that the log of skewness varies from about zero in the coarser grains to both positive and negative values in the finer sediments, some of which, however, still possess a zero value. The points become diffused in the vicinity of median diameter .06, but it is to be noted that only a few sediments possess median diameters between .2 and .06. The skewness of the sediments, however, is very ambiguous

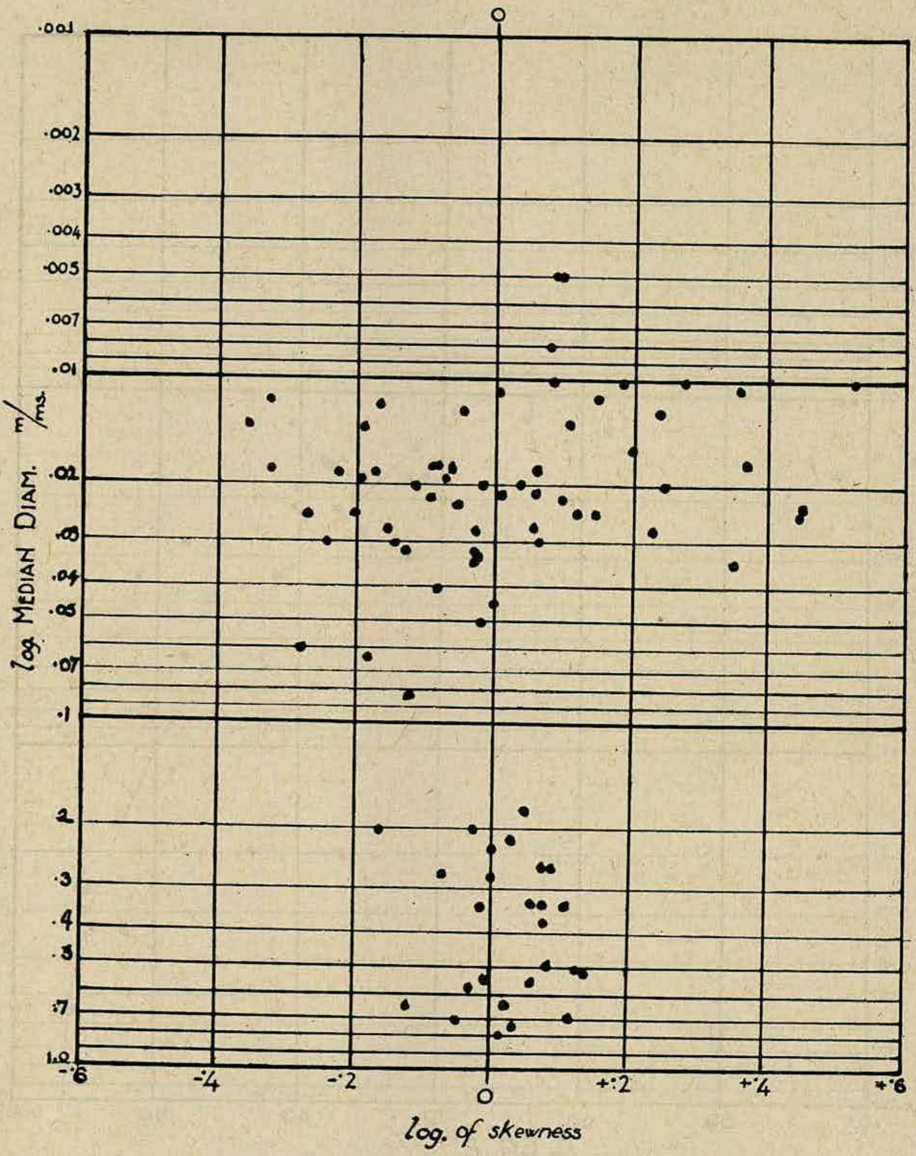


FIG. 17.—Relation between median diameter and log of skewness of Northern Red Sea sediments.

in its interrelation with other properties or with factors of environments as shown later.

Sorting: Skewness:

A graph was drawn to show the relation between sorting and skewness but the plotted points were diffused. They showed, however, that, on the whole, the well sorted samples possess low figures and that the less sorted sediments possess higher figures for log Sk in both negative

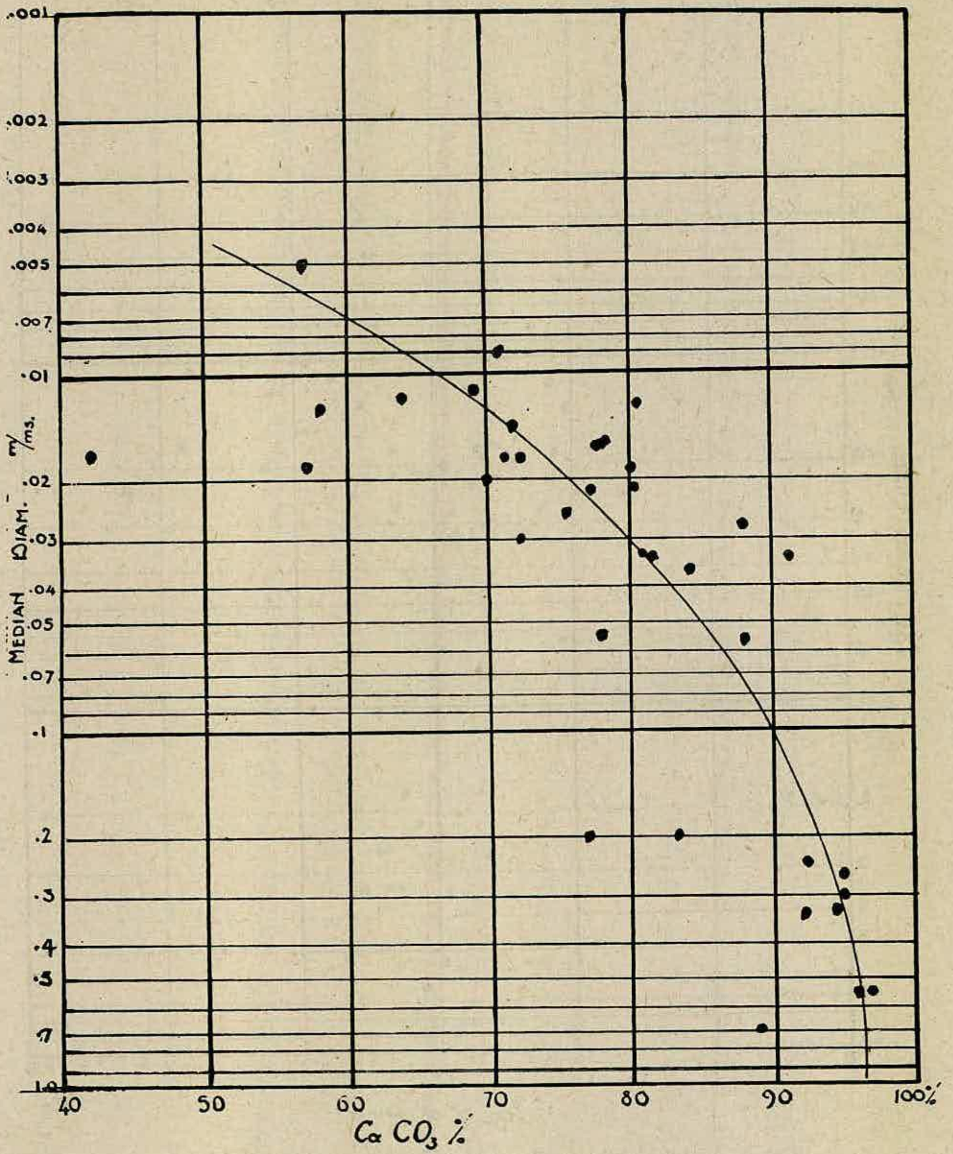


FIG. 18.—Relation between median diameter and $CaCO_3$% of Northern Red Sea sediments.

and positive directions as would be expected from the two previous relations.

Calcium Carbonate Content: Statistical Constants:

Figure 18 shows the relationship between median diameter and calcium carbonate content. The figure clearly shows that the percentage of $CaCO_3$ increases with increase of median diameter, and, as would be expected from the median: sorting relation, a graph drawn to show the interrelation between $CaCO_3$ content and sorting factor showed that the well sorted samples possess the highest content of carbonate whereas the poorly sorted samples possess the lowest. The relation between log of skewness and carbonate content was also investigated by drawing a diagram, which showed that there is no conclusive relation.

Nitrogen and Organic Carbon Content: Statistical Constants:

Graphs were drawn to show the relation between the nitrogen percentages and organic carbon (evaluating the organic matter content of the sediments) on the one hand and the median diameters and sorting factors on the other. The graphs showed that both the nitrogen

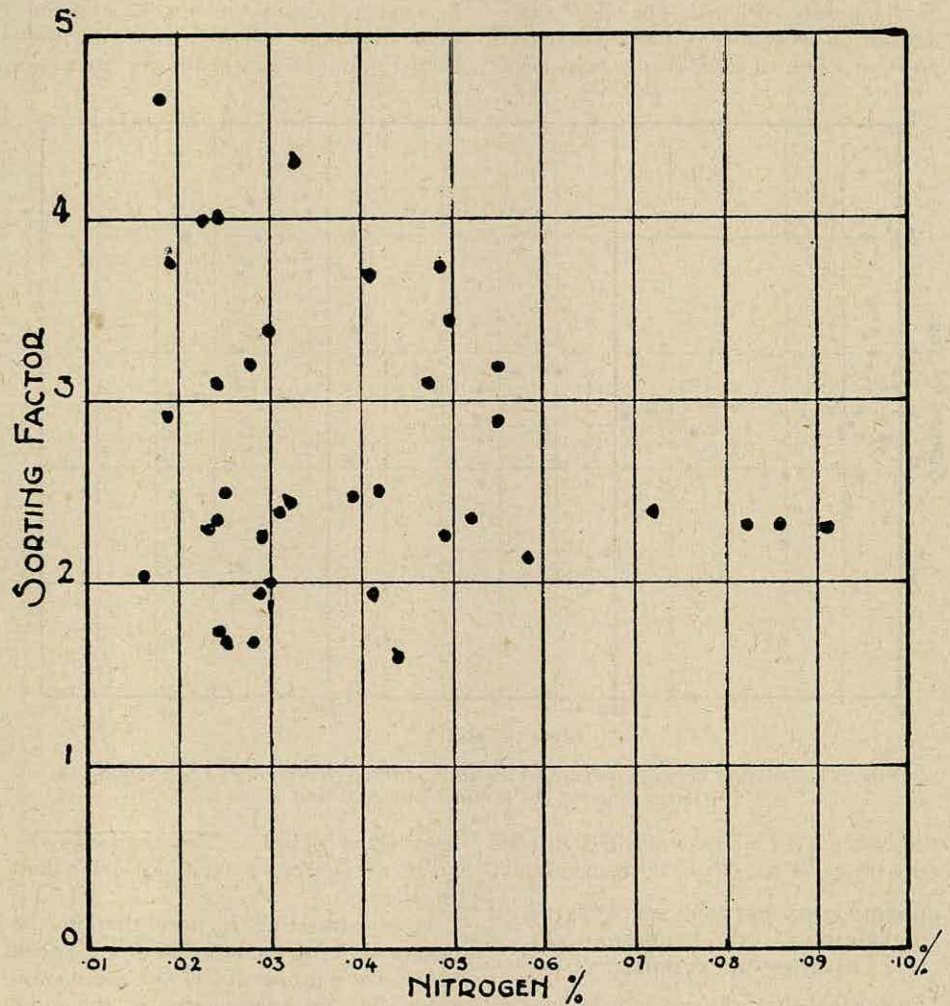


FIG. 19.—Relation between sorting factor and nitrogen percentage of Northern Red Sea sediments.

and organic carbon remain more or less constant irrespective of median diameter or sorting factor, except between median diameters .04–.02 mm. and sorting factors 2–2.5, (fig. 19) when they become conspicuously enriched. The log of skewness graph showed that it changes from a positive value to zero, thence to a negative value with increase of nitrogen content from .01 to .06 to .09 respectively.

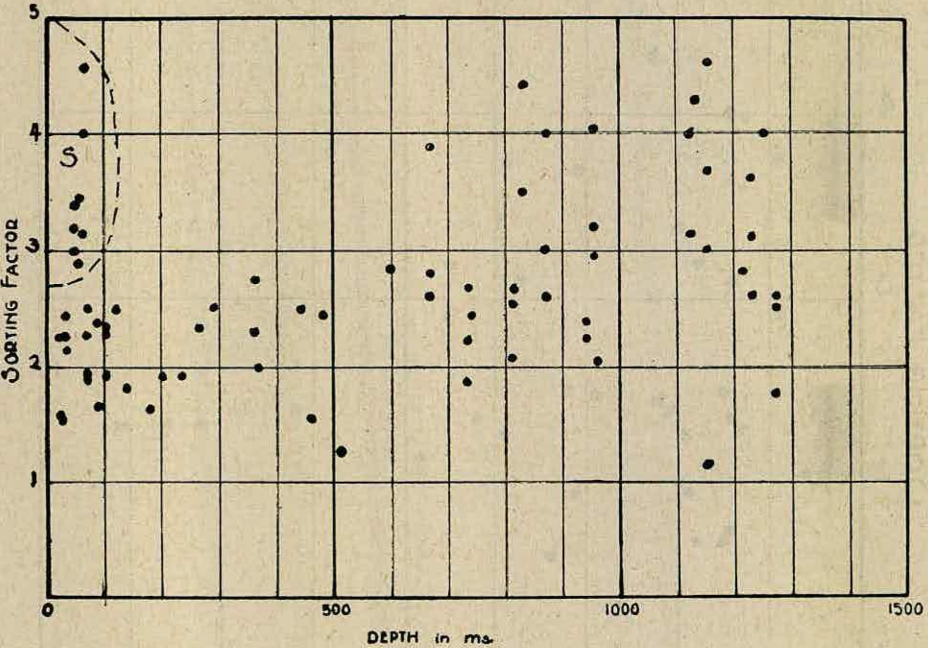


FIG. 20.—Relation between sorting factor and depth of Northern Red Sea sediments. The letter S marks the samples from the Gulf of Suez.

COORDINATION BETWEEN PROPERTIES OF SEDIMENTS AND CORRESPONDING FACTORS OF ENVIRONMENT

Knowing that the various properties of the sediments analyzed are more or less interdependent, with the exception of log of skewness, we can now proceed to coordinate these properties with the corresponding environmental conditions of deposition.

Depth: Statistical Constants:

When the median diameters were plotted against depth it was clearly shown from the curve drawn that on the whole increase in depth meant decrease in median diameter. The depth: sorting coefficient graph (see fig. 20) showed, as would be expected from the interrelation median diameter: sorting, that the well sorted samples are shallower than the less sorted samples. The shallower deposits are better sorted and coarser than the deeper.

It is interesting to note that in the graphs showing the interrelation between the various properties of the sediments, the points are interrelated in the same way irrespective of the environment from which the samples were secured. On the other hand, the points for the Gulf of Suez occupy a unique position in the depth curves. Thus in the depth: sorting factor diagram, for instance, the points for the Gulf of Suez sediments are all located in the field marked "S" in figure

20. The sediments of the Gulf of Suez, though of shallow origin, are finer and less sorted than those from the Gulf of Aqaba or the Red Sea shallow environments. On the other hand, the depth: log of skewness graph showed a confused relation and, in contradistinction with the sorting and median diameter graphs, the plotted points of the Gulf of Suez were not concentrated in a special area of the skewness graph. It seems that skewness is of little genetic value for the Red Sea sediments as judged from the sediments already examined.

Depth: Calcium Carbonate Percentage:

As could be deduced from the depth: median diameter and median diameter: carbonate graphs, the carbonate content was found to decrease with increase of depth.

Depth: Organic Matter Content:

Both nitrogen and organic carbon content of the sediments were plotted against the corresponding depths in two graphs, which showed that the organic content remained more or less constant at different depths, except at the relatively shallow depth of about 100 meters where an increase in organic matter content was apparent. It was previously shown that the sediments enriched in organic matter possess also median diameters between .04 and .02 mm. and sorting factors between 2 and 2.5. It is interesting to note that, though the rule is that the shallow and well sorted sediments are coarse, here the shallow (of depths about 100 meters) and well sorted sediments, which are also rich in organic matter, deviate from the rule, and are fine-grained sediments. It seems that the organic matter concentrates in the finer fractions relative to the carbonate particles, which concentrate in the coarser fractions. The organic matter was also found to accumulate more in basins than on slopes and ridges, as shown by samples collected at station 34 (over a submarine hill) west of Shadwan Island (9). It is interesting to note that the sample from the base of the hill, at the basin, is finer and less sorted than those collected from the slopes.

SUMMARY AND CONCLUSIONS

The paper deals with the mechanical analysis of some bottom samples amounting to fourteen cores and fifty grab samples collected during the Egyptian Preliminary Expedition to the northern part of the Red Sea in the R.R.S. "Mabahith" in 1934–1935. Both sieving and sedimentation methods (the pipette method) were used in the mechanical analysis. The fine sediments were thoroughly deflocculated by washing them free from electrolytes and subsequent stirring in dilute ammonia solution.

The Red Sea is unique amongst the seas of the world in the fact that no permanent streams flow into it and that only winds, mostly northwesterly, and rain torrents[e] contribute material to its bottom. The sea is probably unique also for its very irregular bottom topography (excluding the Gulf of Suez), hence, the nature and distribution of its bottom deposits are unmatched in other seas.

Though it is known that the physical constitution of marine sediments depends on many factors of environment and mode of origin such as the agents of transportation, flocculation effects, transporting influence of currents, depth, nearness to landmasses, amount of slope of bottom, effect of organisms etc., and that sediments deposited in several environments may have identical graphs (14), yet the mechanical analysis of the examined deposits gave many interesting results.

It is already apparent from the evidence that the statistical constants, the calcium carbonate and organic matter contents are interrelated in the same way,

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[e] The authors had many experiences with torrents pouring into the sea, in its northern and southern parts, for several days with such a force as to make the sea water turbid for many kilometers off shore, giving it a similar color to that of the coastal plains.

irrespective of the environment from which the samples were secured. It was even noted that Hough gave a similar relation for median diameter: sorting factor for the sediments of Cape Cod Bay and Buzzards Bay, Massachusetts (5). It was found that, on the whole, the coarser sediments are better sorted and richer in calcium carbonate than the finer. The organic matter content increases between diameters .04–.02 mm. and sorting factors range between 2 and 2.5. It was shown also that the organic matter probably concentrates in the finer fractions relative to the carbonate particles, which concentrate in the coarser fractions. The interrelations of log of skewness and other properties are ambiguous.

As to interrelations of these properties with environmental conditions of deposition, it was found that the sediments are coarser and better sorted when they are secured from shallow or sloping bottoms or from near landmasses (including submarine ridges). The carbonate content has been found to decrease with increase of depth and the organic matter to concentrate in depths about 100 metres, being also greater in basins than on ridges and slopes. The skewness of the sediments, however, is ambiguous in its interrelation with other properties or with factors of environments. It seems that skewness is of little genetic value for the Red Sea sediments, as judged from the sediments already examined.

The topography of the bottom which affects the various factors of environment mentioned above seems to be the important factor in determining the physical constitution of the deposits. The Gulf of Suez, because of its flat bottom, has deposits with but little variation in their statistical data, in contradistincttion with the deposits on the very irregular bottom of the Gulf of Aqaba or the Red Sea which have rapid changes in the corresponding statistical constants. The difference in environment is also shown by the fact that some of the statistical constants for the Gulf of Suez are located in special fields in the corresponding depth diagrams.[f] The sediments of the Gulf of Suez though of shallow origin are finer and less sorted than those of the Gulf of Aqaba or the Red Sea shallow environments. The data for the Gulf of Suez sediments are, in fact, comparable with those given by other normally sorted sediments from continental shelves; the Gulf of Suez is itself a shallow flat shelf filled with the surface water of the Red Sea and descending at its mouth abruptly to a depth five times greater than its own.

Though these results are of value in the reconstruction of paleogeographic conditions of deposition for ancient sediments, yet on account of the small number of samples examined, the results should be considered tentative and must inevitably remain subject to correction in the future. It is earnestly hoped, however, steadily to fill in the lacunae in our knowledge with fresh material to be collected when the main expedition for the exploration of the Red Sea is undertaken, and complete cartographic studies can be consequently accomplished.[g]

The authors wish to express their thanks to Prof. O. Zdansky for laboratory facilities provided at the Geology Department of the Fouad I. University, Cairo. The authors are specially indebted to Dr. A. P. Mohamed for kindly giving permission to use while in press, the chemical data enclosed in the present work.

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[f] It is interesting to note that the same peculiarity was reflected on the mineralogy of the Gulf of Suez sediments, which are much richer in authigenic pyrite than either the Gulf of Aqaba or the Red Sea.

[g] The Egyptian Government postponed the expedition in 1935–1936, because of the Italo-Abbysinian War raging at that time; financial difficulties thereafter caused further delay; the present World War made it impossible for the "Mabahith" to resume its activities.

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PART X

With the authors'
compliments.

THE MINERALOGY OF SOME BOTTOM DEPOSITS OF THE NORTHERN RED SEA

BY

N. M. SHUKRI AND R. A. HIGAZY

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JOURNAL OF SEDIMENTARY PETROLOGY, VOL. 14, NO. 2, PP. 70–85
FIG. 1, TABLES 1–2, AUGUST, 1944

THE MINERALOGY OF SOME BOTTOM DEPOSITS OF THE NORTHERN RED SEA

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ABSTRACT

The present paper deals with the mineralogy of sixty-four samples of bottom deposits from the Northern Red Sea collected during the "Mabahith" Expedition (1934–35). The special character of the wind-borne Red Sea deposits is discussed. The mineralogy of the sediments is uniform over the different provinces and thus contrasts with that of the usual basins of deposition. Local variations are, however, caused by contamination from local source-rocks or variation in the environmental conditions of deposition. The full value of the results can only be estimated when much more work has been done on the contributing rocks of the coastal areas.

INTRODUCTION

In the preceding article the authors gave the results of the mechanical analysis of the bottom deposits of the Northern Red Sea collected during the "Mabahith" expedition in 1934–1935 (9). A map showing the distribution of the samples is given in the same work. The present paper deals with the mineralogy of the deposits, a topic which received but little attention till the present. In fact the only work, as far as the authors are aware which deals with the mineralogy of the Red Sea sediments, is that of Sujkowski (21), who examined the sediments collected by S. S. "Endeavour" from the middle and south-eastern parts of the Sea in 1926–1928. Sujkowsky concentrated his study on the deep water deposits, especially their detrital material, which he considered to be derived from the continental dust by wind and accordingly gave a clue as to the features of sediments derived from desert regions. He recorded the following detritals:—amphiboles, pyroxenes, biotite, lime-soda and potash feldspars, feldspathoids, quartz, rare zircon and very rare tourmaline, but he failed to note garnet or rutile or any authigenic mineral, especially pyrite.[a] These minerals, however, and some other species were noted in the present investigation. Sujkowski concluded that the characteristics of such deposits, because of the absence of any chemical decomposition and lack of water transportation, are:

1—The freshness and angularity of detrital grains.
2—Their small size, which does not exceed 0.06–0.07 mm. (for mica 0.14 mm.).
3—The characteristic mineral composition, with the rareness or absence of common heavy minerals in sediments such as tourmaline, rutile, zircon, etc. and the preponderance of:
  a. colored minerals
  b. common rock-forming minerals (of igneous and metamorphic rocks)
  c. easily weathered minerals.

The authors believe that these characters are not criteria for wind transportation as stated by Sujkowski,[b] though the deposits are actually carried mainly

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[a] The minerals recorded are found in the fraction coarser than .005 mm. Sujkowski treated the sediments with hydrochloric acid before examination.

[b] The criticism of the work of Sujkowski, given in the following pages, does not, in any way, lessen the importance of his paper.

by wind giving them a more or less uniform mineral constitution in very widely separated parts of the Sea, without forming any sedimentary petrographic provinces (10). On the other hand local conditions (mostly depending on provenance) gave rise to variation in the frequencies or types of minerals present without affecting the general characters of the mineralogy of the deposits. Incidentally the evidence showed also that White's statement (23) that wind-borne sediments contain less frequent heavy minerals than water-borne sediments is invalid.

TECHNIQUE USED IN THE LABORATORY

The coarse samples, which are loose, whitish in color, and mainly formed of large organic carbonate particles, were separated by dry sieving into the following fractions: 2001–610, 610–271, 271–135, and 135–84 microns. The finer samples, which are usually gray, buff or rarely yellow in color, were thoroughly dispersed by washing them free from electrolytes, adding a dilute ammonia solution, and the subsequent stirring of the suspensions using a mechanical stirrer. The suspension was then screened through a 200 mesh (.084 mm.) sieve and the coarser material dried and again separated as for the coarser sediments. The finer material (less than the 200 mesh) will be the subject matter of a future publication.

All fractions of three representative samples were then separated by bromoform into heavy and light fractions. The constituents of their different fractions varied as follows:

>2.001 mm.—Shells and shell fragments, mostly of lamellibranchs and gastropods, carbonate particles and rare teeth, brachiopods and echinoid fragments. Quartz was not observed.

>.610 mm.—Do.—together with fragments of corals, bryozoa, foraminifera and annellids.

>.271 mm.—Do.—together with very few quartz grains.

>.136 mm.—Do.—together with mica flakes, iron ores and a few grains of the non-opaque heavy minerals.

>.085 mm.—Do.—the non-opaque heavy minerals are, however, more frequent.

The fraction >.085 mm. of all the samples was accordingly separated into heavy and light fractions. After determining the index figure (11, p. 236 and 239) the residues were mounted in Canada balsam and analyzed microscopically. Four hundred to seven hundred grains were counted from each crop and the relative frequencies of the minerals present were calculated. It is to be noted here that the minerals to be described are found in the fraction .136–.085 mm. and are accordingly coarser than the limits given by Sujkowski i.e. .05–.07 mm.[c], a small size, which he considered as characteristic for marine sediments transported by wind.

DESCRIPTION OF MINERALS

Table I gives the minerals recorded from each station, their percentages[d] and the corresponding index figures, whereas Table 2 shows the average percentages and range of minerals for the samples of each of the sections examined. Table 1 shows that the index figures (varying from 2.0 to .1) of the sediments are comparatively low for recent sediments but this is due to the presence of much non-detrital organic carbonate particles in them. An attempt was made to coordinate environmental conditions of deposition of the sediments and the corresponding index figures. A graph was accordingly drawn to show the relation between depth and index figure but no definite relation was detected, the points being diffused in the graph irrespective of

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[c] Biotite flakes reach approximately twice this size, being exceedingly thin and thus more easily transported.

[d] The percentage of pyrite given is relative to all other minerals, carbonate grains were not counted and biotite was counted with the heavy minerals.

TABLE 1.

A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
Sample No.	University No.	Station No.	Iron ores	Biotite	Amphiboles	Pyroxenes	Epidote	Chlorite	Tourmaline	Sphene	Apatite	Zircon	Rutile	Garnet	Staurolite	Kyanite	Fluorite	Andalusite	Glauconite	Spinel	Olivine	Anatase	Pyrite	Index fig.
Section 1 (Gulf of Suez)																								
1	8503	1—Top	61	7	5	16	3	×	×	—	—	4	—	—	—	×	—	—	—	—	—	—	41	not determined
		—Bottom	61	3	9	20	5	×	×	—	—	4	—	—	—	×	—	—	—	—	—	—	47	
2	8504	2—Top	24	15	18	28	4	×	1	×	×	6	×	1	1	×	—	—	×	—	—	—	45	
		—Middle	25	14	16	26	5	×	1	×	×	7	1	1	1	—	—	—	—	—	—	—	47	
		—Bottom	26	10	11	30	3	×	1	×	×	8	1	1	×	—	—	—	—	—	—	—	49	
3	8505	3—Top	40	13	14	19	2	×	3	—	1	3	×	1	1	—	—	—	—	—	—	—	34	
		—Middle	42	11	16	21	2	×	2	—	1	3	×	1	1	—	—	—	—	—	—	—	38	
		—Bottom	47	9	18	20	2	×	1	—	1	3	×	1	1	—	—	—	—	—	—	—	45	
	Average of section		43	10	13	22	3	×	1	×	×	5	×	1	1	×	—	—	×	—	—	—	43	
Section 2 (Gulf of Aqaba)																								
4	8506	57	14	35	38	2	3	4	×	—	2	1	—	—	—	—	—	×	—	—	—	—	1	.6
5	8507	48	26	23	31	4	1	2	1	6	5	1	1	—	—	—	—	—	—	—	—	×	1	2.0
6	8508	49	23	6	34	9	3	—	4	6	7	3	5	×	×	—	—	×	—	—	—	×	×	2.0
7	8509	52	22	14	32	11	3	3	1	4	5	3	3	×	×	×	—	—	—	—	—	—	×	.6
9	8511	54	39	10	27	5	7	3	2	2	1	2	1	×	—	—	—	—	—	—	—	—	—	.7
10	8512	55	32	7	35	8	3	5	×	1	7	3	×	×	—	—	—	—	—	—	—	—	×	1.9
	Average of section		26	16	33	7	3	3	1	3	4	2	2	×	×	×	—	×	—	—	—	×	×	1.3
Section 3 (Ghardaqa-Shadwan-Senafir)																								
11	8513	43	33	15	28	6	5	3	1	3	3	1	1	1	×	1	1	×	—	—	—	—	1	1.3
12	8514	41	33	9	27	5	7	1	2	2	3	9	1	1	×	—	—	—	—	—	—	—	×	.3
13	8515	58	48	9	28	3	2	1	×	2	3	4	1	×	—	—	—	—	—	—	—	—	×	.2
14	8516	43	32	33	20	3	2	5	1	×	2	3	—	—	—	—	—	—	—	—	—	—	—	.4
15	8517	45	19	49	15	2	2	5	1	2	2	×	2	—	—	—	—	—	—	—	—	—	—	1.1
16	8518	40—Top	28	42	13	4	2	8	×	×	2	×	—	×	—	—	—	—	—	—	—	—	15	.1
		—Middle	21	45	17	4	3	6	—	—	1	2	—	—	—	—	—	—	—	—	—	—	30	.6
		—Bottom	19	58	12	4	—	6	—	1	—	—	—	1	—	—	—	—	—	—	—	—	29	.2

Section 3 (Ghardaqa-Shadwan-Senafir) (continued)																								
17	8519	7—Top	13	49	18	4	1	9	1	×	1	1	—	1	—	—	—	—	—	—	—	—	6	.2
		—Middle	13	43	22	6	1	9	1	1	1	2	×	1	×	—	—	—	—	—	—	—	3	.3
		—Bottom	14	43	22	7	1	8	1	1	1	2	×	1	×	—	—	—	—	—	—	—	3	.8
18	8520	26	33	4	24	15	6	2	4	2	2	5	2	1	—	×	—	—	—	—	—	—	9	.4
19	8521	32	32	5	31	15	7	2	2	1	2	2	1	1	—	—	—	—	—	—	—	—	5	.4
21	8523	21	40	6	20	11	9	3	1	—	5	2	1	1	—	—	—	—	—	—	—	—	11	.6
22	8524	20	24	3	33	24	7	—	—	—	—	1	—	—	—	—	—	—	—	—	—	—	6	.6
24	8526	15	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0
25	8527	27	28	2	34	11	9	2	1	2	3	5	2	1	—	1	—	—	—	—	—	—	6	.4
26	8528	14	25	8	28	20	8	2	1	2	2	1	×	1	—	—	—	—	—	—	—	—	9	.6
28	8530	18	25	22	28	8	9	3	1	1	1	1	—	×	—	—	—	—	—	—	—	—	10	.6
29	8531	19	46	3	28	8	6	×	1	1	3	2	1	1	—	—	—	—	—	—	—	—	12	.7
30	8532	34	27	10	29	9	10	1	2	2	2	2	1	×	×	—	—	—	—	—	—	—	7	.4
39	8541	37—Top	19	48	18	2	3	6	—	—	1	2	—	—	—	—	—	—	—	—	—	—	2	.7
		—Bottom	15	49	20	3	4	6	—	—	×	2	—	—	—	—	—	—	—	—	—	—	3	1.0
40	8542	22	32	9	31	6	7	2	1	1	2	3	×	×	×	—	—	—	—	—	—	—	7	.7
43	8545	23	33	5	30	8	5	3	2	3	3	2	2	—	—	—	—	—	—	—	—	—	8	.3
44	8546	33	33	9	32	8	5	2	1	1	3	3	×	×	—	—	—	—	—	—	—	—	7	.5
	Average of section		28	28	23	6	4	3	1	1	2	2	1	1	×	×	×	×	—	—	—	—	7	.5
Section 4 (Yuba-Mersa-Daba')																								
45	8547	67—Top	24	29	20	3	4	5	4	1	2	×	×	×	—	×	—	—	—	—	—	—	—	.3
		—Middle	27	32	24	4	5	6	3	×	2	×	×	×	—	×	—	—	—	—	—	—	×	.6
		—Bottom	27	29	22	5	6	4	2	1	2	×	×	×	—	—	—	—	—	—	—	—	×	.2
46	8548	66	18	38	20	3	7	6	3	2	1	×	×	×	—	—	—	—	—	—	—	—	×	.2
47	8549	62	20	4	49	10	6	1	1	2	3	1	1	1	—	—	—	—	—	—	—	—	×	.5
	Average of section		23	24	31	6	6	3	3	2	2	1	×	×	—	×	—	—	—	—	—	—	×	.5
Section 5 (Safaga-Mowila)																								
48	8550	75	46	10	24	5	6	1	1	2	1	1	1	×	×	—	—	—	—	—	—	—	×	.8
49	8551	69	47	5	24	4	6	2	2	2	2	2	2	—	—	—	—	—	—	—	—	—	2	.5
50	8552	74	49	4	23	5	5	—	4	4	2	2	—	2	—	—	—	—	—	—	—	—	2	.7
51	8553	76—Top	38	30	20	6	4	6	4	1	1	×	×	×	×	—	—	—	—	—	—	—	1	.2
		—Middle	34	28	18	4	4	5	2	1	1	×	×	×	—	—	—	—	—	—	—	—	×	.3
		—Bottom	27	29	16	5	4	4	3	1	1	1	×	×	×	—	—	—	×	—	—	—	1	.6

TABLE 1. (*continued*)

A Sample No.	B University No.	C Station No.	D Iron ores	E Biotite	F Amphiboles	G Pyroxenes	H Epidote	I Chlorite	J Tourmaline	K Sphene	L Apatite	M Zircon	N Rutile	O Garnet	P Staurolite	Q Kyanite	R Fluorite	S Andalusite	T Glauconite	U Spinel	V Olivine	W Anatase	X Pyrite	Y Sphene
		Section 5 (Safaga-Mowila) (continued)																						
52	8554	77—Top	32	40	14	2	2	4	2	1	×	×	×	×	—	—	—	—	—	—	—	—	6	.2
		—Middle	33	37	12	2	2	3	2	1	×	×	×	×	—	—	×	—	—	—	—	—	7	.2
		—Bottom	34	34	13	2	2	2	2	1	×	×	×	×	—	—	×	—	—	—	—	—	8	1.3
53	8555	78—Top	34	37	14	2	4	3	2	—	1	×	×	—	×	—	—	—	—	—	—	—	3	.2
		—Middle	34	38	13	2	4	2	1	1	1	×	×	—	—	—	—	—	—	—	—	—	4	.3
		—Bottom	34	36	12	2	4	4	3	×	1	×	×	—	×	—	—	—	—	—	—	—	5	.1
	Average of section		42	21	20	4	5	2	2	2	1	1	1	×	×	—	×	—	×	—	—	—	3	.5
		Section 6 (Qoseir-Brothers' No'man)																						
55	8557	88	46	2	13	22	7	1	1	×	1	2	×	×	—	×	—	—	—	—	2	—	3	.6
56	8558	87	40	4	11	26	9	2	1	×	1	2	—	—	—	—	—	—	—	—	1	×	3	.5
57	8559	83	52	8	18	6	6	4	1	×	1	2	—	—	—	—	—	—	—	—	—	—	3	.4
58	8560	82	51	13	12	7	7	1	3	1	1	1	×	×	—	—	—	—	—	×	—	—	3	.3
59	8561	81	40	6	24	17	5	2	2	1	1	1	×	—	—	—	×	—	—	—	—	—	2	.3
	Average of section		47	7	16	16	7	2	2	1	1	2	×	×	—	×	—	×	—	×	×	×	3	.4
		Section 7 (Daedalus-Hanak)																						
60	8562	102	49	20	15	4	5	1	3	—	1	1	—	1	—	—	—	—	—	—	—	—	—	.2
62	8564	103	48	9	25	8	3	1	3	1	1	1	1	×	×	—	—	—	—	—	—	—	—	.3
63	8565	98	30	29	24	8	2	5	1	2	—	×	—	—	—	—	—	—	—	×	—	—	—	.1
64	8566	91	35	6	19	18	4	2	3	3	2	3	2	1	×	—	—	—	—	—	1	—	—	.4
	Average of section		40	16	21	9	4	2	2	2	1	1	1	1	×	—	—	—	—	×	×	—	—	.3
	Total average		36	17	22	10	5	2	2	2	2	2	1	1	×	×	×	×	×	×	×	×	8	.6

The cross means that the mineral is present but is less than 1 %.

depth.[e] This may be attributed to the fact that wind, not water, is the main agent of transportation as there is no diminution of detrital minerals from shore-lines towards basins of deposition.

The authigenic mineral pyrite is to be dealt with first. It was previously mentioned that Sujkowski (p. 1) failed to detect pyrite in the sediments further south. It was, however, identified from the present sediments, and was present in great abundance at some stations, expecially in the Gulf of Suez, which has a special environment as shown in a previous work. Figure 1 gives the distribution of the minerals.

TABLE 2. *Average percentages and range of minerals of samples examined.*

Mineral	Section 1		Section 2		Section 3		Section 4		Section 5		Section 6		Section 7	
	Av.	Range	Av.	Range	Av.	Range	Av.	Range	Av.	Range	Av.	Range	Av.	Range
Iron ores	43	24–61	26	14–39	28	13–48	23	18–27	42	27–49	47	40–52	40	30–49
Biotite	10	3–15	16	6–35	28	2–58	24	4–38	21	4–40	7	2–13	16	6–29
Amphiboles	13	5–18	33	27–38	23	12–34	31	20–49	20	12–24	16	11–24	21	15–25
Pyroxenes	22	16–30	7	2–11	6	2–24	6	3–10	4	2– 6	16	7–26	9	4–18
Epidote	3	2– 5	3	1– 7	4	1–10	6	4– 7	5	2– 6	7	5– 9	4	2– 5
Chlorite	×	×–×	3	— 5	3	×– 9	3	1– 6	2	— 6	2	1– 4	2	1– 5
Tourmaline	1	×– 3	1	×– 4	1	— 4	3	1– 4	2	1– 4	2	1– 3	2	1– 3
Sphene	×	— ×	2	— 6	1	— 3	2	×– 2	2	— 4	1	×– 1	2	— 3
Apatite	×	— 1	4	2– 7	2	— 5	2	1– 3	1	×– 2	1	1– 1	1	— 2
Zircon	5	4– 8	2	1– 3	2	— 9	1	×– 1	1	×– 2	2	1– 2	1	×– 3
Pyrites	43	34–49	×	— ×	7	— 30	×	— ×	3	×– 8	3	2– 3	—	— —

Pyrite—Pyrite is always authigenic and occurs in irregular patches and aggregates of minute crystals filling the hollow spaces of micro-organisms, especially the forams, showing their internal structure in a very striking manner. It is of interest to note that authigenic pyrite forms 34–49% (average of 43%) of the heavy residues of the Gulf of Suez sediments, whereas it is much less frequent or even completely absent in the sediments of both the Gulf of Aqaba and the Red Sea proper (see table 2). This suitable environment for the formation of authigenic pyrite in the Gulf of Suez may be attributed to 1) its richness in organic matter,[f] (16) which, being a reducing medium, will undoubtedly favor the formation of pyrite and not the oxides and, 2) its close proximity to the Egyptian oil fields and sulphur deposits, which are located in the neighborhood of the western coast of the Gulf of Suez at Ras Gharib and Ras Gemsa and on the eastern coast at Abu Durba. Few of the Red Sea samples, however, are rich in pyrite though not as rich as the Gulf of Suez. The richest sample (no. 16) possesses an average of 25% of pyrite and is located east of Shadwan Island in the Strait of Jubal and though the sample was secured from relatively deep waters (941 meters) its richness in organic matter[g] (16) helped in the formation of pyrites.

In the following pages the description and significance of the detrital minerals are given, starting with the light minerals.

A) MINERALS OF THE LIGHT FRACTION

The light fraction is composed mainly of micro-organisms in all the samples examined. These include various species of foraminifera (*Cristellaria*, *Nodosaria*, *Triloculina*, *Globigerina*, etc.) and shells of

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[e] It is assumed that the amount of carbonate particles, which affects the index figure as well as authigenic pyrite, are constant.

[f] This is due to the fact that conditions in the Gulf are favorable to the growth of plankton and on account of the shallowness of the Gulf rapid sedimentation of organic debris takes place.

[g] This is due to the accumulation of organic residues transported from the Gulf of Suez by a strong outgoing current, which slows down west of Shadwan Island on the one hand, and down the continental slope into the great depths in the Strait of Jubal on the other hand.

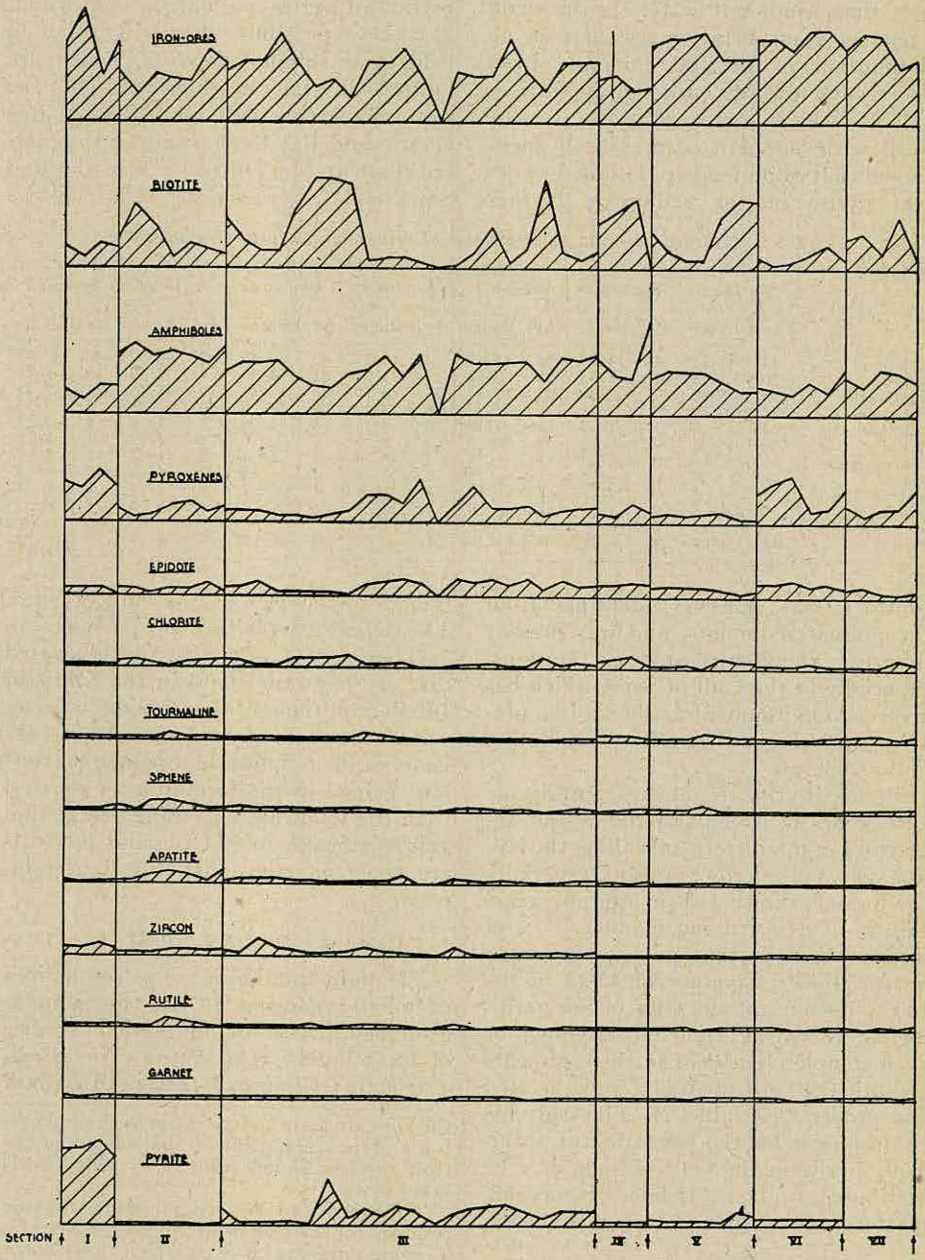

FIG. 1.—Distribution of the minerals in the different sections.

lamellibranchs.[h] Besides these organisms which are dominant, few shells of gastropods, ostracods, echinoid spines and plates, triaxial and monoaxial sponge spicules, bryozoan encrustments, radiolarians and diatoms are also present. A few clear carbonate grains are rhombohedral in shape and may be of authigenic origin.

The other detrital light minerals constitute only a very small percentage of the light fractions. The minerals recorded arranged in a decreasing order are quartz, muscovite and feldspar.

Quartz.—This mineral occurs in two different shapes: one is angular or subangular with inclusions mostly of apatite and zircon crystals, the other is remarkably well rounded. The rounded quartz grains are much more abundant than the angular quartz in the Gulf of Suez sediments but the contrary is the case in the Gulf of Aqaba or the Red Sea proper sediments. The difference in shape may indicate different sources, the rounded from pre-existing sediments, the angular from crystalline rocks. The dominance of pre-Cambrian crystalline rocks on either side of the Sea except to the west of the Gulf of Suez where only Carboniferous and post-Carboniferous sediments are present (together with minor Tertiary basaltic sheets) favors this assumption and may explain the relative abundance of the two varieties of quartz in the Gulf of Suez on the one hand and in both the Gulf of Aqaba and the Red Sea on the other. This is one example for the effect of local variation depending on the type of distributive rocks and some other examples are to be mentioned in the following text but these variations do not affect the mineralogy of the deposits of the Red Sea as a whole to the extent of masking their uniformity, as may be seen from tables 1 and 2 and from the following description. It is to be noted here that Sujkowski stated that the detrital particles exceeding .005 mm. in diameter are only rounded in the sediments obtained from shallow water and near the shore, but such rounded grains, representing different mineral species, were sparsely found in the deep water sediments of the northern Red Sea. It seems that the evidence of angularitymentioned by Sujkowski as one of the characteristic properties of the Red Sea sediments and thereby of desert dusts carried by wind is subject to discussion. The authors believe that further work on the sphericity and roundness of the minerals present is needed before any conclusion is drawn, as the mode of transportation does not seem to affect the angularity of fine mineral-grains (.07–.06 mm.), which Sujkowski worked out.

Some quartz grains show undulose extinction and few others are coated by thin films of yellow and reddish iron oxide. Such coated grains were undoubtedly transported as such (from the Nubian Sandstone or any others similarly stained sandy deposit from the mainland), as it is impossible that the ferric oxide could be formed in a reducing medium, which favored the formation of the sulphide as mentioned above.

Muscovite.—Muscovite, in irregular or rarely oval basal flakes, occurs in less abundance than quartz. The flakes are usually devoid of inclusions and few grains show undulose extinction.

Feldspars.—These are represented by a few grains in each slide. Orthoclase, microcline and plagioclase are recorded and are always fresh and angular. Their freshness is an indication of mechanical weathering but not necessarily of wind transportation as remarkably fresh feldspars and easily weathered ferromagnesian minerals (including the least stable mineral olivine) are present in the water-carried Nile deposits as shown by a recent work carried by the senior author (see also 13). This question of the freshness of the detrital minerals of the Red Sea sediments will be further discussed.

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[h] Some shells give a negative uniaxial figure between crossed nicols due to the concavity of the shells acting itself as a convergent lens.

B) MINERALS OF THE HEAVY FRACTION

The minerals will be described and discussed in the order given in table 1, in which the minerals are arranged, as far as possible, according to their relative abundance.

Carbonates.—Carbonate grains are always abundant in the heavy crops and are not counted. Aragonite is the most common carbonate and is of organic origin, but calcite, not well separated into the light fraction, is also present. Members of the dolomite-ankerite group may possibly be present but no attempt was made to identify them. Some of the aragonite grains are either uniformly stained in pink, mauve or purple colors or only part of the fragments are colored. Some of the stained grains show cleavage and pronounced pleochroism (X = mauve, Z = colorless) and are at first sight mistaken for glaucophane or dumortierite except that they show twinkling.

It is interesting to note that pleochroic aragonite is not recorded in Milner's Sedimentary Petrography. Dispersion of the light along a certain direction in the crystals may be the cause of the apparent pleochroism, but it is difficult to explain the partly "stained" particles by this assumption. It is highly possible that a staining matter arranged its atoms or molecules in definite directions in the crystals and thus formed a part of its crystal lattice.

Iron Minerals.—Under this heading, ilmenite, magnetite, hematite and limonite are grouped together. They are not counted separately because it is not easy to distinguish between ilmenite and magnetite, and again limonite or hematite may be present as thin films enveloping magnetite grains. The grains are rounded and always form an important part of the heavy fractions, ranging from 13 to 61 per cent. It is interesting to note that the percentage of both authigenic pyrite and detrital iron minerals added together is highest in the Gulf of Suez. This is in harmony with the fact that the Gulf of Suez sediments are also the highest in the percentage of iron as proved chemically (16).

Biotite.—The frequency of biotite ranges between 2 and 58 per cent in the different samples as shown in table 2. It is found in two distinct fresh varieties: a) a dark-brown, b) a dirty-green variety, comparable to that usually found in contaminated rocks. Rutile and zircon are the usual inclusions. Few grains are either completely or partially altered to chlorite. The flakes are mostly irregular but perfectly oval grains of both varieties are present in the Gulf of Suez. Such perfectly oval grains were observed by the senior author from the Nile sediments and, as mentioned later, the authors state that the Nile sediments of the Delta may have contributed easily weathered ferromagnesian minerals, including the oval shaped biotite, to the Gulf of Suez in a similar fresh state. If this is true it shows that biotite and other ferromagnesian minerals can survive two cycles of sedimentation and even survive them without affecting their freshness. In fact, there is no reason why the remarkaby fresh ferromagnesian minerals of the Nile, which stood one cycle of sedimentation, could not be carried once more by wind and deposited in the Gulf of Suez in a similar state of freshness.

Variation in the relative frequencies of biotite in the different sections and in samples of the same section seems to depend on changes in wind velocity during transportation and on the degree of quietness of their marine environment. On the other hand local variation in the distributive rocks undoubtedly played a part in this respect (3, chapter VII). The samples west of Shadwan Island, for instance, which is formed of mica schists and acid and intermediate rocks as observed by the senior author during the present Expedition caused enrichment of biotite in these neighboring sediments (nos. 16 and 17), whereas the sediments collected from the Brothers' slopes, which are formed of basic rocks nearly devoid of mica (18) are relatively poor in biotite.

Amphiboles.—Uhder this heading four "species" are recorded and described namely: dirty-green hornblende, bluish-green hornblende, brown hornblende and actinolite. The frequency of amphiboles varies from 5 to 48 per cent in the different sediments; the dirty-green variety always exceeds the others; whereas the brown variety and actinolite are very rare and the latter is usually the least abundant.[i] All the grains are remarkably fresh and are very rarely decomposed into chloritic material. It was noted that in the Gulf of Suez, for instance, the completely altered crystals of amphibole, as well as pyroxene, became more abundant as the downward trend of the core increased (percentage of decomposed amphibole varies from .2 to 1.8 as shown in Table 3. This might be due to post-depositional processes (4, 8, 17 and 21), which will yield simplification of the mineral detritus during geological time. If this is correct, because there is the possibility that these decomposed grains were transported as such and that their increase downward is accidental, the hydrogen sulphide generated during diagenetical processes undoubtedly helped in the alteration of the mineral particles, because the slightly alkaline seawater is a stabilizing medium rather than a destructive one (18).

TABLE 3. *Showing percentage of decomposed amphiboles and pyroxenes.*

No. of samples		% of decomposed amphiboles	% of decomposed pyroxenes
1	Top	.2	.4
	Bottom	.9	1.4
2	Top	.6	1.4
	Middle	.8	2.0
	Bottom	1.2	3.0
3	Top	.4	.6
	Middle	1.0	1.4
	Bottom	1.8	2.1

The hornblende crystals are compact and angular and show some tendency for prismatic habit. The grains show marked pleochroism from yellowish-green to dirty-green, from green to bluish-green (with $-2V=82^\circ$ and $Z\ c=30^\circ$)[j], and from pale-brown to dark-brown in the three varieties of hornblende. Black iron minerals are present as inclusions. Actinolite is fibrous, very pale green in color and unpleochroic. The amphiboles summed together are always more abundant than the pyroxenes, except in the sediments from the slopes of the Brothers' Islets in the south (nos. 55 and 56) and from the Gulf of Suez. These are two other examples of the effect of local variations on the mineralogy of the sediments. The abundance of the pyroxenes on the slopes of the Brothers' is due to the fact that they are formed of basic rocks (18). It was difficult at first to account, however, for the relative abundance of pyroxenes in the Gulf of Suez, especially as the Gulf is bounded in its immediate vicinity by sediments on its eastern side and mainly by both sediments and acid and intermediate types on its western side, but this may be explained by the suggestion that the important north-westerly winds passing over the Delta of the Nile carried its fine detritals during the frequent sand storms and subsequently deposited them in the Gulf of Suez. The Nile sediments contain more abundant pyroxenes than amphiboles as shown in a recent work by the senior author.

Pyroxenes.—Both monoclinic and rhombic pyroxenes are recorded. Their total relative frequencies vary from 2 to 30 per cent. The monoclinic pyroxenes comprise five varieties: grayish-brown augite, yellowish augite,[k] colorless augite, diopside and diallage. They are all unpleochroic and the grayish-brown variety

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[i] The same relative abundance is recorded from the Nile sediments at Cairo.

[j] Data determined by the use of a Fedorov stage. They compare fairly well with those of a bluish-green hornblende from the Nile sediments, as determined by the senior author.

[k] With $+2V=56^\circ$, the cleavage is not clear.

is always dominating. The colorless augite and diopside are very rare and are completely absent in some sections. The diallage is also very rare and is schillerized and the inclusions are mostly reddish iron oxides. The grains are angular to sub-angular and are very fresh with but few grains partially altered into a yellowish serpentinous material. The colorless and diopsidic varieties were not seen in a decomposed state.

The rhombic pyroxenes are very rare and are represented by both hypersthene and enstatite. The hypersthene shows marked pleochroism from green to pink and is rarely altered along cleavage planes into a brownish serpentine. Black iron ores are common inclusions. The colorless rhombic pyroxenes were identified as enstatite.

Epidotes.—Pistachite, zoisite, clinozoisite, thulite and a much turbid rounded variety were recorded. The total frequency of the epidotes varies from 1 to 10 per cent. Pistachite, which occurs in angular or sub-angular broken crystals is the most abundant except in the sediments of the Gulf of Suez and few samples from near Tiran Island where the turbid and rounded grains are more abundant than pistachite. It is believed that the turbid and rounded variety is derived from pre-existing sediments. The abundance of sediments on the western side of the Gulf may thus explain the dominance of the rounded turbid variety over the fresh pistachite. Zoisite and clinozoisite, occurring also in angular crystals are very rare. Thulite, showing pleochroism from rose to colorless, was recorded only from the sediments located on the slopes of the Brothers' Islets. It is interesting to note that thulite was identified from the basic rocks of the Brothers' (sample no. 3472 housed in the Geological Department of Fouad I University).

Chlorite.—Chlorite varies from less than 1 to 9 per cent. Besides its occurrence as alteration product after biotite, other grains seem to be primary. These are pale-green, non-pleochroic and occur in rounded or oval grains and may be derived from pre-existing sediments, but irregular flakes are present, some of which show undulose extinction and suggest derivation from crystalline rocks. The rounded grains are dominant in the Gulf of Suez.

Tourmaline.—The percentage of this mineral varies from less than 1 to 4 per cent. It occurs in four varieties differing in color, namely brown, bluish, violet and green varieties, exhibiting marked pleochroism. The brown variety is the commonest. Most of the particles are prismatic with rounded or angular edges but well rounded grains are occasionally observed. The presence of these two varieties, namely the prismatic and rounded, suggest derivation from crystalline and sedimentary formations respectively. Inclusions, including zircon crystals, rutile needles and opaque particles are more abundant in the brown variety than in the others. A rare light indigo-blue variety (indicolite) in very clear grains is also present. It is interesting to note that exactly similar grains were observed in the Nubian Sandstone of the Eastern Desert of Egypt (19).

Sphene.—Sphene varies from less than 1 to 6 per cent. It is faint brownish in color. The grains possess pitted surfaces and are sub-angular or angular but rare, nearly complete spindle-shaped crystals are present. Some grains contain iron minerals as inclusions. Sphene is more abundant in the Gulf of Aqaba than in the Gulf of Suez or Red Sea sediments.

Apatite.—Two varieties of apatite were recorded, namely, 1) a clear angular to sub-angular prismatic variety, which is devoid of inclusions and 2) rounded or oval grains, which are crowded with inclusions composed mainly of opaque material. The relative frequencies of the two varieties vary in the different samples.

Zircon.—The frequency of zircon varies from less than 1 to 9 per cent. Colorless, purple and yellow varieties are distinguished. It ranges from water-clear crystals devoid of any inclusions except for some fluid cavities to grains possessing numerous inclusions (comprising apatite crystals and smaller zircon grains). Worn, rounded and oval grains (usually of the purple and yellow varieties) as well as idiomorphic crystals (usually the colorless) are present. The presence of these two varieties suggests that they are derived from two different sources, the rounded from sediments and the idiomorphic from crystalline rocks. The rounded grains are more abundant than the idiomorphic crystals in the Gulf of Suez, whereas the reverse is the case in the Gulf of Aqaba or the Red Sea sediments. This may be due to local variation related to the dominance of sediments on the sides of the Gulf of Suez.

Rutile.—This mineral is recorded from most of the sediments and its frequency reaches up to 5 per cent. It occurs in ovoid, deep reddish-brown or yellowish grains, showing marked pleochroism. Less frequently angular to sub-angular prismatic crystals, often striated parallel to the vertical axis are present. Some of the angular crystals show polysynthetic or heart-shaped twinning.

Garnet.—The freqency of garnet varies from less than 1 to 2 per cent. Three varieties were recognized, colorless, pink, and yellowish-brown. The colorless usually dominates. The grains are rounded and inclusions are rare. A few etched grains, having a scaly patterned surface and similar to those figured by Wilgus (23, p. 86) were seen. Exactly similar grains were recorded from the Nubian Sandstone of the mainland to the west (19). Broken dodecahedrons are also present. At least two sources of the garnet are suggested: the Nubian Sandstone on the one hand and crystalline rocks on the other.

Staurolite.—Staurolite when present always forms less than 1 per cent except in some samples of the Gulf of Suez where it forms up to 1 per cent of the heavy minerals. It is angular and exhibits strong pleochroism (X = nearly colorless, Y = pale yellow and Z = golden yellow). Inclusions, commonly carbonaceous matter, are rarely present and a few grains show a pitted scaly patterned surface[1] which is more pronounced than that shown by the pitted garnets mentioned above. Staurolite seems to have been derived from the Nubian Sandstone where it forms about 20 per cent of the heavy non-opaque minerals of the sandstones (19). Staurolite is, however, recorded from a few localities in the Eastern Desert but is very rare in the Pre-Cambrian of Egypt (1).

Kyanite.—Kyanite is, on the whole, slightly less frequent than staurolite. It occurs in colorless stout prismatic grains with rounded edges and shows the two rectangular cleavages. Inclusions are absent. Kyanite like staurolite is recorded from a few localities in the Eastern Desert of Egypt.

Fluorite.—This mineral was recorded from only three samples (from the entrance to the Gulf of Aqaba, Safaga-Mowila and Qoseir-Brothers' sections) It is always less than 1 per cent and occurs in very rare sub-angular colorless grains. Fluorite is recorded from the Pre-Cambrian of Sinai and the Eastern Desert.

Andalusite.—Andalusite is recorded from three samples located in the Gulf of Aqaba and at its entrance. It is very rare and occurs in clear prismatic grains with their edges rounded. Pleochroism from pink to colorless is displayed by all the grains. It is interesting to note that Hume recorded contact-altered pelitic rocks bearing andalusite, showing the characteristic pink pleochroism, from the south-eastern part of Sinai (12, p. 607), otherwise andalusite is not recorded from Egypt. This is another example showing the effect of source-rocks on the mineralogy of the neighboring sediments.

Glauconite.—Glauconite is represented in two samples only by two grains, one from the Gulf of Suez section and the other from Safaga-Mowila section. The two grains are unpleochroic green in color and rounded, showing aggregate polariza-

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[1] Similar staurolite grains are recorded from the Nubian Sandstone (6 and 20).

tion colors. The grains are most probably detrital in origin. Glauconite was not seen either filling the hollow spaces of organisms or forming after biotite.

Spinel.—This mineral is recorded from two samples in the two southernmost sections. It is represented in the two samples by a bluish-green isotropic angular variety, represented by a very few grains.

Olivine.—Olivine was also recorded from the same two sections, from the slopes of the Brothers' Islets and from station no. 64, north-west of Sheibara Island, but in greater abundance than spinel as it forms 1 or 2 per cent of the heavy minerals. The mineral is present in angular colorless fresh grains on the Brothers' slopes and exhibits a yellowish tinge in the other occurrence. The optic axial angle of the colorless olivine from the Brothers' slopes equals 85° and it is interesting to note that remarkably fresh olivine crystals (with $-2V = 84° - 78°$) were described from the shore-debris and from a compact conglomerate on the Brothers' Islets (18). The presence of olivine in the bottom sediments as well is another example of the effect of local variations on the mineralogy of the Red Sea deposits.

Anatase.—This mineral occurs in three samples, two from the Gulf of Aqaba and one from the slopes of the Brothers' Islets and is represented by a very few grains. It occurs in angular dark bluish-gray, nearly opaque grains.

Rock-fragments.—Besides the separate mineral grains recorded in the previous pages a few rock-fragments are occasionally present in the heavy crops. A hornblende schist is recorded from the Gulf of Aqaba, whereas a fragment of a dolerite is recorded from the slopes of the Brothers' sediments. Dolerite is recorded from the Islets by the senior author (18).

SUMMARY AND CONCLUSIONS

The present paper deals with the mineralogy of the bottom deposits collected during the "Mabahith" Expediton to the northern part of the Red Sea in 1934–1935. The sediments were fractionated and the fraction lying between .135 and .085 mm. was separated by bromoform into light and heavy fractions and was examined microscopically. Carbonate particles of organic source form the greater part of the sediments and the following minerals are recorded: pyrite, calcite, quartz, moscovite, orthoclase, microcline, members of the plagioclase series, pleochroic aragonite,[m] ilmenite, magnetite, hematite, limonite, biotite, hornblende (three varieties), actinolite, augite (three varieties), diopside, diallage, hypersthene, enstatite, pistachite, zoisite, clinozoisite, thulite, chlorite, tourmaline, sphene, apatite, zircon, rutile, garnet, staurolite, kyanite, fluorite, andalusite, glauconite, spinel, olivine and anatase, amounting to about 38 species.

The characteristics of the minerals present in the middle and south eastern parts of the Red Sea are beautifully summarized by Sujkowski and his description agrees in its essential parts with the minerals found farther to the north. The relative frequencies of the minerals recorded show that the common heavy minerals of sediments (especially of the older formations), such as tourmaline, rutile, zircon, etc. are rare or even absent in some parts of the Sea, whereas the easily weathered, colored minerals, and the common rock-forming minerals of crystalline rocks are present in abundance in a fresh state.

Sujkowski stated that such an assemblage of minerals characterizes sediments derived from desert regions by wind. This statement is, however, subject to discussion and the authors believe that these characters are neither criteria for wind transportation nor of desert regions. The minerals of the bottom sediments of the Red Sea exhibit these characters mainly, or at least in part, because they were derived in their greater part from crystalline rocks, which bound the Sea on both sides. In fact, the recent dunes of the great

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[m] Pleochroic aragonite (X = mauve, Z = colorless) is not recorded in Milner's sedimentary petrography.

African Sahara, where conditions that favor mechanical disintegration rather than chemical decomposition of source-rock prevail, but where sediments and not crystalline rocks dominate (14) contain a totally different assemblage (rich in iron minerals, tourmaline, zircon, rutile, etc.) from that of the Red Sea sediments (2 and 23). On the other hand, the Nile sediments, worked out by the senior author and which are water-borne, gave an assemblage of minerals with the same characteristics as those of the Red Sea bottom deposits. Both formations, though of two different modes of origin, are remarkable examples for the richness of recent sediments (derived from crystalline rocks) in vulnerable minerals. The sediments near Cairo, though carried for hundreds of kilometres, contain over thirty mineral species in a very fresh state, many of which stand at the top of a list of minerals arranged in an increasing order of stability.

The angularity of the grains and their small size, stated by Sujkowski to be characteristic for the mode of origin of the Red Sea sediments, seems to be invalid and further evidence is wanted on the subject before any conclusion is drawn. It was noted that the minerals recorded in the present work are coarser than the limits given by Sujkowski, who considered their fineness as characteristic for wind transportation.

The mineral assemblage of a sediment depends on three main factors:

1. Nature of distributive rocks.
2. Type of weathering and mode of transportation.
3. Post-depositional processes, leading to simplification of detrital grains and increase in authigenic minerals.

Sujkowski took into account the second factor mentioned but not the first, which is of great importance in the case of the Red Sea sediments. The third is not working in recent sediments or is of negligible importance. The characteristics of sediments derived from deserts by wind are, accordingly, not those given by Sujkowski. At the same time the statement of White (23) that wind-borne sands contain less frequent heavy minerals than water-borne sands and that the heavy minerals are less frequent in larger deserts than in smaller desert areas is invalid as he did not take into account the factor of distributive rocks in this case also.

The detrital minerals of the Red Sea sediments were transported to the sea mainly by wind, mostly from the rocks in its immediate vicinity,[n] though rain-torrents and waves undoubtedly contributed smaller amounts of material. The mineral constituents of the sediments are uniform[o] in all parts of the Sea and they all show the same general characters, whether collected from the southern, middle or northern portions of the Sea.[p] The usual heterogeneity of the mineralogy of marine sediments, producing well defined "sedimentary" petrographic provinces (10) and which are in many cases due to transportation by rivers, is not known in the Red Sea bottom deposits. Again, no diminution of detrital minerals from shore-lines towards basins of deposition was detected and this may also be due to wind transportation. On the other hand, local conditions gave rise to variation in the frequencies or types of minerals present without affecting the general characters of the mineralogy of the deposits. Variation in authigenic minerals is due to variation of the environmental conditions of deposition, on the other hand, variation in detrital minerals is mainly attributed to differences in the source-rocks, but varia-

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[n] It is interesting to note that Wade (22) showed that the sands round Gebel Zeit, in the northern Eastern Desert of Egypt are mostly derived from rocks in its vicinity, the sand itself playing a part in the disintegration of the source-rocks.

[o] Sujkowski (21) states that it is not possible to differentiate between one sediment of deep water bottom and another by a study of their minerals.

[p] It is interesting to note that the shallow and near-shore sediments gave the same general characters as those of the deeper samples.

tion of wind velocity and direction, as well as of environments of deposition (such as strength and direction of currents, etc.), played a part.

Authigenic pyrite is present in great abundance (average of 43 per cent of the heavy minerals) in the Gulf of Suez, which has a special environment as shown in the preceding article and is much less frequent or even completely absent in the sediments of both the Gulf of Aqaba and the Red Sea proper. The suitable environment for the formation of authigenic pyrite in the Gulf of Suez is attributed to its shallowness, richness in organic matter and its close proximity to the Egyptian oil-fields and sulphur deposits, located on its sides. It was noted that the percentage of both authigenic pyrite and detrital iron minerals added together is highest in the Gulf of Suez; this is in harmony with the fact that the Gulf of Suez sediments are also the highest in the percentage of iron as proved chemically (16).

Examples of the effect of local variations on the detrital grains were discussed. The presence of 1) feldspathoids in the sediments described by Sujkowski from the middle and south-eastern parts of the Sea and their presence in the Yamano-Abbyssinian Tertiary alkaline volcanic provinces as well, and their absence in the bottom sediments and extreme rarity in the source rocks from the north, 2) the presence of olivine, thulite,[a] and dolerite in both the Brothers' Islets and the bottom sediments collected from their submarine ridge, 3) the presence of andalusite in the Gulf of Aqaba sediments and in those from its entrance on the one hand and its record in a similar variety from the south-eastern part of the Sinai Peninsula on the other and 4) the dominance of rounded quartz, zircon and turbid epidote grains over angular or idiomorphic crystals of the same species in the Gulf of Suez (contrary to the Gulf of Aqaba and Red Sea sediments) and the abundance of sedimentary formations on its sides, are some examples of the effect of local variations.

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[a] This mineral and others, though of extreme rarity, are of great provenance significance (7).

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TABLE 1a

Chemical composition of the chief rocks of the Loch Doon Complex

	A	B	C	D	E	F	G	H	I	J	K	L
	214	485	414	206	18	333	685/5	506	507	404	401	666
SiO_2	59.82	68.68	56.92	55.78	55.34	60.06	60.29	67.79	64.20	58.70	61.62	71.34
Al_2O_3	16.84	12.84	16.57	16.36	16.18	16.14	17.53	13.83	15.86	16.56	16.44	15.13
Fe_2O_3	0.46	0.16	0.76	0.53	0.97	0.98	tr.	0.41	0.71	0.49	0.46	0.34
FeO	5.88	5.58	6.84	6.41	6.13	4.85	5.31	5.77	4.57	5.28	4.16	1.66
MgO	4.97	2.95	5.88	5.42	6.02	4.65	4.49	3.03	2.81	5.48	4.23	1.21
CaO	5.68	1.32	5.76	7.34	6.06	5.64	5.02	1.38	2.35	5.14	4.06	1.80
Na_2O	2.49	2.04	3.15	3.32	3.92	3.43	2.69	3.06	3.64	2.98	3.18	3.36
K_2O	1.73	1.47	1.36	1.78	2.21	2.04	2.28	1.96	3.62	2.56	2.72	4.28
H_2O+	1.16	2.98	1.20	1.22	0.36	0.32	0.36	0.94	0.82	1.36	1.18	0.55
H_2O-	0.42	0.10	0.24	0.17	0.38	0.04	0.18	0.22	0.16	0.29	0.73	0.15
CO_2	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
TiO_2	0.58	1.12	0.86	1.42	1.68	1.07	0.98	0.98	0.96	0.84	0.74	0.37
P_2O_5	0.09	0.17	0.12	0.21	0.25	0.21	0.20	0.13	0.22	0.14	0.13	0.06
MnO	0.14	0.23	0.15	0.31	0.33	0.26	0.26	0.27	0.14	0.12	0.14	tr.
	100.26	99.64	99.81	100.27	99.83	99.69	99.59	99.77	100.06	99.94	99.79	100.25

Analyst: W.H. Herdsman.

A = Mobilised sediment about 18 ft. from the contact quartz-diorite, at a height of approximately 800 ft., on the south slope of Buchan Hill (Rutledge, 1950, Table II, Analysis C).

B = Greywacke from south side of Craiglure Hill (McIntyre, 1947, Table 2, Analysis 1).

C = Biotite-hornblende-plagioclase-hornfels, 55 yds. from the marginal granodiorite at a height of approximately 800 ft. on the south slope of Buchan Hill (Rutledge, 1950, Table II, Analysis B).

D = Potash-feldspar-poor "norite" from south side of Shiel Hill (McIntyre, 1947, Table 2, Analysis 8).

E = Coarse-grained opdalite, 100 yds. south of Balloch Lodge (McIntyre, 1947, Table 2, Analysis 7).

F = Fine-grained opdalite, west shore of Loch Cornish (McIntyre, 1947, Table 2, Analysis 5).

G = Opdalite pod in the aureole south of summit of Craigbrock (McIntyre, 1947, Table 2, Analysis 4).

H = Slightly feldspathised greywacke, Cow Craig (McIntyre, 1947, Table 2, Analysis 2).

I = Highly feldspathised greywacke, Cow Craig (McIntyre, 1947, Table 2, Analysis 3).

J = Contact quartz-diorite, transitional to marginal granodiorite at a height of approximately 800 ft., on the south slope of Buchan Hill (Rutledge, 1950, Table II, Analysis D).

K = Marginal hornblende-biotite-granodiorite, about 15 yds. from the contact-quartz-diorite at a height of approximately 800 ft., on south slope of Buchan Hill (Rutledge, 1950, Table II, Analysis E).

L = Biotite-adamellite, Craignaw. New analysis.

TABLE I.

Chemical and spectrographic composition in weight per cent.

Oxide	A	B	C	Average BC	D	E	Average DE	Average of all rocks
SiO_2	60.52	53.05	68.05	60.55	50.63	53.02	51.83	57.07
Al_2O_3	17.45	21.74	15.69	18.71	28.86	23.35	26.10	21.42
FeO	7.11	5.13	6.84	5.99	4.95	5.94	5.45	5.99
Fe_2O_3	0.48	3.12	0.26	1.69	3.32	1.88	2.60	1.81
TiO_2	1.10	1.14	0.50	0.82	1.06	1.14	1.10	0.99
MnO	0.07	0.09	0.18	0.13	0.23	tr.	0.12	0.11
CaO	0.93	0.54	0.48	0.51	0.94	1.33	1.13	0.84
MgO	2.89	2.87	1.77	2.32	2.32	2.62	2.47	2.49
K_2O	2.27	6.59	2.23	4.41	2.25	4.89	3.57	3.64
Na_2O	2.94	0.82	0.37	0.59	1.92	2.06	1.99	1.62
H_2O-	0.39	0.20	0.14	0.17	0.05	0.18	0.12	0.19
H_2O+	3.48	4.55	3.34	3.95	2.97	3.22	3.09	3.51
CO_2	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
P_2O_5	0.17	0.18	0.10	0.14	0.28	0.16	0.22	0.18
Rb_2O	0.011	0.05	0.011	0.031	0.016	0.033	0.025	0.022
Li_2O	0.022	0.07	0.012	0.041	0.026	0.024	0.025	0.031
BaO	0.1	0.33	0.1	0.22	0.11	0.22	0.17	0.17
SrO	0.007	0.006	0.002	0.004	0.009	0.014	0.012	0.008
Cr_2O_3	0.009	0.022	0.007	0.015	0.018	0.016	0.017	0.014
CoO	0.004	0.006	0.003	0.0045	0.005	0.005	0.005	0.005
NiO	0.007	0.006	0.005	0.005	0.015	0.009	0.012	0.008
ZrO_2	0.11	0.12	0.01	0.07	0.04	0.04	0.04	0.06
La_2O_3	*	*	*	*	0.004	0.004	0.004	0.001
Y_2O_3	0.006	0.004	0.004	0.004	0.008	0.01	0.009	0.006
CuO	0.0007	0.002	0.001	0.0015	0.002	0.001	0.0015	0.001
V_2O_5	0.016	0.016	0.012	0.014	0.016	0.017	0.016	0.015
Ga_2O_3	0.005	0.007	0.003	0.005	0.01	0.008	0.009	0.006
Tl_2O	*	*	*	*	*	*	*	*
SnO_2	*	*	*	*	*	*	*	*
PbO	0.001	0.004	0.001	0.0025	0.002	0.002	0.002	0.002
Sc_2O_3	*	*	*	*	*	0.002	0.001	*
MoO_3	0.0002	0.0002	0.0005	0.0004	0.0003	0.0003	0.0003	0.0003
GeO_2	*	*	*	*	*	*	*	*
BeO	0.001	*	*	*	0.001	0.001	0.001	0.0006
Ag_2O	0.0003	0.0002	0.0001?	0.0002	0.0001	0.0002	0.0002	0.0002
In_2O_3	*	*	*	*	*	*	*	*

A = quartz-chlorite-schist (Skatie shore)

B = quartz-biotite schist (south side of Perthumie Bay)

C = quartz-garnet-biotite-schist (north of Red Man, Perthumie Bay)

D = quartz-staurolite-schist (Perthumie Bay)

E = quartz-sillimanite-biotite-gneiss (Earnsheugh Bay)

A, BC and DE = low, medium and high grades of metamorphism respectively

Chemical analyst: W.H. Herdsman

Spectrographic analyst: R.A. Higazy

* = Element if present is in amount below its limit of sensitivity. The limits of sensitivity in ppm. are as follows:

Rb 1;	Li 1;	Ba 5;	Sr 5;	Cr 1;	Co 2;
Ni 2;	Zr 10;	La 30;	Y 30;	Cu 3;	V 5;
Ga 1;	Tl 30;	Sn 5;	Pb 10;	Sc 10;	Mo 1;
Ge 10;	Be 5;	Ag 1;	In 10.		

TABLE 1b

Trace-element contents in ppm. of the chief rocks of the Loch Doon Complex.

Element	Sensitivity	A	B	C	D	E	F	G	H	I	J	K	L
		214	485	414	206	18	333	685/5	506	507	404	401	666
Rb	1	65	100	50	100	150	130	110	90	180	110	120	380
Li	1	80	80	70	100	80	90	15	85	100	90	80	350
Ba	5	600	750	800	1000	1000	1200	1900	1400	2000	2000	1600	1800
Sr	5	950	200	1000	2200	1900	2000	1100	850	900	1200	2200	900
Cr	1	250	250	450	280	320	260	290	240	70	400	300	70
Co	2	60	35	65	45	45	35	40	30	40	40	45	5
Ni	2	100	115	120	120	200	110	120	90	60	150	110	35
Zr	10	290	500	350	450	1200	350	700	600	1000	1100	800	400
La	30	<30	30	<30?	<30	30	30	<30	40	50	30	40	60
Y	30	70	65	40	70	80	50	75	65	100	60	60	60
Cu	3	3	280	12	250	320	240	150	110	300	5	8	3
V	5	170	105	180	200	180	120	150	110	120	130	140	100
Ga	1	25	30	35	35	35	30	40	30	35	35	40	45
Tl	30	*	*	*	*	*	*	*	*	*	*	*	*
Sn	5	40	20	<5	15	25	10	8?	5	30?	<5	<5	<5
Pb	10	10	35	<10	25	25	32	30	12	35	10	10	20
Sc	10	10	*	10	<10	<10	<10	*	*	<10	<10?	<10?	<10
Mo	1	<1	1	<1?	<1	<1	1	*	<1	<1	<1	<1	1
Ge	10	*	*	*	*	*	*	*	*	*	*	*	*
Be	5	*	*	*	*	*	*	*	*	*	*	*	*
Ag	1	2	<1	2	<1	3	2	1	<1	2	4	6	8
In	10	*	*	*	*	*	*	*	*	*	*	*	*

Analyst: R.A. Higazy

* = Element if present is in amounts below its limit of sensitivity.

A - L as given in Table 1a.

TABLE 2a

Chemical composition of katungite, mafurite, ugandite and ouachitite

	Katungites								Mafurite	Ugandite	Ouachitite
	Katwe-Kikorongo		Bunyaruguru				Katunga	Average Katungite			
	A	B	C	D	E	F	G		H	I	J
SiO_2	35.51	37.93	33.89	34.23	33.22	35.52	35.37	35.09	39.06	40.47	38.94
Al_2O_3	6.83	6.59	8.27	8.02	9.71	8.04	6.50	7.70	8.18	5.38	6.92
Fe_2O_3	9.68	6.81	7.03	6.62	6.68	5.88	7.23	7.13	7.13	4.61	5.27
FeO	2.70	4.37	5.21	5.34	5.30	5.50	5.00	5.06	4.98	6.47	5.09
MnO	0.22	0.18	0.26	0.22	0.52	0.15	0.24	0.26	0.26	0.23	0.23
MgO	11.67	14.54	10.93	9.92	12.12	13.54	14.08	12.40	17.66	24.84	11.58
CaO	16.00	15.23	16.98	16.54	15.64	15.22	16.79	16.06	10.40	8.06	15.95
Na_2O	1.56	0.88	1.42	1.20	1.51	1.42	1.32	1.33	0.18	0.68	1.01
K_2O	3.30	2.65	3.65	3.39	3.54	4.26	4.09	3.56	6.98	3.46	3.96
H_2O+	3.11	3.38	2.08	2.80	3.28	2.34	2.78	2.82	1.42	1.11	2.26
H_2O-	1.31	1.42	1.19	1.72	0.80	1.68	1.15	1.32	0.50	0.57	1.20
CO_2	1.47	0.50	3.27	4.02	0.42	0.96	0.09	1.53	tr.	0.36	2.12
TiO_2	4.88	4.12	4.43	4.56	6.08	6.04	3.87	4.86	4.36	3.52	3.88
P_2O_5	1.18	1.03	0.97	0.96	1.12	0.82	0.74	0.97	0.61	0.29	0.91
Cl	tr.	0.01	-	-	-	-	0.02	-	-	0.01	-
F	0.27	0.16	0.18	0.14	0.08	-	0.16	-	0.13	0.10	0.13
S	-	-	0.14	0.12	-	-	0.35	-	0.13	0.04	0.14
SO_3	0.13	0.06	-	-	-	-	-	-	-	-	-
Cr_2O_3	0.02	0.05	-	-	-	-	0.01	-	0.08	0.11	-
V_2O_3	0.04	0.02	-	-	-	-	0.03	-	-	0.03	-
NiO	0.02	0.03	-	-	-	-	0.19	-	tr.	0.23	0.09
BaO	0.27	0.30	0.21	0.20	0.17	0.15	0.25	-	0.32	0.27	0.18
SrO	0.24	0.25	0.29	0.23	0.05	0.44	0.04	-	0.18	0.02	0.19
Li_2O	tr.	-	-	-	-	-	none	-	-	-	-
CuO	-	-	-	-	-	-	0.06	-	-	-	-
Total	100.41	100.51	100.40	100.23	100.24	99.96	100.36	100.09	100.04	100.18	100.05
Less O	0.11	0.07	0.11	0.11	0.03	-	0.24		0.10	0.05	0.09
	100.30	100.44	100.29	100.12	100.21	99.96	100.12		99.94	100.13	99.96

A = Katungite. Lapilli from tuff, G 21, Katwe crater (Holmes, 1937, p. 207). Analyst: H.F. Harwood.

B = Biotite-katungite (Alnöite). Ejected block, G. 56, Katwe crater (Holmes, 1937, p. 207). Analyst: H.F. Harwood.

C = Proto-katungite. Ejected block, C 6065, from the rim of one of the oldest craters, Lugazi, Bunyaruguru (Holmes, 1950, p. 784). Analyst: W.H. Herdsman.

D = Katungite. Lapilli separated from the first volcanic horizon of the Upper Kaiso Series, C 5945, near M.P. 75 on the Fort Portal Road, N.W. edge of the Bunyaruguru field (Combe and Holmes, 1945, p. 367). Analyst: W.H. Herdsman.

E = Katungite. Ejected block, C 3509, from Chamakumba crater, Bunyaruguru (Holmes, 1942, p. 212). Analyst: W.H. Herdsman.

F = Kalsilite-katungite. Lapilli separated from tuff, C 4012, N.W. rim of Changabe crater, Bunyaruguru (Combe and Holmes, 1945, p. 367). Analyst: W.H. Herdsman.

G = Katungite, western flow, C 4407, Katunga (Holmes, 1937, p. 205). Analyst: A.W. Groves.

H = Mafurite. Ejected block from the tuffs above the lava sheet of Mafuru, C 6073 (Holmes, 1942, p. 212). Analyst: W.H. Herdsman.

I = Olivine-rich ugandite, C 3052. Old rest camp of Kichwamba, adjoining Kachuba crater, Bunyaruguru (Holmes and Harwood, 1932, p. 415). Analyst: H.F. Harwood.

J = Olivine-ouachitite, C 5844. Ejected block 20 ft. below S.E. rim of Katwe crater, Katwe-Kikorongo (Holmes, 1950, p. 780). Analyst: W.H. Herdsman

TABLE 2b

Trace-element contents of katungites, mafurite, ugandite and ouachitite.

Element	Katungites								Mafurite	Ugandite	Ouachitite
	Katwe-Kikorongo		Bunyaruguru				Katunga	Average Katungite			
	A	B	C	D	E	F	G		H	I	J
Rb	200	150	240	220	150	380	200	220	450	450	100
Li	10	12	8	7	6	6	8	8	5	7	13
Ba	2800	2600	7000	2000	1800	4500	2900	3370	7500	2000	1700
Sr	7500	3800	>1%	7500	4000	9500	4500	6685	7000	1800	2500
Cr	700	800	290	650	500	1200	900	720	1300	1200	550
CO	85	70	60	80	80	70	65	73	70	110	60
Ni	230	140	100	200	160	180	270	185	300	900	250
Zr	800	1100	1100	850	1200	800	1200	1000	900	300	1200
La	30	<30	100	50	30	70	40	50	80	35	<30
Y	< 30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Cu	80	60	200	70	60	50	70	85	25	60	65
V	320	350	170	260	350	210	250	275	220	110	320
Ga	25	30	25	25	30	20	25	25	15	5	25
Tl	*	*	*	*	*	*	*	*	*	*	*
Sn	*	*	< 5?	*	*	35	*	*	*	*	*
Pb	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Sc	<10	*	*	<10	<10?	*	*	*	*	*	*
Mo	*	*	*	*	*	*	*	*	*	*	*
Ge	*	*	*	*	*	*	*	*	*	*	<10?
Be	*	*	*	*	*	*	*	*	*	*	*
Ag	*	8	*	*	*	2	*	1	*	1	*
In	*	*	*	*	*	*	*	*	*	*	*

Analyst: R.A. Higazy

* = Element below its limit of sensitivity given in Table 1b

A - J as in Table 2a

TABLE I

Major and Trace Element Contents in ppm. of the Rocks of the Braefoot Sill(*)

	A	B	C	D	E	F	G	H	I	J	Sensitivity
Si	214,000	196,000	220,000	209,000	210,000	214,000	225,000	196,000	221,000	287,000	
Al	79,400	58,700	84,500	82,400	69,400	77,900	79,300	63,300	80,600	73,500	
Fe^3	23,600	12,800	11,000	22,800	38,800	17,300	14,300	12,200	19,800	19,900	
Fe^2	68,000	70,000	56,000	62,300	60,000	90,000	42,700	57,800	53,600	30,200	
Mg	41,700	90,000	43,300	36,200	29,900	29,900	36,200	17,600	35,400	17,200	
Ca	56,500	41,400	47,700	47,000	66,400	29,000	77,100	101,000	77,200	13,600	
Na	21,800	17,500	32,000	34,500	21,200	19,700	19,100	14,000	20,200	33,800	
K	8,300	5,800	11,400	14,400	10,600	11,800	10,500	10,900	8,800	34,000	
P	1,222	830	960	1,050	1,090	2,050	740	960	1,050	870	
Mn	1,550	1,550	774	1,160	1,550	2,162	774	1,160	1,160	465	
Ti	13,300	9,700	13,200	12,800	18,400	17,700	11,700	10,500	13,000	5,200	
S	960	2,770	2,180	2,400	2,180	4,900	1,970	1,120	1,330	1,170	

	A	B	C	D	E	F	G	H	I	J	Sensitivity
Rb	5	3	18	25	10	15	20	18	9	100	1
Li	12	20	40	32	3	20	28	40	9	50	1
Ba	950	650	2,600	1,250	450	400	500	550	800	1,200	5
Sr	900	300	950	950	1,200	300	1,000	650	1,000	450	5
Cr	750	950	180	40	*	<1	400	400	550	*	1
Co	90	85	60	80	55	55	50	55	70	10	2
Ni	340	430	70	90	50	45	110	100	120	40	2
Zr	290	220	240	240	160	180	280	220	290	1,100	10
La	*	*	*	*	*	*	*	*	*	75	30
Y	50	25	50	70	60	60	50	45	60	200	30
Cu	40	25	70	50	80	60	40	35	35	10	3
V	330	220	360	360	450	220	390	250	340	8	5
Ga	30	6	40	40	35	32	35	12	30	40	1
Tl	*	*	*	*	*	*	*	*	*	*	30
Sn	*	*	*	*	*	*	*	*	*	*	5
Pb	<10	<10	<10	<10	<10	<10	<10	50	<10	10	10
Sc	<10	10	*	*	*	*	*	20	<10	*	10
Mo	*	3	*	*	*	2	*	*	*	4	1
Ge	*	*	*	*	*	*	*	*	*	*	10
Be	*	*	*	*	*	*	*	*	*	5	5
Ag	1	10	1	1	2	1	4	10	1	2	1
In	*	*	*	*	*	*	*	*	*	*	10

(*) Chemical analyses (T.C. Day, analyst) in Campbell et al (1933 and 1934) include

		Locality	H_2O+	H_2O-	CO_2	Total
A	Olivine basalt	Braefoot Bay, Fife.	4.74	0.92	0.15	100.08
B	Picroteschenite	" " "	4.97	4.40	0.29	99.96
C	Medium-grained teschenite	Quarry, near summit of Braefoot promontory, Fife	4.67	0.69	0.12	99.76
D	Coarse-grained teschenite	Birkhill Wood Railway cutting, Fife	4.27	0.60	1.19	99.76
E	Chlorophaeite-dolerite-pegmatite	Braefoot Pier, Fife	1.70	2.07	3.02	100.57
F	Chloritised-dolerite pegmatite	80 yards north-west of Braefoot Pier, Fife	4.64	0.82	2.27	99.96
G	Dolerite	Braefoot Plantation, Fife	2.56	0.57	2.80	100.07
H	Ocellar basalt	Dalgety Bay, Fife, 330 yards north of Braefoot Pier	3.30	0.99	10.11	100.46
I	Upper basalt	" " " 370 yards " " " "	2.05	0.92	1.16	99.88
J	Microsyenite	330 yards north of Braefoot pier, Dalgety Bay, Fife	1.84	0.51	0.93	100.03

Spectrographic analyst: R.A. Higazy

*Element if present is in amount less than its limit of sensitivity