

THE GEOCHEMISTRY OF THE MARANGUDZI COMPLEX,
SOUTHERN RHODESIA .

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by

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A B S T R A C T

The Marangudzi igneous ^{complex}, S . Rhodesia, consists of a gabbro mass intruded by quartz syenite ring dykes, nepheline syenite cone sheets and phonolitic dykes.

Typical specimens of the main rock types have been analysed for major elements and the results discussed with reference to possible differentiation trends. The most striking property of the complex is its potash rich character. The crystallisation of the rocks is discussed in relation to the syrtetic system Ne-Ks-Qu. The chemistry and mineralogy of feldspars, nephelines, pseudoleucites, amphiboles and magnetites have been studied. Trace elements Li, V, Cr, Co, Ni, Cu, Ge, Rb, Sr, Y, Zr, Nb, Cs, Ba, Yb and Ta have been determined in selected rocks and minerals.

The petrogenesis of the quartz and nepheline syenites from a common parent magma is discussed with reference to the crystallisation of leucite, hastingsitic amphibole and biotite and the influence of volatiles is also considered. The porphyritic quartz syenites are more closely associated with the nepheline syenites than with the main oversaturated ring quartz syenites. The juvites although of late intrusion, crystallised from a comparatively early formed liquid.

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C H A P T E R 1

GEOLOGY OF THE MARANGUDZI RING COMPLEX

The Marangudzi ring complex is located near the southern border of Southern Rhodesia, 50 miles east of Beitbridge. It was mapped and the structural geology and petrology described by Rees (1960) and Gifford (1961). The following description of the geology of the complex is mostly summarised from the work of these two authors. However, on the basis of petrographic and chemical evidence, I have reclassified some of the rock types. I have used chemical evidence to modify the order of intrusion given by Rees and Gifford, especially where the field evidence is inconclusive.

The complex extends over an area of approximately 33 square miles and is intruded into the high grade metamorphic basement. The complex consists essentially of a gabbro mass, quartz syenite ring dykes, nepheline syenite cone sheets and phonolite dykes radiating from the undersaturated centre of intrusion (Fig. 1). Rocks intermediate in composition between the gabbros and the syenitic rocks have, so far, not been found.

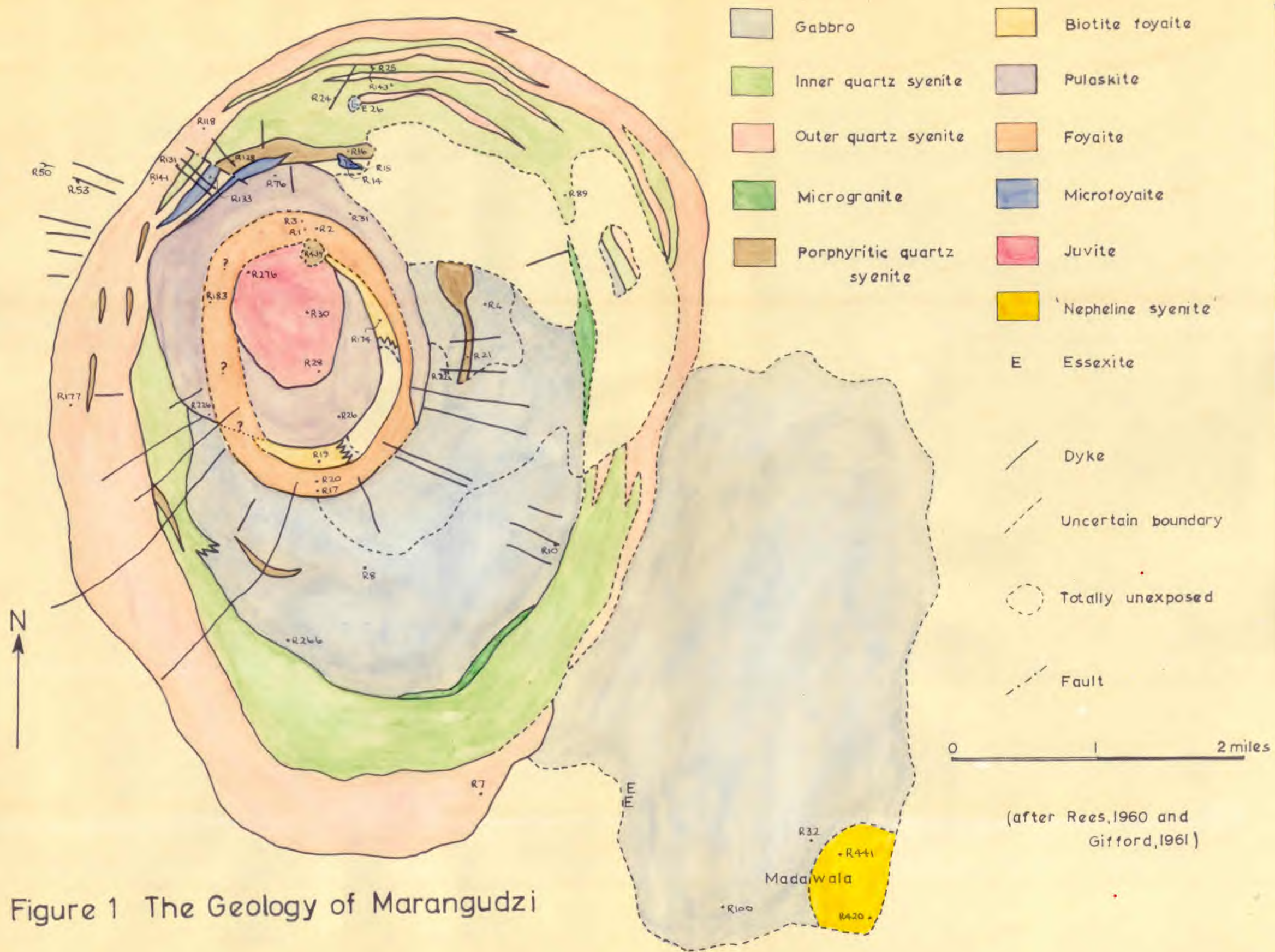


Figure 1 The Geology of Marangudzi

(after Rees, 1960 and Gifford, 1961)

The major intrusions

The suggested order of intrusion of the major rock types is:-

1. Gabbro.
2. Inner quartz syenite, outer quartz syenite and microgranite ring dykes, i.e. the main oversaturated ring.
3. Porphyritic quartz syenite ring dyke and plug.
4. Biotite foyaite, pulaskite, foyaite and microfoyaite cone sheets.
5. Juvite core.

1. The gabbro, which occupies half the area of the complex, is elongated in a N.W.-S.E. direction and is a medium grained rock consisting essentially of plagioclase and pyroxene with frequent biotite and small amounts of olivine. Xenoliths of basic material occur in most rock types in varying amount and extent of assimilation.
2. The gabbro is cut by steep sided rocks of the main oversaturated ring which takes up three-eighths of the total area of the complex. The outer quartz syenite was originally mapped as granite but the samples chosen by Rees and Gifford as typical specimens contain less than 10% quartz and are quartz syenites. The quartz content in rocks of the outer quartz syenite ring is extremely variable and quartz rich syenites and granites are found to a limited extent at the periphery of the ring. These syenites are medium grained and consist essentially of alkali

feldspar and amphibole with variable amounts of quartz.

The inner quartz syenite is a medium to coarse grained rock which consists mostly of green alkali feldspar with minor quantities of quartz and mafics which are interstitial to the feldspar. The inner quartz syenite seems to be an earlier intrusion than the outer quartz syenite.

The microgranite is exposed along the inner contact of the main oversaturated ring and forms a narrow discontinuous arc. It consists mostly of alkali feldspar and quartz and seems to be the youngest member in this group of rocks.

The main oversaturated ring contains many basic xenoliths especially to the N and N.W. Some of these have sharp margins but others show effects of assimilation with development of alkali feldspar and quartz in the basic matrix.

3. The porphyritic quartz syenites occur as two separate intrusions. The first is a discontinuous ring dyke whose centre of intrusion is offset to the N.W. of the main oversaturated ring centre. This rock varies in grain size and quartz content. It typically has porphyritic alkali feldspar and xenocrystic plagioclase set in a matrix of feldspar, amphibole and quartz. It contains abundant small oval fragments of mafic material which may be the remnants of assimilated gabbro xenoliths. The age of this ring is uncertain. Although it is seen as masses in the

main oversaturated ring, it is uncertain whether these are intruded into the main ring or whether they are screens of older rock caught up in younger magma which crystallised to give the inner and outer quartz syenites. The other intrusion of porphyritic quartz syenite is seen as a single mass in the undersaturated rocks. The rock is medium grained with phenocrysts of alkali feldspar and quartz is usually a minor constituent. This rock mass is most likely a plug, connected with the porphyritic quartz syenite ring dyke, which was enveloped by younger undersaturated rocks.

4. Nepheline syenite cone sheets cut both the oversaturated rocks and the gabbro, their centres of intrusion being to the N.W. of the main oversaturated ring centre.

The biotite foyaite, from chemical evidence, seems to be the oldest undersaturated rock type. It is intruded around an inlier of gabbro which is considerably broken up at the contact and the biotite foyaite contains many xenoliths of gabbro, especially near the contact. The typical rock is medium to coarse grained with only small amounts of nepheline.

The pulaskite occurs as a steeply inclined cone sheet. The typical rock is medium to coarse grained equigranular and consists essentially of alkali feldspar and amphibole with smaller amounts of plagioclase and nepheline. Basic xenoliths, in various stages of assimilation, are found within the pulaskite mass.

The pulaskite ring is cut by foyaite. These range in texture from coarse grained granular rocks to porphyritic types with alkali feldspar phenocrysts set in a fine grained groundmass. The large feldspars often show a sub-parallel arrangements giving the rock a typically foyaitic texture. The normal foyaite consists of alkali feldspar, nepheline (in greater amount than in pulaskite) and amphibole. In places it contains pseudoleucites but these are rather rare.

The microfoyaite is intruded into the pulaskite and main oversaturated ring as a discontinuous cone sheet. It is a fine grained porphyritic rock with phenocrysts of feldspar and amphibole and contains rare pseudoleucites. The phenocrysts show a sub-parallel arrangement and give the rock a foyaitic texture.

Gifford (1961) found difficulty in mapping the boundaries between the pulaskite and foyaite as the main difference between these rock types is that of nepheline content. He suggested that, on the basis of petrographic evidence, part of the undersaturated intrusion to the N.E., although mapped as pulaskite, might be foyaite. He also suggested that the foyaite ring might be continued in the western part of the undersaturated intrusion; this also was originally mapped as pulaskite. Chemical evidence from the western part of the undersaturated intrusion substantiates Gifford's suggestion and the foyaite is shown as a complete ring on the map (Fig. 1).

The age relations between the biotite foyaite, pulaskite, foyaite and microfoyaite are rather complex. This is reflected in their field occurrence and chemistry and the latter suggests considerable overlap between the various rock types.

5. The juvite, which is a nepheline rich syenite, is found in the core of the pulaskite and foyaite rings. It seems to be the youngest of the major intrusions, however, certain aspects of its chemistry cast doubt on this. It is very variable and consists of two main types. The first is a coarse grained pseudoleucite bearing rock. At some localities the rock is very rich in pseudoleucites (up to 10 cm diameter) and at others they are comparatively rare. The second is a medium to coarse grained rock which does not contain pseudoleucites. These two rock types are intimately intruded.

The minor intrusions

Two small intrusions of essexite are seen in the northern part of the main oversaturated ring. There is a similar small essexite mass intruded into the gabbro in the S.E. of the complex. The essexites show considerable brecciation and may represent volcanic pipes. Dolerites and microgabbro dykes make up the other basic minor intrusions.

Trachytic dykes intrude all the oversaturated rock types but are never seen in the undersaturated rocks.

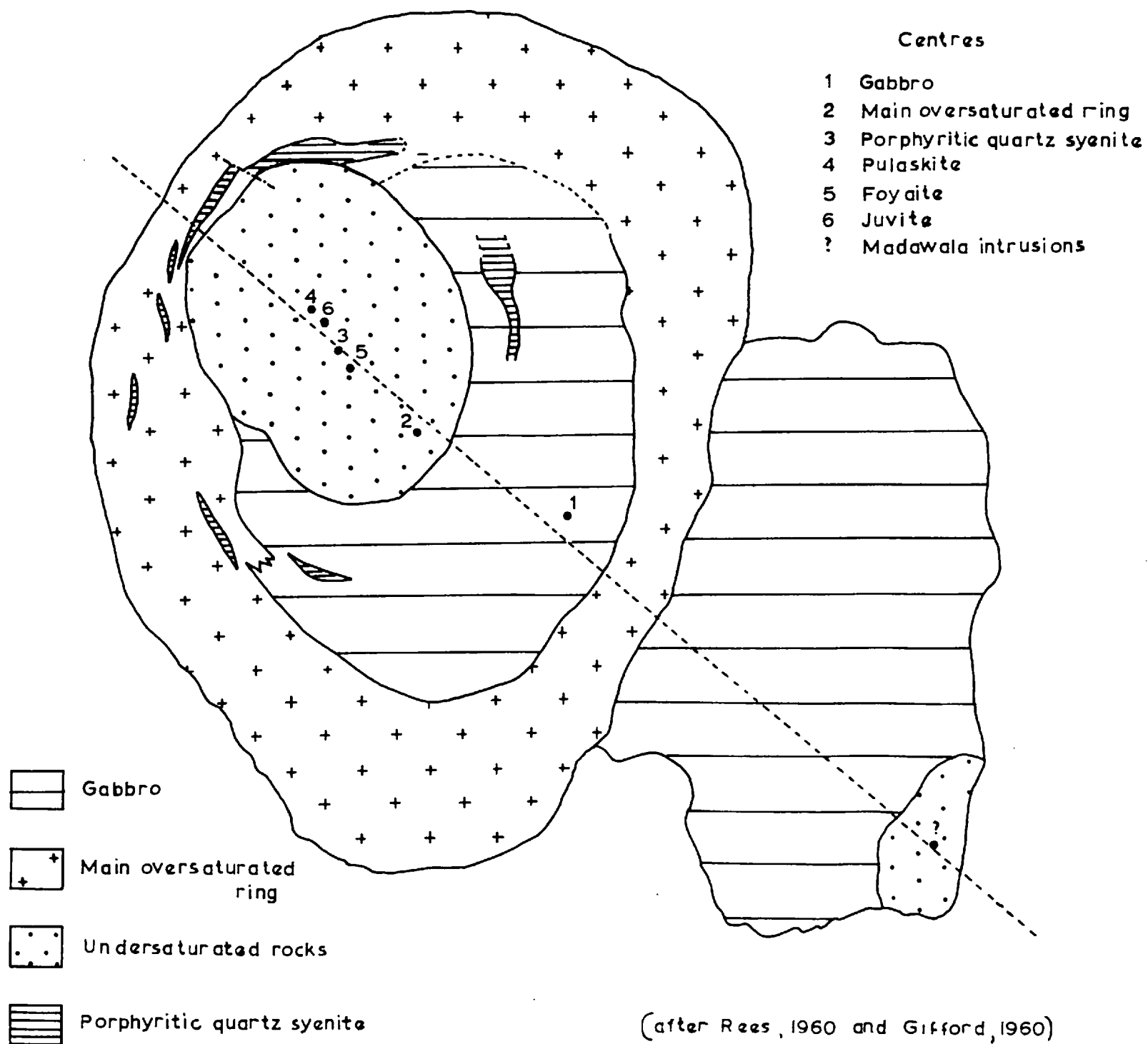
The dominant minor intrusives are phonolitic dykes which are of several types: (1) Non-porphyrific phonolites, (2) Porphyritic phonolites with alkali feldspar phenocrysts, and (3) Phonolites with pseudoleucites which vary in size up to 10 cm. diameter and which make up about 10% of the rock. These dykes radiate from the alkali centre and usually have sharp and parallel sides. Their main concentration is along E-W lines and they often extend up to 16 miles into the basement. All varieties of phonolitic dykes cut the oversaturated rocks, biotite foyaites, pulaskites, foyaites and microfoyaites. Only a few pseudoleucite bearing phonolites are seen cutting the juvite and this seems to confirm that the juvite is the latest intrusion.

Other rocks are poorly exposed at Madawala to the S.E. of Marangudzi. They consist of nepheline syenites, pseudoleucite bearing syenites and nepheline bearing ultrabasic rocks (malignites). The relationship between these rocks and the Marangudzi rocks is uncertain.

Structure

The centres of intrusion of the various rings lie in a S.E.-N.W. line and there was a progressive shift of activity to the N.W. (fig. 2). The centre of the porphyritic quartz syenite ring dyke is nearer to those of the undersaturated intrusions than to that of the main oversaturated ring.

Figure 2 Centres of intrusion



(after Rees, 1960 and Gifford, 1960)

Rees (1960) and Gifford (1961) suggested that the presence of (a) flow banding, (b) lack of clean contacts, and (c) evidence of contamination in the various rock types, indicate that intrusion occurred while the earlier rock types were still rather mobile.

CHAPTER 2

PETROGRAPHY OF THE ROCKS

The descriptions of the typical rock types given here are largely summarised from the work of Rees (1960) and Gifford (1961). Where the analysed rocks differ from the typical rock types I have given separate descriptions. The modes (volume %) of the rocks analysed for major elements are given in Table 1. Owing to the alteration of the essexite, inhomogeneity of the juvites and fine grain size of the phonolites it was impractical to determine their modes. Although the essexite and the gabbro mass seem to be unrelated, it is convenient to discuss their petrography (and chemistry) in the same section.

The basic rocks

The gabbro has laths of plagioclase up to 1 cm. long which show carlsbad, albite and pericline twinning. The range in composition is from An_{90} to An_{60} . Pyroxene is anhedral and occurs as grains and patches interstitial to the plagioclase; these minerals often occur in poikilitic texture. The pyroxene is pale green and is near augite in composition. Olivine occurs as small grains interstitial to the plagioclase and sometimes shows alteration to serpentine and ore. The range of composition is from Fa_{20} to Fa_{45} . Biotite is interstitial to plagioclase and is often seen rimming olivine, pyroxene and ore. Accessory

1

[illegible]

minerals are iron ore and apatite.

Analysed specimens R.4, R.8, R.75, R.100 and R.266 are similar to the typical rock type described above. R.4 has plagioclase of composition An_{83} and olivine Fa_{43} . Plagioclase from R.8 is An_{65} and that from R.266 is An_{83} . The latter co-exists with olivine of composition Fa_{33} .

The essexite contains phenocrysts of augite (up to 1 cm. across), olivine (4mm.) and plagioclase (3mm.). The ground mass is fine grained and consists of an intimate intergrowth of plagioclase, alkali feldspar, nepheline, pyroxene, olivine, biotite, ore and apatite. Pyroxene and olivine are usually altered to amphibole, biotite, chlorite and serpentine.

E.26 has been analysed and is a typical essexite. Gifford (1961) gives the composition of the plagioclase phenocrysts as An_{90} and the groundmass plagioclase as An_{66} .

The dolerites R.25 and R.50 are fine grained rocks with plagioclase and pyroxene in ophitic texture. The pyroxene in both rocks is augite. R.25 has a high modal content of biotite and has accessory olivine and ore. R.50 is rich in pyroxene which shows alteration to chlorite. Ore is abundant as skeletal grains.

The oversaturated rocks

The inner quartz syenite is inequigranular with large subhedral alkali feldspars, smaller subhedral mafics and plagioclase and small grains of olivine and interstitial quartz. The alkali feldspar forms tabular grains up to 5mm. long and is a microperthite. The exsolution grains of plagioclase are often large enough to show albite twinning. Discrete grains of plagioclase in the oligoclase-andesine range of composition also occur. Pale green clinopyroxene is of variable size up to 3mm. long. It is a diopside and shows alteration to hastingsitic amphibole which is pleochroic with X pale brown, Y brown-green, Z dark green. The pyroxene contains inclusions of ore and apatite and is intergrown with ore mineral. Small amounts of altered olivine and quartz are present, the latter varying from 0 to 10 %. Accessory minerals are allanite and zircon.

Analysed samples R.89, R.103, and R.143 are typical specimens with R.89 containing very little quartz. None of them contain any discrete plagioclase.

The outer quartz syenite is inequigranular with subhedral alkali feldspar forming the largest grains (up to 4mm. long). The feldspar is a microperthite which often shows carlsbad twinning. Some of the larger perthite grains have cores of soda rich plagioclase which may, or may not, be twinned. The interstices between the larger feldspars are filled by finer grained subhedral alkali feldspar, anhedral amphibole and quartz. The grain size

of the amphibole is variable, the largest grains being 1mm. across. It sometimes has small cores of diopsidic pyroxene and has inclusions of ore, zircon and allanite. It is pleochroic with X pale brown, Y green, Z dark olive-green and is a hastingsite. Quartz content is extremely variable and infrequently is as high as 30%. Accessory minerals are ore, allanite and zircon.

Analysed samples R.7, R.118, R.141 and R.177 are typical examples. All of them have less than 10% quartz and are lacking pyroxene and discrete plagioclase.

The microgranite is a fine grained rock consisting essentially of an intergrowth of perthitic alkali feldspar and quartz. Amphibole is anhedral with X yellow-green, Y green, Z dark green and is rather altered to biotite. Accessory minerals are allanite, zircon and ore.

R.753 is a medium grained inequigranular granite. Perthitic alkali feldspar forms the largest grains (5 mm. long). The groundmass is a finer grained intergrowth of perthite, quartz and exsolved albite. Ore and biotite are present in small amount. This sample was loaned by the Research School of African Geology, Leeds University, and its precise location is not known.

The porphyritic quartz syenite ring dyke has phenocrysts of tabular alkali feldspar (up to 5mm. long) which is a micro-perthite. The plagioclase xenocrysts (2mm. long) are strongly

zoned in the andesine-oligoclase range of composition and have reaction rims of alkali feldspar. These plagioclases often have bleb-like inclusions of mafic minerals at their cores. The groundmass is composed of a variable grain size intergrowth of alkali feldspar, plagioclase (albite-oligoclase), quartz and amphibole. Amphibole generally occurs as ragged crystals and aggregates and is a hastingsite with X pale green, Y green-brown, Z dark green. It contains inclusions of apatite and ore and sometimes shows alteration to biotite. Quartz occurs as small grains interstitial to the other minerals and varies in amount from 0 to 20%, therefore some of these rocks are more properly described as granites. Accessory minerals are ore (usually associated with amphibole) and zircon.

Analysed samples are R.16 and R.21 . R.16 has a high modal content of quartz, whereas R.21 contains only a trace.

The porphyritic quartz syenite plug has tabular phenocrysts of microperthitic feldspar up to 2cm. long; these sometimes have cores of plagioclase (andesine). The groundmass consists of a medium grained intergrowth of microperthite , lath like grains of weakly zoned plagioclase (andesine), amphibole and quartz. The amphibole is pleochroic with X pale straw, Y brown, Z olive-green and is a hastingsite. It sometimes shows alteration to biotite. Quartz is interstitial to the other minerals and varies from 0 to 10 modal %. Accessory minerals are ore, allanite, zircon and apatite.

Analysed sample R.439 contains an amphibole which is much altered to biotite and ore. Some of the larger biotite grains are zoned from brown at the core to green at the rim. Quartz is present in very small amount and secondary calcite occurs in the groundmass.

The Undersaturated Rocks

The biotite foyaites are a rather variable series of rocks. They are usually medium grained and subhedral alkali feldspar forms the largest grains (up to $2\frac{1}{2}$ mm. long). Plagioclase in the composition range oligoclase-labradorite is present and often has reaction rims of alkali feldspar. Nepheline is present in small amount and is rather altered to cancrinite. Sodalite is also present in small amount. In the plagioclase rich types nepheline is usually absent. The rocks vary from pyroxene rich to biotite rich. The pyroxene is a green diopside which has reaction rims of amphibole and biotite. Discrete grains of biotite are coloured a deep brown. Amphibole also occurs as discrete grains and is a hastingsite with X straw, Y green-brown, Z dark olive-green. Accessory minerals are apatite and ore (usually associated with the mafics). Other facies of this rock type vary from normal foyaites to altered gabbros and the latter types occur near the gabbro inlier.

R.19 is an analysed rock. It is medium grained with tabular perthitic alkali feldspar up to 5mm. long. Plagioclase occurs as small subhedral grains and is labradorite.

Nepheline is present in small amount and is intergrown with, and interstitial to, the alkali feldspar. Green pyroxene shows alteration to hastingsite and biotite is abundant as laths up to 4 mm. long; these biotites show effects of strain. Ore occurs in intimate association with the mafics and accessory apatite is abundant. A mafic free area consisting of an intimate intergrowth of alkali feldspar and nepheline is a pseudoleucite. R.174 is similar to R.19 but has a large amount of amphibole present.

The pulaskite is equigranular with tabular grains of alkali feldspar up to 5mm. long, this may, or may not, be perthitic. Subhedral plagioclase occurs as discrete grains up to 1mm. long and is of oligoclase composition. Amphibole grains occur as subhedral laths up to 5mm. long and also as much smaller irregular grains. The larger grains sometimes have cores of a green diopsidic pyroxene. The amphibole is a hastingsite with X pale straw, Y brown, Z dark green-brown. Nepheline is anhedral and is interstitial to the other minerals, it may show considerable alteration to sericite, cancrinite and zeolites. The nepheline content is rather variable but is usually less than 5%. Accessory minerals are apatite, ore and allanite.

Analysed specimens are R.26, R.31 and R.76. R.26 has a slightly zoned plagioclase which sometimes shows alteration to scapolite. The large grains of amphibole tend to collect in

aggregates and have inclusions of ore and apatite. They are colour zoned from brown at the centre to green at the periphery and infrequently have cores of diopside. Nepheline is the principal feldspathoid and is usually altered. Sodalite is also present in small amount. R.31 and R.76 are similar and have more modal pyroxene (at the cores of the larger amphiboles) and less plagioclase than R.26. The amphiboles are zoned as in R.26 but are coloured a much darker brown and sometimes show alteration to biotite.

The foyaites vary, in texture, from medium grained granular to fine grained porphyritic. The porphyritic types have elongated phenocrysts of alkali feldspar (up to 1 cm. long) and amphibole (4mm. long) and these show a sub-trachytic (foyaitic) texture. The alkali feldspar, whether as phenocrysts or smaller prismatic grains, varies from homogeneous to cryptoperthitic. Nepheline never occurs as phenocrysts but occurs as subhedral grains or irregular patches interstitial to the groundmass feldspar and amphibole. The nepheline grains are typically about 1mm. across with a maximum size of 2mm. Sodalite is also present and feldspathoids make up more than 10% of the rock. Amphibole occurs as subhedral laths and is a hastingsite with X pale green, Y dark olive-green, Z green. In the porphyritic types amphibole also occurs as small grains and blebs in the groundmass. Accessory minerals are apatite and ore. The hastingsites in

the foyaïtes differ from those of the pulaskites in that they have green pleochroism. The pulaskite hastingsites have brown pleochroism. Pesudoleucites have been found in the foyaïtes but are rather infrequent.

Analysed foyaïtes R.2, R.3, R 20 and R.183 are all porphyritic types. The phenocrystic amphibole often occurs in glomeroporphyritic texture. It is zoned from pale brown at the centre to green at the periphery and has inclusions of ore. The groundmass feldspars have clear cores and cryptoperthitic rims. R.3 has a small amount of aegirine present. R.17 has a similar texture to the above types but contains discrete plagioclase. It has a higher amphibole and a lower nepheline content than the other foyaïtes. The plagioclase is often untwinned and has thick rims of alkali feldspar. This rock has certain affinities with the pulaskites but its high nepheline content and the green pleochroism of its amphibole warrant its classification as a foyaïte. R.226 is similar mineralogically to the other foyaïtes but is a medium grained granular rock.

R.183 and R.226 were originally mapped as pulaskites but, on the basis of their high nepheline content and green pleochroism of the amphiboles, they have been reclassified as foyaïtes.

The microfoyaite is inequigranular with subhedral alkali feldspars (up to 2 mm. long) which have a foyaitic texture. The feldspar can either be homogeneous or cryptoperthitic. Nepheline occurs as equidimensional grains intergrown with the alkali feldspar and sodalite shows similar textures. Amphibole occurs as small laths and blebs and is sometimes included in the feldspar and nepheline grains. It is a hastingsite with X pale brown, Y green, Z dark green. The amphibole laths also show a foyaitic texture. Iron ore is an accessory mineral.

R.14, R.15 and R.133 are analysed microfoyaite. R.14 and R.15 have sodalite as the dominant feldspathoid and nepheline shows alteration to sericite. The amphibole in all three rocks is zoned from brown at the centre to green at the periphery and the feldspar is cryptoperthitic.

The juvite is a very inhomogeneous rock and contains pseudoleucites in variable amount and all stages of alteration. In some, the original boundaries have been completely lost and the pseudoleucite is only recognisable in that it forms a roughly circular and mafic free area. The matrix between the pseudoleucites is a feldspathoid rich syenite. It varies from fine to coarse grained and consists of feldspar, nepheline, pyroxene and amphibole. The alkali feldspar is usually homogeneous. The nepheline is much altered to cancrinite, sericite and zeolites and these show intimate intergrowths with the alkali feldspar.

Pyroxene and amphibole occur in roughly equal proportions and a small amount of biotite is also present. The pyroxene is a green diopside and the amphibole is a hastingsite with X pale brown, Y dark brown, Z green-brown. Biotite is zoned from brown at the centre to green at the rim. The pseudoleucites consist of intergrowths of nepheline (altered) and feldspar with included mafics.

Analysed rocks are R.28, R.30, R.276 and R.730. The approximate mode of R.28 is 45% feldspar, 40% nepheline (and alteration products) and 15% mafics. Pseudoleucites are of variable size. Pyroxene and amphibole are present in equal proportions and show slight alteration to chlorite. Ore is associated with the mafics and accessory apatite is present; secondary calcite occurs in the groundmass. R.30 is similar to R.28 and contains small pseudoleucites. The amphibole is zoned. R.276 is a medium grained rock and is mineralogically similar to R.28. It has 40% feldspar, 40% nepheline and 20% mafics. R.730 is richer in mafic minerals than the other juvites. Nepheline is present as euhedral grains and pseudoleucites are absent. Diopside (dark green) and hastingsite are present in equal proportions. The hastingsite has X golden-brown, Y brown, Z dark brown. The mafic minerals show glomeroporphyritic texture and are associated with ore. R.730 was loaned by the Research Institute of African Geology, Leeds University, and its precise locality is unknown.

The undersaturated dyke rocks are dominantly phonolites, the most distinctive type being a pseudoleucite phonolite. The phonolites are fine grained, dark grey-green rocks which may have phenocrysts of alkali feldspar (up to 5mm. long), nepheline (2mm.) or pseudoleucite (10 cm. diameter). Micro-phenocrysts of diopside and biotite also occur. The alkali feldspar is homogeneous and shows carlsbad and baveno twinning. Nepheline phenocrysts often form glomeroporphyritic aggregates and the mafics typically have dark rims. The pseudoleucites usually make up about 10% of the rock. They consist of a fine grained intergrowth of nepheline and feldspar and show extensive alteration even though the original crystal shape is maintained. The groundmass is very fine grained and consists of an intergrowth of alkali feldspar, nepheline, pyroxene, amphibole and ore.

R.10, R.22, R.24, R.53, R.128 and R.129 are analysed phonolites. Pseudoleucites are usually up to 2 cms. diameter and have well shaped boundaries. R.131 is a pseudoleucite bearing dyke which contains a hastingsitic amphibole.

The Madawala rocks

Nepheline syenites vary from fine grained to medium grained types. Some are porphyritic with phenocrysts of alkali feldspar, nepheline and pseudoleucite. Groundmass feldspar and nepheline are intergrown and both show alteration;

feldspar to sericite, nepheline to cancrinite and zeolites. Nepheline and its alteration products usually make up about 10% of the rock. Mafic minerals are augite, amphibole and biotite. R.420 and R.441 are analysed types; both are much altered and have secondary calcite in the groundmass.

The malignite is a dense, medium grained, dark grey rock. Subhedral clinopyroxene and phlogopite are the most abundant minerals. The interstices between these are filled with an intergrowth of nepheline and alkali feldspar. The pyroxene is usually a titaniferous augite with rims of aegirine-augite and inclusions of ore and apatite. The phlogopite occurs as laths up to 3mm. long and is coloured a golden-brown. Ore and apatite are accessory minerals.

R.32 is an analysed specimen. The phlogopite laths are strained and accessory apatite is abundant.

Rocks analysed for major and trace elements

(see figure 1 for localities)

R.4	Gabbro
R.8	Gabbro
E.26	Essexite
R.89	Inner quartz syenite
R.143	Inner quartz syenite
R.7	Outer quartz syenite
R.141	Outer quartz syenite
R.177	Outer quartz syenite
R.16	Porphyritic quartz syenite (ring dyke)
R.21	Porphyritic quartz syenite (ring dyke)
R.439	Porphyritic quartz syenite (central plug)
R.753	Granite (sample locality unknown).
R.19	Biotite foyaite.
R.26	Pulaskite
R.31	Pulaskite
R.76	Pulaskite
R.2	Foyaite
R.3	Foyaite
R.17	Foyaite
R.20	Foyaite

R.183	Foyaite
R.226	Foyaite
R.15	Microfoyaite
R.133	Microfoyaite
R.28	Juvite
R.276	Juvite
R.730	Juvite (sample locality unknown).
R.10	Phonolite
R.22	Phonolite
R.131	Pseudoleucite dyke
R.32	Malignite, Madawala
R.420	Nepheline syenite, Madawala

Rocks analysed for trace elements

R.75	Gabbro
R.100	Gabbro
R.266	Gabbro
R.25	Dolerite
R.50	Dolerite
R.103	Inner quartz syenite
R.118	Outer quartz syenite
T.14	Aplite

R.174 Biotite foyaite

R.1 Foyaite

R.14 Microfoyaite

R.30 Juvite

R.24 Phonolite

R.53 Phonolite

R.128 Phonolite

R.129 Phonolite

R.441 Nepheline syenite, Madawala.

CHAPTER 3

MAJOR ELEMENT GEOCHEMISTRY

The quartz and nepheline syenites are of very different compositions to the gabbros and rocks of intermediate mineralogical and chemical composition have not been found. I decided that it was impractical to attempt making a detailed chemical study of both the gabbros and syenites and therefore only briefly studied the gabbroic rocks.

I have analysed two gabbros, one essexite, eight oversaturated rocks and seventeen undersaturated rocks, all from the main Marangudzi complex. I have also analysed a malignite and a nepheline syenite from the Madawala complex, to the S.E. of Marangudzi. The Research Institute of African Geology, Leeds University, loaned me the analyses of a granite (R.753) and a nepheline syenite (R.730) both from the main complex. Analytical data are given in Table 2.

As the analysed quartz and nepheline syenites show little chemical variation within the two rock types the presentation of the analyses is difficult. I found it most convenient to discuss the variation in chemical composition with respect to the differentiation index $\frac{1}{3}\text{SiO}_2 + \text{K}_2\text{O} - \text{CaO} - \text{MgO} - \text{FeO}$

Table 2 : Major element analyses of Marangudzi igneous rocks

	R4	R8	E26	R89	R143	R16	R21	R439	R7	R141	R177	R26	R31	R76	R183	R226	R2	R3	R20	R17	R19	R15	R133	R28	R276	R10	R22	R131	R32	R420	R753	R730	
SiO ₂	46.40	46.62	49.00	61.98	63.20	67.56	59.06	62.02	64.00	63.05	63.98	53.96	56.85	56.65	54.96	55.31	53.45	56.42	56.03	51.60	48.13	57.18	55.92	51.49	51.22	51.12	50.55	54.59	39.90	46.02	73.51	46.82	SiO ₂
Al ₂ O ₃	24.02	22.57	14.51	16.67	15.51	15.12	18.13	17.83	16.23	17.31	15.81	19.42	17.72	17.98	21.16	22.50	19.90	21.77	18.43	18.54	19.55	19.57	19.69	23.06	22.63	21.01	20.48	19.54	10.27	20.21	13.05	23.46	Al ₂ O ₃
Fe ₂ O ₃	1.57	2.00	1.19	1.66	2.74	0.69	1.54	2.16	1.20	0.89	1.35	1.62	2.26	3.03	1.85	1.35	2.42	1.35	1.61	2.42	2.37	2.26	1.83	0.68	1.24	3.31	2.07	2.34	6.45	4.38	1.98	2.22	Fe ₂ O ₃
FeO	3.75	4.13	7.54	3.88	3.41	2.71	3.65	2.29	3.73	4.32	3.88	4.27	4.20	3.98	3.75	1.67	4.67	2.44	4.93	5.69	4.94	3.05	4.00	1.79	2.15	1.01	2.76	3.41	7.08	2.05	0.88	4.16	FeO
MgO	4.52	5.28	9.50	0.09	0.16	0.62	1.24	0.76	0.36	0.38	0.36	1.38	0.96	1.06	0.56	0.35	0.92	0.44	0.69	2.03	2.68	0.25	0.96	0.57	0.93	0.38	0.55	0.50	10.16	0.54	*	1.39	MgO
CaO	15.97	15.47	11.08	2.52	2.20	1.72	3.35	1.89	1.63	1.75	1.58	4.79	3.31	3.45	2.51	1.40	2.93	1.77	3.15	5.08	8.63	2.08	2.92	2.09	2.59	2.27	2.90	2.36	14.92	8.35	1.07	5.23	CaO
Na ₂ O	1.67	1.57	2.54	5.55	5.48	4.20	4.62	5.57	5.54	5.05	5.48	4.69	4.16	4.41	6.49	7.74	6.59	6.84	5.24	4.79	2.20	7.05	4.62	5.99	5.43	8.36	7.64	7.46	0.89	4.21	3.46	7.56	Na ₂ O
K ₂ O	0.56	0.69	1.74	6.73	5.85	6.02	6.69	6.41	6.64	6.80	6.28	6.90	7.95	7.60	7.97	8.10	7.04	8.31	8.49	6.49	7.30	6.69	8.09	11.16	10.45	7.49	7.79	8.13	3.77	9.58	5.58	6.13	K ₂ O
H ₂ O+	0.35	0.41	0.80	0.54	0.12	0.46	0.11	0.52	0.06	0.22	0.20	0.43	0.72	0.62	0.56	0.68	0.61	0.21	0.25	0.75	0.91	0.53	0.75	1.77	1.64	1.39	1.76	0.34	0.97	0.46	0.15	1.22	H ₂ O+
H ₂ O-	0.10	0.12	0.07	0.06	0.28	0.05	0.02	0.08	0.14	0.04	0.04	0.07	0.08	0.02	0.06	0.05	0.09	0.07	0.10	0.10	0.10	0.07	0.05	0.18	0.11	0.21	0.14	0.12	0.10	0.08	0.13	0.13	H ₂ O-
CO ₂	0.39	-	0.20	-	-	-	-	-	-	-	-	-	-	-	-	0.60	-	-	-	-	-	0.60	-	0.20	0.70	1.90	1.20	0.09	0.40	2.14	-	0.48	CO ₂
TiO ₂	0.27	0.58	0.67	0.32	0.43	0.46	0.42	0.31	0.41	0.51	0.45	0.48	0.77	0.66	0.21	0.10	0.30	0.16	0.38	0.62	0.88	0.15	0.34	0.19	0.23	0.37	0.26	0.16	1.92	0.35	0.22	0.52	TiO ₂
P ₂ O ₅	0.10	0.08	0.18	0.09	0.04	0.09	0.14	0.14	0.10	0.10	0.10	0.30	0.28	0.34	*	*	0.15	*	0.17	0.24	0.62	0.04	*	0.08	0.14	0.06	0.08	0.13	1.51	0.28	0.05	0.24	P ₂ O ₅
MnO	0.08	0.09	0.16	0.15	0.14	0.09	0.13	0.12	0.12	0.13	0.12	0.18	0.17	0.14	0.19	0.12	0.21	0.12	0.21	0.22	0.12	0.19	0.18	0.07	0.07	0.21	0.22	0.18	0.17	0.24	0.02	0.15	MnO
BaO	0.02	0.01	0.08	0.04	0.01	0.14	0.27	0.07	0.02	0.04	0.01	0.62	0.14	0.16	0.14	0.01	0.11	0.11	0.27	0.79	1.44	0.02	0.15	0.70	0.16	0.49	0.40	0.10	0.52	0.34	-	-	BaO
F	-	-	0.25	0.05	0.10	0.10	0.35	0.15	-	0.20	0.20	0.25	0.25	0.25	0.25	0.25	0.35	0.15	0.35	0.45	0.30	0.45	0.25	0.10	0.15	0.30	0.50	0.40	0.75	-	-	-	F
less O=F	-	-	0.10	0.02	0.04	0.04	0.15	0.06	-	0.08	0.08	0.11	0.11	0.11	0.11	0.11	0.15	0.06	0.15	0.19	0.13	0.19	0.11	0.04	0.06	0.13	0.21	0.17	0.32	-	-	-	less O=F
Total	99.77	99.62	99.41	100.31	99.63	99.99	99.57	100.26	100.18	100.71	99.76	99.83	99.71	100.24	100.54	100.12	99.59	100.10	100.15	99.72	100.04	99.99	99.75	100.08	99.78	99.75	99.09	99.68	99.46	99.23	100.10	99.71	Total

- absence of data * not detected

(Larsen, 1938). In the text this index will be denoted DI.

The DI has low values for early formed rocks and higher values for rocks formed progressively later. This index can be misleading in that it assumes a decrease in modal amount of mafic minerals with differentiation and ignores any iron enrichment in the mafic minerals with differentiation. However, in the Marangudzi rocks the iron enrichment in the amphiboles is accompanied by a decrease in modal % of amphibole. The increase in proportion of felsic minerals is therefore the dominant differentiation process.

The D.I. should only be used for rocks with similar mineral assemblages and therefore the values given for the quartz syenites cannot be directly compared with those for the nephelines syenites.

Thornton and Tuttle (1960) suggested the use of a differentiation index consisting of the sum of normative Qu, Or, Lc, Ks, Ab and Ne. This index is a measure of the nearness of the rocks to the system Ne-Ks-Qu (Petrogeny's residua system). It is inconvenient to use this index as over and undersaturated rocks have similar values to each other.

Variation of D.I.

Values of D.I. for the analysed rocks are given in Table 3. The gabbros and the essexite have values close to -10 but the malignite has a value of -20.9. The inner and outer quartz syenites show little variation in D.I., the former

Table 3 : Data for Marangudzi rocks

	R4	R8	E26	R89	R143	R16	R21	R439	R7	R141	R177	R26	R31	R76	R183	R226	R2	R3	R20	R17	R19	R15	R133	R28	R276	R10	R22	R131	R32	R420	R730	R753	
Larsen Index $(\frac{1}{3}\text{SiO}_2 + \text{K}_2\text{O}) - (\text{CaO} + \text{MgO} + \text{FeO})$	- 9.6	-10.5	-11.2	19.4	18.7	22.9	16.8	20.2	21.2	20.5	20.6	13.0	16.4	15.4	17.8	21.8	14.2	21.2	17.0	8.7	4.9	18.4	17.0	23.3	20.8	17.8	16.6	17.9	-20.9	10.0	8.9	26.3	Larsen Index $(\frac{1}{3}\text{SiO}_2 + \text{K}_2\text{O}) - (\text{CaO} + \text{MgO} + \text{FeO})$
Thornton and Tuttle Index $\text{Qu} + \text{Or} + \text{Lc} + \text{Ks} + \text{Ab} + \text{Ne}$	15.8	16.8	30.2	85.2	85.7	86.1	76.9	85.1	87.5	85.5	86.6	69.6	77.2	76.8	82.6	90.4	78.5	87.6	80.1	65.3	50.1	85.2	77.2	85.7	81.5	81.6	79.1	79.9	19.8	66.1	69.4	92.5	Thornton and Tuttle Index $\text{Qu} + \text{Or} + \text{Lc} + \text{Ks} + \text{Ab} + \text{Ne}$
FeO/MgO (wt%)	0.8	0.8	0.8	43.1	21.3	4.37	2.94	3.0	10.4	11.4	10.8	3.1	4.4	3.7	6.7	4.8	5.1	5.5	7.1	2.8	1.8	12.2	4.2	3.1	2.3	2.7	5.0	6.8	0.7	3.8	3.0		FeO/MgO (wt%)
Co-ordinates in system Ne - Ks - Qu																																	Co-ordinates in system Ne - Ks - Qu
Ne	-	-	-	29.7	29.6	22.4	27.8	30.0	28.6	27.4	28.9	31.0	24.6	26.2	36.2	38.9	38.3	35.7	29.7	33.5	20.1	37.5	27.2	32.2	30.6	42.1	41.2	37.4	-	28.0	50.4	17.2	Ne
Ks	-	-	-	25.8	22.8	23.4	29.2	25.2	25.6	27.1	24.5	33.2	34.8	33.3	32.6	30.0	30.2	31.7	35.5	33.4	48.9	26.0	35.2	43.8	43.1	29.7	32.1	34.4	-	46.7	29.5	20.5	Ks
Qu	-	-	-	44.6	47.6	54.2	43.0	44.8	45.8	45.5	46.7	35.8	40.6	40.5	31.2	31.1	31.5	32.6	34.8	33.1	31.0	36.5	37.6	24.0	26.3	28.2	26.7	28.2	-	25.3	20.1	62.3	Qu
Niggli Values																																	Niggli Values
c + fm.	64	66	73	27	29	24	34	26	26	26	26	36	34	36	26	15	32	19	32	44	52	24	31	17	22	21	25	25	82	40	34	19	c + fm
alk.	4	4	8	36	35	36	30	35	37	35	37	28	31	30	35	42	33	39	33	25	18	37	31	41	37	40	38	39	6	28	30	39	alk.
al.	32	30	19	37	36	40	36	39	37	39	37	36	35	34	39	43	35	42	35	31	30	39	38	42	41	39	37	36	12	32	36	42	al.

average 19 and the latter average 20.8 . The porphyritic quartz syenites vary from 16.8 (R.21) to 22.9 (R.16). and the granite R.753 has the highest value of 26.4 . The rock series biotite foyaite-pulaskite-foyaite-microfoyaite shows increasing values for D.I. and this agrees with the suggested order of intrusion. However, within each nepheline syenite cone sheet there is a considerable range of values. Biotite foyaite R.19 has a D.I. of 4.9 and is clearly an early formed rock. The pulaskites vary from 13.0 (R.26) to 16.4 (R.31) while the foyaites have a larger range from 14.2 (R.2) to 21.8 (R.226) . The plagioclase bearing foyaite R.17 has a D.I. of 8.7 and is an early formed rock. Microfoyaites R.15 and R.133 have values of 18.4 and 17.0 and fall in the late stage foyaite range. Rees (1960) and Gifford (1961) suggested that the foyaite ring was the product of multiple and continued intrusion of foyaitic magma. This is substantiated by the chemistry of the rocks and the variation of D.I. within the foyaites. The same seems to be true for the biotite foyaite, pulaskite and microfoyaite rings. The juvites may show a similar relationship as R.730 has a D.I. of 8.9 while R.28 and R.276 have values of 23.3 and 20.8 respectively. R.28 and R.276 are peculiar in that although they have high values for D.I., they contain mafic minerals with compositions typical of early formed rocks (i.e. low FeO/MgO ratios). These rocks are rich in pseudoleucites and therefore have high K_2O ; causing them to have anomalously high values for D.I. The phonolites have an average value for D.I. of 17.2 and the pseudoleucite bearing dyke R.131 has a value of 17.9 .

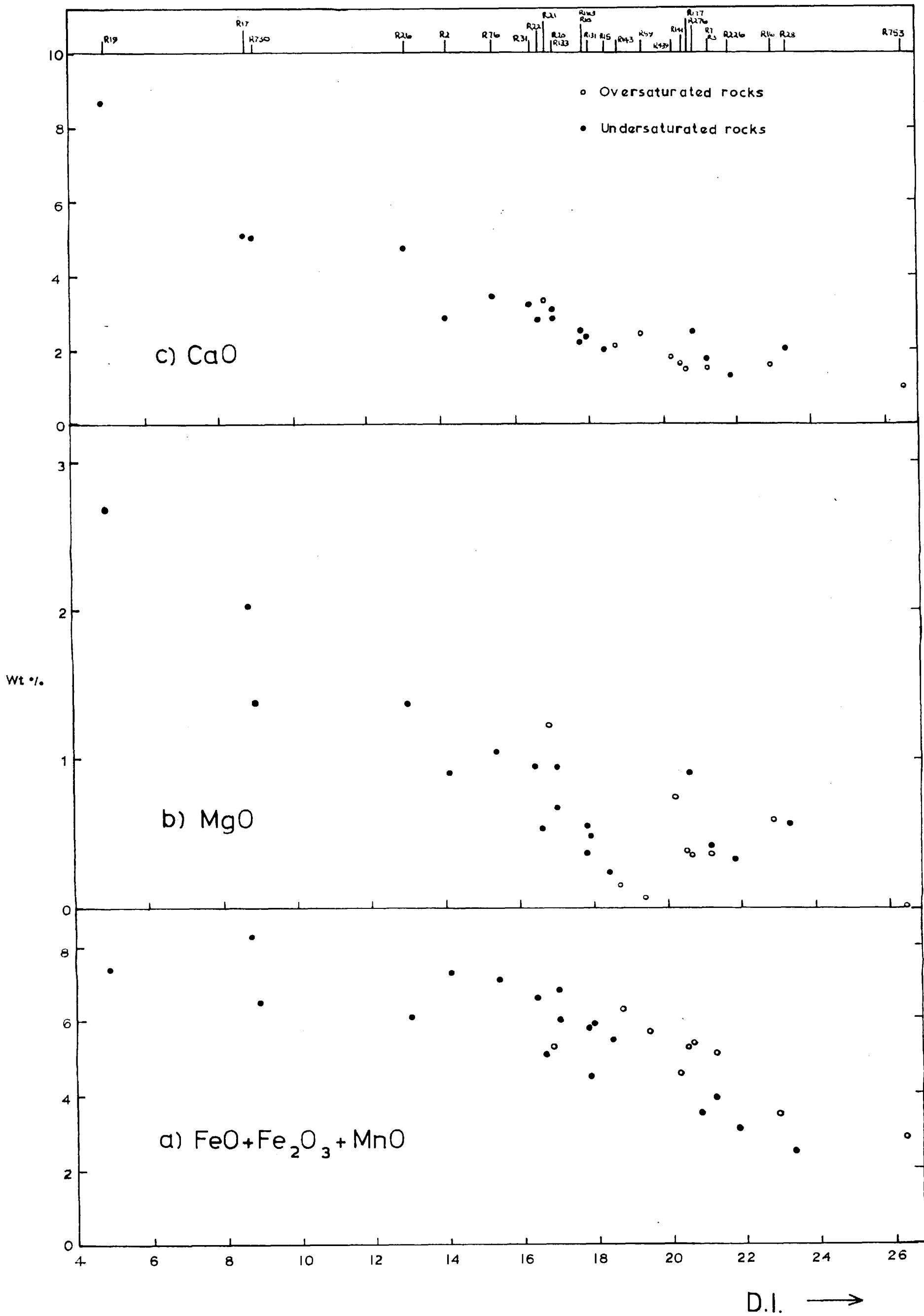
Systematic chemistry of the rocks

SiO₂ The analysed gabbros have similar SiO₂ concentrations (average of 46.5%) and the essexite is slightly higher with 49.0%. The malignite R.32 has the lowest SiO₂ (40%). Rocks of the inner and outer quartz syenite rings show only a small range in SiO₂ concentration from 62 to 64 % SiO₂. The porphyritic quartz syenites show a much larger range from 59.1 (R.21) to 67.6% (R.16) and the granite R.753 has 73.5% SiO₂. The rock series biotite foyaite, microfoyaite shows an increase in SiO₂ from 48.1 (R.19) to 57.2% (R.15) with increasing D.I. The juvites and phonolites have SiO₂ from 50.5 to 51.5 %.

Al₂O₃ The gabbros have higher Al₂O₃ contents than the essexite and the malignite has very low Al₂O₃. The felsic rocks show little systematic variation with D.I. but the quartz syenites have lower Al₂O₃, and the juvites and phonolites higher Al₂O₃, than the biotite foyaite - microfoyaite series.

FeO + Fe₂O₃ + MnO The malignite has much higher content of iron plus manganese than the gabbros and the essexite slightly higher. The felsic rocks show a general decrease of iron plus manganese with increase in D.I. (Fig. 3a). The oversaturated rocks show a decrease from 6.3 (R.143) to 2.9% (R.753). The series biotite foyaite - microfoyaite shows a decrease from 7.4 to 5.5 % but foyaite R.3 and R.226 have respectively 3.9 and 3.1 % and

Figure 3



are clearly late formed rocks. Foyaite R.17 has 8.3% and is an early formed rock. Juvites R.28 and R.276 and the phonolites have lower totals of iron and manganese than the other undersaturated rocks but juvite R.730 has 6.5% and is an early formed rock.

MgO The gabbros are lower in MgO than the essexite, malignite R.32 is slightly higher with 10.2%. Rocks of the main oversaturated ring have less than 0.5% MgO but the porphyritic quartz **syenites** have up to 1.2% . The rock series biotite foyaite - microfoyaite shows a decrease of MgO from 2.7 to 0.2% with increasing D.I. (Fig. 3b). Microfoyaite R.133 has 1% MgO and is an older rock than R.15. Juvites R.28 and R.276 have rather high MgO for their values of D.I. and this reflects the magnesium rich composition of their mafic minerals.

CaO The gabbros have CaO above 15%, the essexite is lower with 11% and the malignite has 14.9%. Rocks of the inner quartz syenite ring average 2.4% CaO while those of the outer quartz syenite ring are lower with an average of 1.7%. The porphyritic quartz syenites range from 1.7 (R.16) to 3.3% CaO (R.21). Undersaturated rocks show a decrease of CaO with D.I. (Fig. 3c) from 8.6% in the biotite foyaite to 1.4% in the late stage foyaite R.226.

Na₂O The gabbros contain an average of 1.6% Na₂O but the essexite is higher with 2.5% and the malignite has 0.9%. Oversaturated

rocks show little variation from 5.1% Na_2O but the porphyritic quartz syenites R.16 and R.21 are lower with an average of 4.4%. Under-saturated rocks have variable contents of Na_2O but the foyaites with the highest D.I. have the highest soda contents and the biotite foyaites is very low with 2.2% Na_2O . The phcholiths have the highest Na_2O concentrations (up to 8.4%).

K_2O The gabbros and essexite contain 0.6 and 1.7 % K_2O respectively and the malignite has 3.8%. The most striking property of the felsic rocks is their high potash content and all except R.730 contain an excess of K_2O over Na_2O (weight %). The oversaturated rocks show little variation in K_2O from 6.1% but the undersaturated rocks are higher than this and show an increase of K_2O with D.I. (microfoyaite R.15 has low K_2O for its D.I.). Pseudoleucite bearing juvites R.28 and R.276 contain especially high K_2O with greater than 10%. Pseudoleucite dykes R.10, R.22 and R.131 have lower K_2O than the juvites and this reflects the soda rich nature of their pseudoleucites.

TiO_2 The gabbros have 0.3 and 0.6 % TiO_2 and the essexite has 0.7%. The malignite is exceptionally high with 1.9% TiO_2 . The oversaturated rocks show little variation and average about 0.4% TiO_2 . The rock series biotite foyaites - microfoyaite shows a decrease in TiO_2 from 0.88 to 0.15 %. Microfoyaite R.133 has 0.34% TiO_2 and is an earlier rock than R.15.

P₂O₅ The gabbros contain 0.1%, the essexite 0.2% and the malignite is very high with 1.5% P₂O₅. The oversaturated rocks show little variation from 0.1% but the undersaturated rocks have decreasing concentrations with D.I. Biotite foyaite R.19 is especially rich with 0.6% and the microfoyaite R.15 has 0.04% P₂O₅.

CO₂ The juvites have 0.2 and 0.7 % CO₂ and the phonolites are very high with 1.2 and 1.9 %.

BaO The gabbros have less than 0.02% BaO, the essexite is higher with 0.08% and the malignite is very high with 0.52%. Rocks of the main oversaturated ring have less than 0.04% BaO but the porphyritic quartz syenites are higher with up to 0.27%. Rocks of the biotite foyaite - microfoyaite (late stage foyaite) series generally show a decrease in BaO content with increase in D.I. Biotite foyaite R.19 is exceptionally high with 1.4% BaO and the late stage foyaite R.226 has 0.01%. The juvites and phonolites have variable contents of BaO.

F The essexite has 0.25% and the malignite has 0.75% F. The oversaturated rocks generally have less than 0.2% F but porphyritic quartz syenite R.21 has 0.35%. The undersaturated rocks generally have rather higher F contents and vary from 0.25 to 0.5% but the juvites have less than 0.2%.

FeO/MgO Values for this ratio are given in Table 3. The oversaturated rocks show a haphazard variation in this ratio. The rock series biotite foyaite - microfoyaite shows a ^{increase} ~~decrease~~ in FeO/MgO, with increasing D.I., from 1.8 to 12.2. This must be due to the iron enrichment of the mafic minerals with differentiation. Foyaite R.17 has a FeO/MgO ratio of 2.8 and is clearly older than the other foyaites; microfoyaite R.133 has a ratio of 4.2 and is older than R.15. Juvites R.28 and R.276 have ratios typical of comparatively early formed rocks (3.1 and 2.3 respectively).

Comparison of modal and chemical data

The gabbros High CaO and Al_2O_3 reflect the large modal % of plagioclase and low MgO and FeO reflect the relatively low modal olivine and pyroxene. Biotite accounts for the fairly high K_2O .

The essexite Lower CaO and Al_2O_3 can be correlated with lower modal plagioclase than in the gabbros. Higher K_2O indicates a higher content of biotite and the presence of orthoclase.

The malignite Low Al_2O_3 reflects the absence of plagioclase and high CaO, MgO and FeO show a high modal content of pyroxene. High K_2O and P_2O_5 reflect the presence of biotite and apatite.

The oversaturated rocks High alkalis reflect the large amount of alkali feldspar and the potash rich character must be attributed to a potash rich alkali feldspar. The inner quartz syenites have

fairly high CaO but no modal plagioclase; the bulk of the CaO must be carried by the diopside and amphibole. Outer quartz syenites have less than 2% CaO and this is mostly carried by the amphibole as plagioclase is absent. The porphyritic quartz syenites have rather high CaO and this is accounted for by the presence of xenocrystic plagioclase. The relative constancy of FeO and MgO (except in R.753) is due to there being little variation in the amount of modal pyroxene and/or amphibole.

Rees (1960) and Gifford (1967) suggested that the low quartz content of the oversaturated rocks was caused by the assimilation of gabbroic rocks by a magma of granitic composition. This assimilation would cause the magma to become enriched in CaO, MgO, Al_2O_3 and impoverished in SiO_2 and alkalis. It is likely that the contaminated quartz syenite would contain xenocrysts of plagioclase and augite. The rocks of the main oversaturated ring show no evidence of xenocrystic minerals and have comparatively low CaO and MgO. Most of the CaO is carried by the amphibole. Only the inner quartz syenite contains modal pyroxene and this is an iron rich diopside. It is significant that the gabbro pyroxene is a magnesium rich augite. The analysed outer quartz syenites come from different parts of the ring but all have similar compositions; if contamination had been extensive this would be unlikely. For a reduction in SiO_2 of several %, the concentration of alkalis would also be considerably lowered. Uncontaminated granitic magma would therefore have to be extremely rich in alkalis to give quartz syenites of the present composition.

The porphyritic quartz syenites contain xenocrystic plagioclase and clots of mafic minerals, these rocks could have suffered considerable contamination.

Apart from the physical difficulty of extensive reaction between granitic magma and gabbroic rocks (considerable superheat would be needed) the chemistry of the rocks indicates that, for the main oversaturated ring, the contamination by basic material is a minimum. However, it may have been more extensive on a local scale and the porphyritic quartz syenites are certainly much contaminated.

The undersaturated rocks Low SiO_2 , high Al_2O_3 and high alkalis indicate the presence of nepheline and sodalite and, in the juvites and phonolites, the presence of pseudoleucite. High K_2O in the biotite foyaite is due to the large modal % of biotite. Comparatively high CaO in the pulaskites, biotite foyaite, foyaite R.17 and juvite R.730 indicates the presence of modal plagioclase. Generally higher FeO and MgO than in the oversaturated rocks reflects the higher modal content of mafic minerals. High TiO_2 in the biotite foyaite, pulaskite and foyaite R.17 indicates high TiO_2 in the contained amphiboles, biotites and ore. This is supported by the brown pleochroism of the amphiboles in these rocks. The foyaite and microfoyaite have lower contents of TiO_2 and have amphiboles with green pleochroism. High P_2O_5 in the biotite foyaite, pulaskite and foyaite R.17 indicates comparatively high accessory apatite.

Gifford (1961) suggested that the biotite foyaite originated from the assimilation of gabbroic rocks by a magma of foyaitic composition. Due to the presence of modal biotite the biotite foyaite R.19 has a completely different ratio of alkalis to the foyaite and contains much higher TiO_2 , P_2O_5 and BaO than any of the analysed foyaite. The pyroxene in R.19 is a diopside and those of the gabbros are augites. By a similar argument to that used above, it seems that biotite foyaite R.19 has not originated by the contamination of a normal foyaitic magma and it seems to be an early member of the differentiation series. However, there is considerable evidence of assimilation of gabbro near the gabbro inlier to the west of the juvite core.

Foyaite R.183 and R.226 were originally mapped as pulaskites. I have given petrographic evidence to justify their reclassification as foyaite. Their chemical compositions substantiate this as they have higher alkalis, lower TiO_2 , and lower P_2O_5 than any of the pulaskites. This evidence supports Gifford's (1961) suggestion that the foyaite ring cuts the pulaskite to the west of the juvite core.

The analysed microfoyaite have chemical properties typical of late stage foyaite but R.133 is an older type than R.15. Foyaite R.17 contains plagioclase and its chemical characters are typical of an early formed rock type, e.g. high TiO_2 , moderately high P_2O_5 , high BaO and low FeO/MgO. R730 has chemical characters

typical of an early formed juvite.

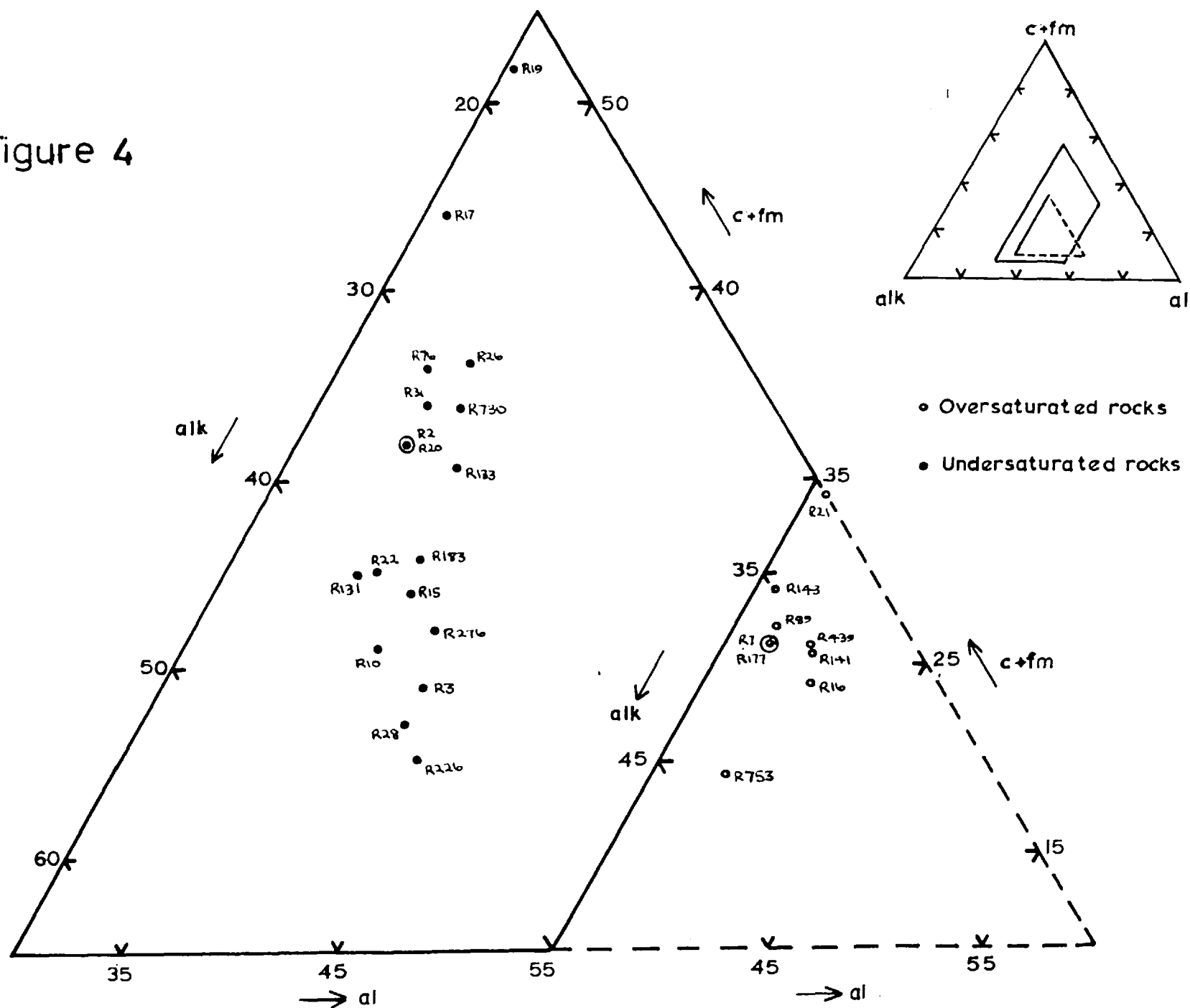
The undersaturated cone sheets, although mapped as separate cone sheets, are clearly the result of complex processes of magmatic differentiation and intrusion. The origin of the juvites and phonolites relative to the other alkali rock types is uncertain but they must be associated in some way.

Rock compositions plotted as Niggli values The variation in chemical composition of the rock types can be represented by plotting Niggli values (Table 3) on a triangular diagram (Figure 4). The co-ordinates used are al , alk and $c + fm$.

The oversaturated rocks (except R.21 and R.753) fall in a relatively small area. R.21 has higher and R.753 lower values for $c + fm$ than the other oversaturated rocks. Assuming a decrease of $c + fm$ with differentiation, the order of formation would be: prophyritic quartz syenite R.21 - inner quartz syenites - outer quartz syenites - porphyritic quartz syenites R.46 and R.439 - granite R.753. Apart from R.21 this agrees with the order of intrusion.

The undersaturated rocks show a wide range in composition and plot as a fairly narrow band from high to low $c + fm$. Early formed rocks have high values for $c + fm$ and rocks formed progressively later show enrichment of al and alk .

Figure 4



The rock series biotite foyaite - plagioclase bearing foyaite (R.17)-pulaskites - foyaites - microfoyaite - late stage foyaites (R.3 and R.226) has decreasing values of $c + fm$ with alk increasing at about twice the rate of al. The juvites follow this trend with R.730 (an early formed type) having high values for $c + fm$ and R.28 and R.276 (later formed types) having lower values. The phonolites are displaced from the general trend towards the alk apex.

I have shown above that the trend of differentiation in the undersaturated rocks is one of decreasing $FeO + Fe_2O_3 + MnO$, MgO and CaO . This is due to a decrease in the modal proportion of mafic minerals. The assumption that $c + fm$ would decrease with differentiation is therefore valid.

Normative composition of rocks

Norms of the analysed rocks are given in Table 4. In the discussion normative minerals are abbreviated thus Qu, Or etc. and modal minerals are written in full, e.g. quartz, orthoclase etc.

The basic rocks The gabbros have high An, high Ab and small amounts of Or and Ne. Di and Ol are magnesium rich types. The essexite has higher Or, Ab, Ne, Di and Ol but lower An than the gabbros. The malignite is characterised by Ks, Lc and Ne and very high Di. The essexite and gabbros have similar amounts of Mn, Il and Ap but the malignite is much higher.

Table 4 : C.I.P.W. Norms for Marangudzi rocks.

	R4	R8	E26	R89	R143	R16	R21	R439	R7	R141	R177	R26	R31	R76	R183	R226	R2	R3	R20	R17	R19	R15	R133	R28	R276	R10	R22	R131	R32	R420	R753	R730	
<u>Qu</u>	-	-	-	-	4.6	14.9	-	0.1	1.9	1.6	3.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	<u>Qu</u>
<u>Or</u>	3.3	3.9	10.6	39.5	34.5	35.6	39.5	37.8	39.5	40.0	37.3	40.6	47.3	45.0	47.3	47.8	41.7	48.9	50.0	38.4	27.8	39.5	47.8	31.4	44.5	44.5	46.1	48.4	Ks 5.7	23.9	33.4	28.4	<u>Or</u>
<u>Lc</u>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	12.2	-	-	27.6	13.5	-	-	-	9.6	25.7	-	6.1	<u>Lc</u>
<u>Ab</u>	12.3	12.7	17.3	44.5	46.6	35.6	35.1	47.2	46.1	42.4	46.1	16.2	23.8	25.4	12.1	16.2	14.7	16.2	13.6	11.0	-	32.0	18.3	-	-	10.5	4.2	4.2	-	-	29.3	-	<u>Ab</u>
<u>Ne</u>	1.0	0.2	2.3	1.2	-	-	2.3	-	-	-	-	12.8	6.1	6.4	23.3	26.4	22.2	22.4	16.5	15.9	10.1	15.1	11.1	27.2	25.0	30.1	31.3	27.6	4.3	19.3	-	34.9	<u>Ne</u>
<u>An</u>	56.5	52.5	22.8	1.1	0.3	4.5	8.9	4.7	-	4.7	-	11.4	6.1	6.7	4.7	2.8	3.9	4.5	2.0	9.7	21.8	2.0	9.2	2.8	6.4	-	-	-	12.8	7.8	3.3	11.7	<u>An</u>
<u>Wo</u>	8.3	9.7	12.5	4.6	3.5	1.4	3.1	1.6	3.0	1.3	3.0	4.9	3.7	3.5	3.4	0.1	4.2	2.0	5.6	6.4	8.2	1.9	2.3	3.0	0.6	-	3.0	4.4	21.2	1.6	-	3.8	<u>Wo</u>
<u>Di</u> <u>En</u>	5.3	6.6	7.9	-	0.4	0.4	1.2	0.8	0.5	0.2	0.5	1.8	1.3	1.4	0.8	0.1	1.2	0.5	1.1	2.6	4.1	0.3	0.8	1.1	0.3	-	0.8	0.8	15.9	1.3	-	1.5	<u>En</u> <u>Di</u>
<u>Fs</u>	2.4	2.5	3.8	5.3	3.4	1.1	2.0	0.8	2.8	1.2	2.8	3.2	2.5	2.1	2.8	0.1	3.2	1.6	4.9	3.8	3.9	1.7	1.6	2.0	0.3	-	2.4	4.0	3.0	-	-	2.4	<u>Fs</u>
<u>Hy</u> <u>En</u>	-	-	-	-	-	0.9	-	1.1	0.5	0.8	0.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	<u>En</u> <u>Hy</u>
<u>Fs</u>	-	-	-	-	-	2.8	-	1.3	2.8	5.4	2.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	<u>Fs</u>
<u>Ol</u> <u>Fo</u>	4.2	4.6	11.1	-	-	-	1.3	-	-	-	-	1.2	0.8	0.9	0.4	0.7	0.8	0.4	0.4	1.8	1.8	0.2	1.1	0.2	1.4	0.7	0.4	0.4	6.6	-	-	1.4	<u>Fo</u> <u>Ol</u>
<u>Fa</u>	2.2	1.9	6.3	0.1	-	-	2.3	-	-	-	-	2.2	1.7	1.5	1.9	1.6	2.5	1.3	2.0	3.1	1.6	1.6	3.3	0.4	1.8	-	1.2	1.8	1.4	-	-	2.2	<u>Fa</u>
<u>Ac</u>	-	-	-	-	-	-	-	-	0.5	-	0.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.2	2.3	6.9	-	-	-	-	<u>Ac</u>
<u>Mn</u>	2.3	3.0	1.9	2.6	3.9	0.9	2.3	3.3	1.6	1.4	1.6	2.3	3.3	4.4	2.8	1.9	3.5	1.9	2.3	3.5	3.5	3.3	2.6	0.9	1.9	2.8	1.9	-	9.3	6.5	2.3	3.3	<u>Mn</u>
<u>Hm</u>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5	-	<u>Hm</u>
<u>Il</u>	0.5	1.2	1.2	0.6	0.8	0.9	0.8	0.6	0.8	0.9	0.9	0.9	1.5	1.2	0.5	0.2	0.6	0.3	0.8	1.2	1.7	0.3	0.6	0.5	0.5	0.8	0.5	0.3	3.7	0.6	0.5	0.9	<u>Il</u>
<u>Ap</u>	0.3	0.3	0.3	0.1	-	0.3	0.3	0.3	0.3	0.3	0.3	0.7	0.7	0.8	-	-	0.3	-	0.3	0.7	1.5	0.1	-	0.2	0.3	0.1	0.2	0.3	3.7	0.7	-	0.7	<u>Ap</u>
<u>Z</u>	-	-	-	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	-	-	-	-	-	-	-	-	-	-	0.1	-	-	-	-	-	-	-	0.1	-	-	<u>Z</u>
<u>Wo</u>	-	-	-	-	0.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1	-	-	<u>Wo</u>
<u>Ct</u>	0.9	-	0.5	-	-	-	-	-	-	-	-	-	-	-	-	1.4	-	-	-	-	-	1.4	-	0.5	1.6	4.3	2.7	0.2	0.9	4.9	-	1.1	<u>Ct</u>

The oversaturated rocks Inner quartz syenites are characterised by high Or, Ab and low An. The extent of saturation is variable and R.143 has 4.6% Qu while R.89 has 1.2% Ne. Di is poor in En. Outer quartz syenites R.7 and R.177 have small amounts of Ac but R.141 has An. They all have low Qu but Or and Ab are high and are similar to the other oversaturated rocks. Di and Hy are rich in Fs. Porphyritic quartz syenites have higher An than the other oversaturated rocks. The extent of saturation is variable and R.16 has 14.9% Qu while R.21 has 2.3% Ne and 3.6 % Ol. Di, Hy and Ol are low in En and Fo. The quartz syenites have variable Mn but similar Il, Ap and Z. Granite R.753 has high Qu, Or and Ab and contains small amounts of Wo and Hm.

The undersaturated rocks Biotite foyaite R.19 is characterised by the presence of Lc. It also has high An, Di, Ol, Il and very high Ap. The pulaskites have variable amounts of Ne and An; Or, Di and Ol are present in larger amount than in the oversaturated rocks. Di and Ol are iron rich. R.31 and R.76 are very similar but have lower Ne and An than R.26. The foyaite have lower An, Il and Ap; higher Ne, and similar Or, Di and Ol to the pulaskites. Di and Ol are iron rich types. Foyaite R.17 has higher An, Di, Ol, Il, Ap but lower Or and Ne than the other foyaite. Microfoyaite R.15 has similar An, but higher Ab and lower Ne, Or, Di and Ol than the foyaite. R.133 is more similar to the foyaite but has lower Ne, Di and Ol.

In the series biotite foyaite - **pulaskite** - foyaite - microfoyaite there is generally a decrease of ^An, Di, Ol, Il and Ap and an increase of Ne to a maximum in the late stage foyaite.

The juvites have large amounts of Lc, Ne and Ct, they also have Or, An and variable amounts of Di and Ol which are comparatively rich in En and Fo. The pseudoleucite dykes have Ac up to 7% and very high Ne. Or is similar to other undersaturated rock types and Ct is variable. R.10 lacks Di and has only a trace of Ol but R.22 and R.131 are richer in these minerals.

Comparison of mode and norm The presence of modal hastingsite affects the comparison of the mode and norm in three ways.

(1) Hastingsites from both over and undersaturated rocks are very undersaturated with respect to SiO_2 . This causes the normative mineral assemblage to be less saturated than the mode (i.e. $\text{Qu} < \text{quartz}$ or $\text{Ne} > \text{nepheline}$).

(2) The hastingsites contain up to 5% total alkalis. Because of this the normative alkali feldspar will be greater than that in the mode ($\text{Or} + \text{Ab} > \text{alkali feldspar}$).

(3) The hastingsites contain approximately 10% CaO and some of this will be calculated as An even in rocks which contain no modal plagioclase ($\text{An} > \text{plagioclase}$).

Table 5 shows the comparison of the mode and norm.

The hastingsite bearing quartz syenites with low modal quartz, either contain only a little Qu (R.7, R.141 and R.439) or might even contain Ne and Ol (R.89 and R.21). It is interesting to note that R.89 contains a little modal fayalite. Plagioclase free quartz syenites show rather close agreement between alkali feldspar and Or + Ab; the latter is slightly greater than the former owing to the presence of hastingsite. Plagioclase bearing quartz syenites have Ab + Or + An rather ^{more} ~~less~~ than total modal feldspar due to the presence of hastingsite.

Undersaturated rocks show variable relationship of Ne to modal feldspathoid. Accurate modal analysis is difficult because of the mineralogical inhomogeneity of the rock and the difficulty of recognising nepheline in unstained sections. In the plagioclase free foyaite, Or + Ab is usually slightly higher than modal alkali feldspar. In the plagioclase bearing pulaskites and foyaite R.17, Or + Ab + An is higher than total modal feldspar, again owing to the presence of modal hastingsite.

Table 5 : Comparison of mode and norm

	Quartz	<u>Qu</u>	Alkali Feldspar	<u>Or</u> + <u>Ab</u>	Plagio- cline	<u>An</u>	Alkali Feldspar & Plagioclase	<u>Or</u> + <u>Ab</u> + <u>An</u>	Nepheline and Sodalite	<u>Ne</u>
R.89	0.6	-	86.5	84.0	-	1.1	86.5	85.1	-	1.2
R.143	2.6	4.6	78.0	81.1	-	0.3	78.0	81.4	-	-
R.16	17.2	14.9	50.6	71.2	12.4	4.5	63.0	75.7	-	-
R.21	<0.1	-	64.5	74.6	17.6	8.9	82.1	83.5	-	2.5
R.439	3.6	0.1	73.4	85.0	7.4	4.7	80.8	89.7	-	-
R.7	6.1	1.9	80.0	85.6	-	-	80.0	85.6	-	-
R.141	6.8	1.6	81.7	82.4	-	4.7	81.7	87.1	-	-
R.177	8.6	3.2	79.2	83.4	-	-	79.2	83.4	-	-
R.26	-	-	54.2	56.8	12.7	11.4	66.9	68.2	5.8	12.8
R.31	-	-	64.6	71.1	10.0	6.1	74.6	77.2	4.2	6.1
R.76	-	-	59.2	70.4	5.9	6.7	65.1	77.1	10.1	6.4
R.183	-	-	65.7	59.4	-	4.7	65.7	64.1	17.0	23.3
R.226	-	-	65.2	64.0	-	2.8	65.2	66.8	27.7	26.4
R.2	-	-	56.3	56.4	-	3.9	56.3	60.3	23.5	22.1
R.3	-	-	64.5	65.1	-	4.5	64.5	69.6	19.1	22.4
R.20	-	-	62.8	63.6	-	2.0	62.8	65.6	18.5	16.5
R.17	-	-	49.8	49.4	7.9	9.7	57.7	59.1	12.8	15.9
R.15	-	-	70.8	68.6	-	2.0	70.8	70.6	18.0	16.6
R.133	-	-	72.0	66.1	-	9.2	72.0	75.3	10.9	11.1

The system Ne-Ks-Qu

Phase relations Bowen and Schairer (1935) showed the existence of a reaction point in this system (point r in Fig. 7). Schairer (1957) continued work on the system at atmospheric pressure and found the composition of the reaction point to be $\text{Ne}_{47}\text{Ks}_{20}\text{Qu}_{33}$ at a temperature of 1020°C . In the dry system the minimum on the feldspar - nepheline boundary curve falls very close to the reaction point. Fudali (1963) studied the system at 1000 bars H_2O pressure and found that the leucite field was much reduced and the liquidus temperatures considerably lowered. The reaction point occurs at $\text{Ne}_{38}\text{K}_{31}\text{Qu}_{31}$ at a temperature of 800°C and the minimum is at $\text{Ne}_{50}\text{Ks}_{19}\text{Qu}_{31}$ at 750°C .

Equilibrium crystallisation Figure 5 is similar to Fudali's Figure 6 and shows the paths of equilibrium crystallisation for various compositions lying within the leucite field. Only for those compositions lying within the area aRbc will the liquid reach R and only for those in the triangle aRb will the liquid move past R towards the minimum M. For a composition s leucite crystallises first and the liquid moves on a curved path to t at which point feldspar joins the leucite. Between t and R feldspar crystallises and leucite is redissolved until at R nepheline crystallises and the liquid is all used up. R is an invariant point and before the liquid can cool further, one of the phases must disappear; in this case liquid disappears first.

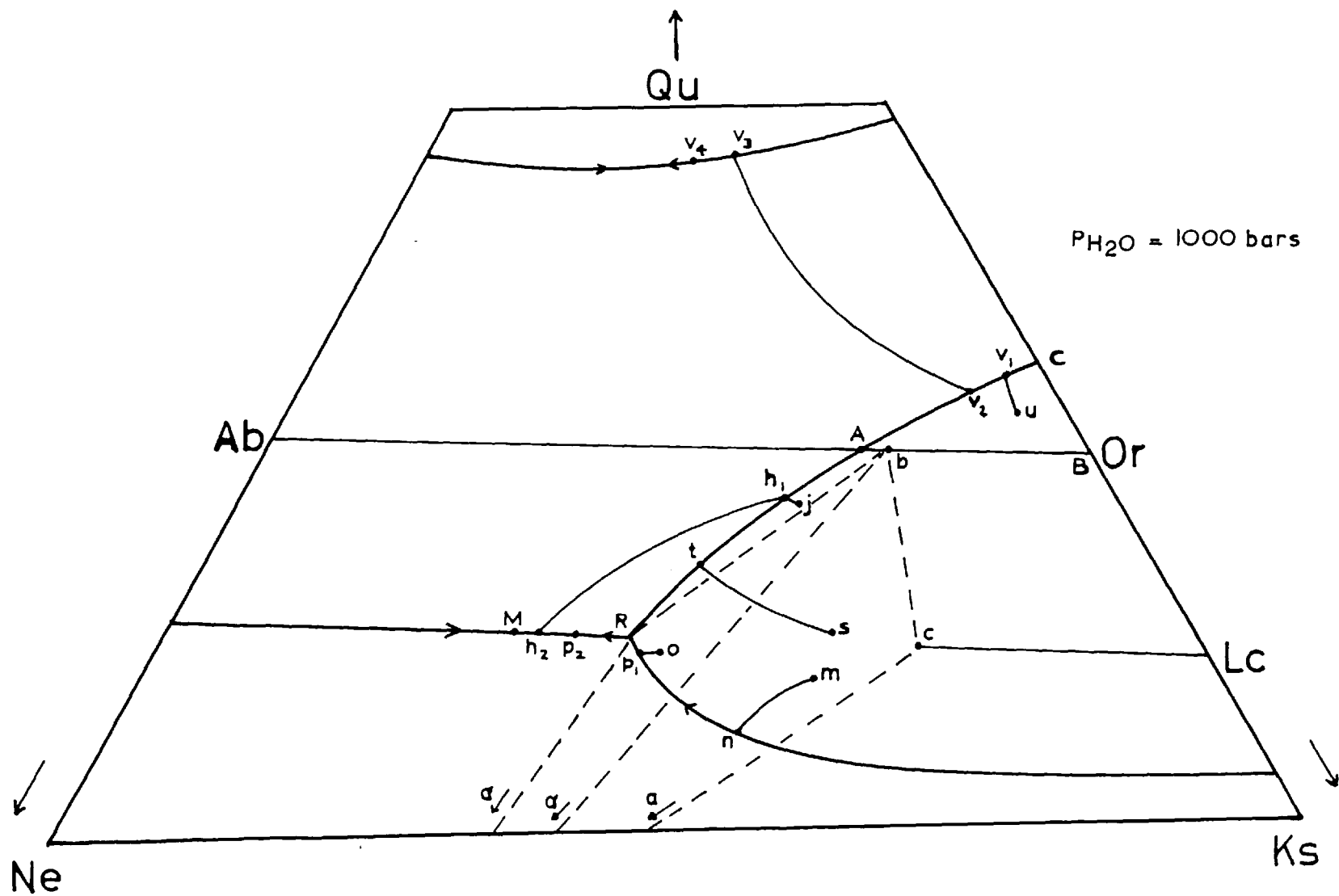


Figure 5

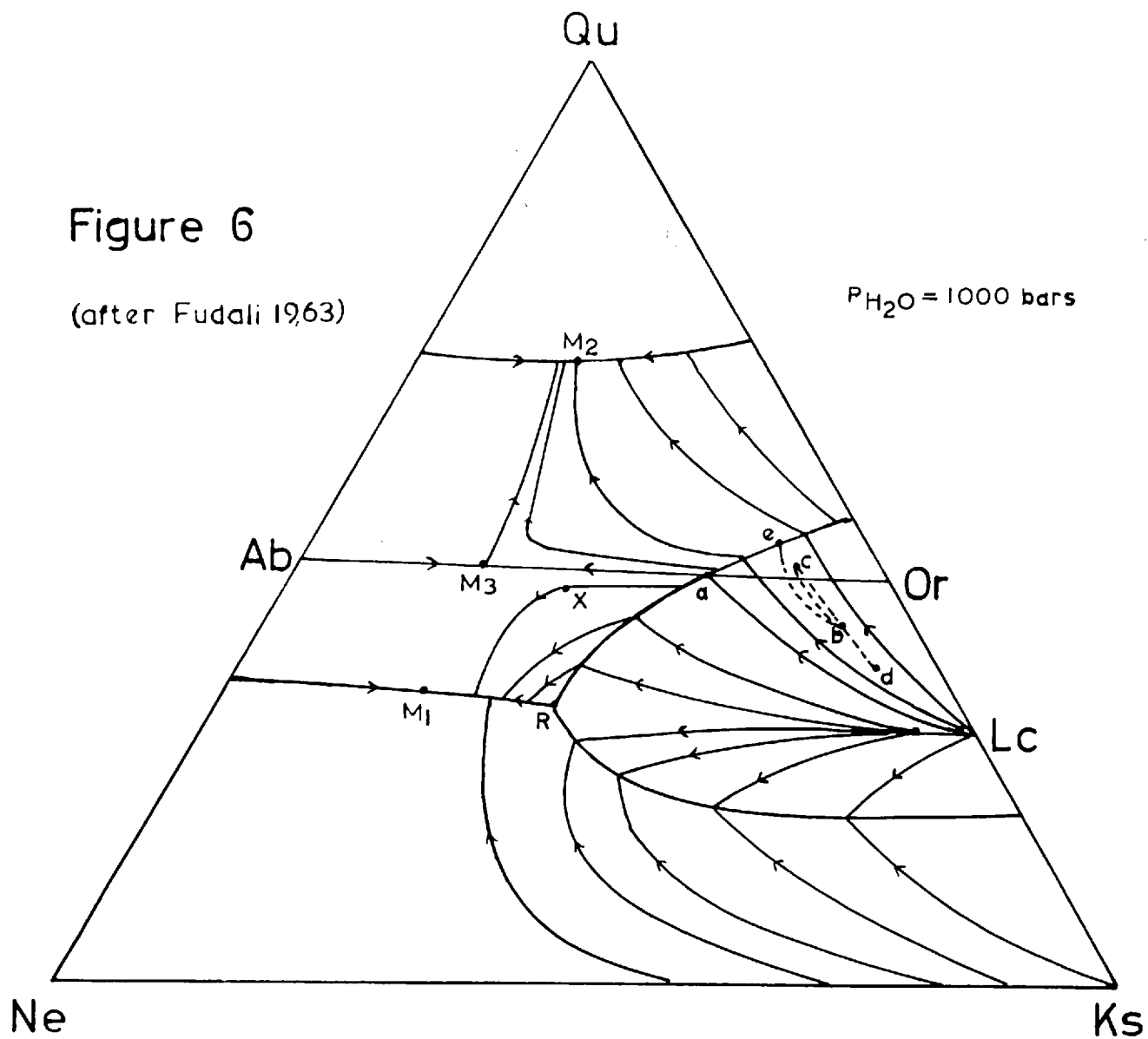
(after Fudalij, 1963).

When the temperature falls again leucite alters to feldspar and nepheline, by sub-solidus reaction, and these minerals make up the final assemblage. Composition m is similar to s except that nepheline is the second mineral to crystallise (at n). Liquid is again used up at R and the final assemblage is again nepheline and feldspar. For a composition o leucite disappears at R and the liquid moves along the nepheline - feldspar boundary curve towards M completing crystallisation at some point p₂. The final assemblage is nepheline and feldspar. A composition u, in the triangle ABC, crystallises leucite until V₁ at which point feldspar crystallises. The liquid cools along the boundary curve as feldspar crystallises and leucite redissolves. At V₂ leucite disappears, the liquid leaves the field boundary and moves in a curved path to V₃ at which point feldspar is joined by quartz. The liquid completes crystallisation at V₄ with a final assemblage at feldspar and quartz. A composition j is similar except that at h₁ the liquid leaves the field boundary joining the feldspar - nepheline boundary curve at h₂. The liquid then moves towards M and the final assemblage is nepheline and feldspar.

Fractional crystallisation Fudali (1963) determined fractionation curves for the system Ne-Ks-Or-Ab and these are shown in Figure 6 (Fudali's Fig. 10). Fractionation curves for the system Ab-Or-Qu are from Tuttle and Bowen (1958). With complete fractionation there is no reaction between crystals and liquid and all

Figure 6

(after Fudali 1963)



compositions in the system will move to one of the three minima. There will be one fractionation curve which will reach the leucite field boundary at its intersection with the Ab-Or join (point a in Figure 6). The liquid in this case will move along the feldspar join from a towards M₃.

Magmatic crystallisation With slow cooling of a magma equilibrium crystallisation should be dominant while for rapid cooling fractional crystallisation would be expected to be the dominant process.

Composition of natural rocks related to the system Ne - Ks - Qu

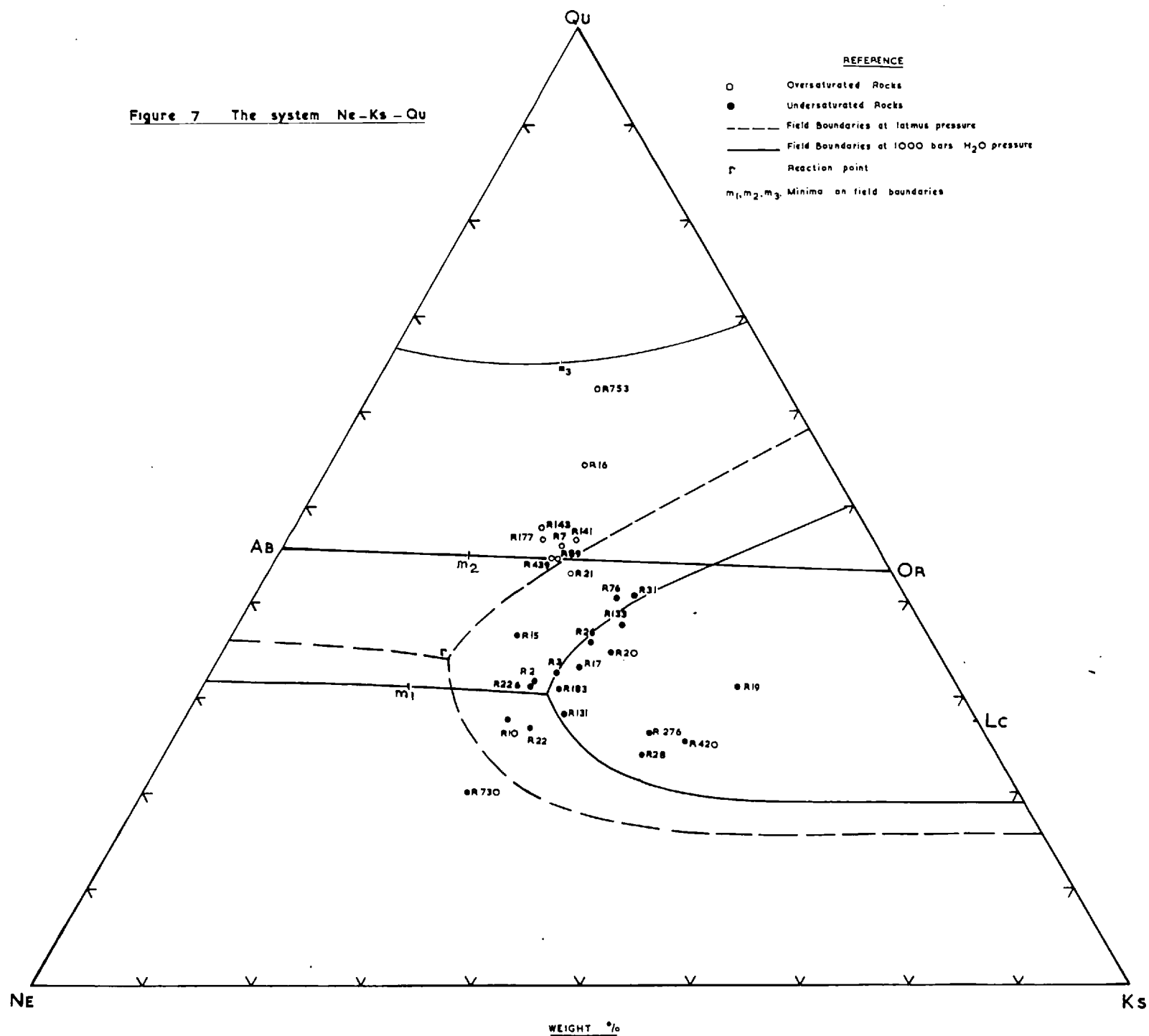
Thornton and Tuttle (1960), on the basis of recent experimental studies, corroborated Bowen's suggestion that the fractional crystallisation of complex magmas produces liquids that move towards the system Ne - Ks - Qu in which ^{they}/complete their crystallisation. They define their differentiation index as the sum of the normative constituents Qu, Or, Lc, Ks, Ab and Ne. Tuttle and Bowen (1958) plotted analysed granites and rhyolites in the system but only chose those rocks which had a total of more than 80 for the normative constituents listed above. These compositions were thought most likely to give an undistorted picture of the phase relations. Hamilton (1960) plotted analysed plutonic and volcanic rocks in the undersaturated part of the system Ne - Ks - Qu and again chose only those rocks

with more than 80% of the above normative constituents.

Values for the Thornton and Tuttle (1960) index for the analysed Marangudzi rocks are given in Table 3. The oversaturated rocks usually have values in excess of 85 but R.21 has a value of 77. The undersaturated rocks show more variation and vary from 50, for the biotite foyaite R.19, to 90 for the late stage foyaite R.226. The only rocks with less than 75 for the index are R.19, pulaskite R.26 and foyaite R.17. Although these rocks have been plotted with the others, it must be remembered that they fall further from the plane of projection and allowance made for this.

The analysed rocks have been calculated in terms of Ne - Ks - Qu and plotted on a triangular diagram (Figure 7). Most of the oversaturated rocks plot in a relatively small area but R.16 and R.753 fall nearer to the feldspar-quartz phase boundary. R.21 and R.89 plot just on the undersaturated side of the feldspar join even though they contain modal quartz. This is because of the presence of modal hastingsite (R.21) and fayalite (R.89) and will be discussed later (Chapter 6). The undersaturated rocks plot well inside the undersaturated field and show more variation. When the experimental phase relations for the system at atmospheric pressure (Schairer, 1957) are considered (Figure 7) the undersaturated rocks are seen to fall within the leucite field. Of the undersaturated rocks analysed

Figure 7 The system Ne-Ks-Qu



only the phonolites, biotite foyaite R.19 and juvites R.28 and R.276 are seen to contain pseudoleucites.

The pulaskites, foyaite and microfoyaite do not contain pseudoleucites and show no evidence of having crystallised leucite at any time in their history. Fudali (1963) suggested that plutonic rocks, whose compositions plot in the leucite field, owe their final nepheline-feldspar assemblage to the sub-solidus breakdown of leucite solid solutions. He suggested that these rocks must have carried recognisable pseudoleucites the evidence of which may, or may not, have been obliterated by the subsequent history of the rock. It is unlikely that the analysed Marangudzi pulaskites, foyaite and microfoyaite ever contained pseudoleucite as the obliteration of this 'mineral' would require extensive sub-solidus re-arrangement within the rock. The alkali feldspars in these rocks are crypto-perthites and some have cores of X-ray perthite. This is clear evidence that the rocks have suffered little sub-solidus reaction otherwise the feldspars would be much more exsolved. There seems to be reasonable evidence that most of the Marangudzi nepheline syenite compositions never contained pseudoleucite.

When the data for the system at 1000 bars H_2O pressure (Fudali, 1963) are considered (Figure 7) the leucite field is seen to be much contracted and now most of the nepheline syenites fall outside this field. At higher pressures the

leucite field would be further contracted, and at some pressure just above 1000 bars the pulaskites, foyaite and microfoyaite would all fall outside the leucite field. I suggest that the Marangudzi nepheline syenites crystallised at some pressure a little in excess of 1000 bars. This pressure would be equivalent to a depth of about 3.5 kilometres. Additional evidence for this is provided by the pulaskites, foyaite and microfoyaite R.133 falling in a band which parallels the leucite-alkali feldspar field boundary in the direction of falling temperature. If these rocks had crystallised at a lower pressure such that their bulk compositions fell within the leucite field, there would be no reason for this regular distribution and a more haphazard one would be expected.

Biotite foyaite R.19 and juvites R.28 and R.276 plot inside the leucite field and contain pseudoleucites which can only be recognised by their round shape and felsic composition. The pseudoleucite bearing dyke R.131 also plots inside the leucite field. Microfoyaite R.15 and phonolites R.10 and R.22 plot outside the leucite field at 1000 bars. There is no evidence that R.15 ever contained pseudoleucite and it contains a cryptoperthitic feldspar. However, the two phonolites contain pseudoleucites which have good crystal shape and are set in a fine grained groundmass. These rocks also contain phenocrysts of nepheline and alkali feldspar and their crystallisation history must have been rather complex. Juvite

R.730 plots outside the leucite field even in the system at atmospheric pressure and does not contain pseudoleucites. It falls inside the field of primary nepheline crystallisation and it is significant that the rock contains abundant euhedral grains of nepheline.

The Marangudzi pulaskites, foyaite and microfoyaite R.133 have plotted compositions typical of magmas formed by a process intermediate between fractional and equilibrium crystallisation (Figure 6) of some parent falling within the leucite field. This crystallisation seems to have occurred at a water vapour pressure of approximately 1000 bars. The origin of microfoyaite R.15 is doubtful. It could either be a composition derived by crystallisation at lower pressure than the other nepheline syenites or the product of extreme fractionation under similar conditions to the other rocks.

Considering the positions of the isotherms in the system Ne - Ks - Qu - H₂O (Fudali, 1963, Figure 1) relative to the plotted rock compositions, the foyaite is lower temperature liquids than the pulaskites and this would be expected from the order of formation and intrusion.

The oversaturated rocks also have plotted compositions possible for magmas formed by fractional crystallisation of some parent composition falling in the leucite field. This will be discussed further at a later stage (Chapter 6). The abundance

of rock compositions close to the feldspar join is difficult to explain, if their origin was due to this process, as there would be a greater tendency for the rocks to show more extreme enrichment of SiO_2 due to the fractionation process.

Shape of the liquidus surface Bowen and Schairer (1935)

described a low temperature trough in the system Ne - Ks - Qu and suggested that liquids falling in this system should cool into the trough. Tuttle and Bowen (1958) plotted analysed granites and rhyolites in this system and found a concentration of points lying in the oversaturated region of the trough. Hamilton (1960) plotted intrusive and extrusive rocks of nepheline syenite composition and found a similar concentration of points in the undersaturated part of the trough. Potash rich rocks plot outside this and show no tendency to cool into the trough. This is shown by the Marangudzi over- and undersaturated rocks which fall in a band outside, but parallel to, the trough. Water pressure does not affect the position of the low temperature trough (Fudali, 1963). However, the effect of mafic minerals might modify the shape of the liquidus by moving the minima to higher potash contents.

Comparison of Marangudzi to other complexes .

The felsic rocks of the Marangudzi complex are essentially syenitic in character. Quartz syenites make up about three-quarters of the felsic rock types and granites are comparatively rare. Nepheline syenites make up the remainder

of the felsic rocks. This predominance of syenite is also seen in other igneous complexes amongst which are: S.W. Greenland Province (Kûngnât, Ilimaússaq and Nunarssuit); Oslo Province, Norway; and Sandyk Mountains Massif, U.S.S.R.

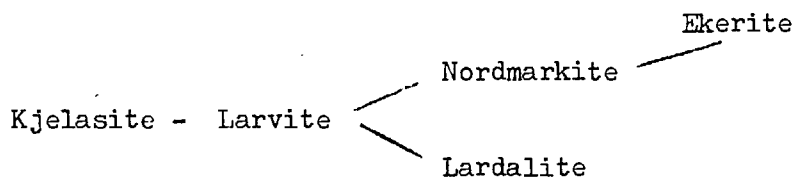
The Kûngnât syenites (Upton, 1960) are slightly oversaturated rock types which are intruded as several bodies. Early syenites tend to be quartz free while later rocks become quartz bearing. The most common rock type is augite-fayalite syenite. Soda granite is present in very small amount and is a product of extreme differentiation. Upton suggested that the intrusions were emplaced in order of increasing basicity, the final intrusion being a ring dyke of alkali gabbro composition.

The Ilimaussaq massif (Hamilton, 1964) consists essentially of augite syenite which can be either quartz or nepheline bearing. Hamilton suggested that the normal trend of differentiation is towards undersaturated rock types (foyaïtes) and that quartz rich syenites owe their origin to the contamination of syenite magma by sandstone or acid basement rocks. The remainder of the complex consists of agpaitic nepheline syenites.

The Nunarssuit complex (Harry and Pulvertaft, 1963) also has large amounts of augite syenite and biotite granite is common.

These three intrusions are of similar age (1100 million years) and there must have been large volumes of augite syenite magma present at this time.

The Oslo Province (Barth, 1944) has larvikite (augite syenite) and nordmarkite (quartz syenite) making up 61% of the complex. Ekerite (soda granite) and biotite granite make up 32% and the remainder of the complex consists of essexite, kjelåsité (mica syenite) and lardalite (nepheline syenite). Barth recognised a branching differentiation giving both over- and undersaturated series of rocks:



The Sandyk massif (Zlobin, 1960) consists essentially of saturated syenites with quartz present only in small amount. Nepheline syenites are formed at a late stage in the differentiation process and some of these are pseudoleucite bearing. Zlobin recognised two phases of intrusion (the figures in the brackets refer to the % of the complex taken up by the various rock types).

Phase 1 (a) Alkali gabbroids (11.4)

(b) Alkaline-earth syenites(35.7)

(c) Leucocratic alkaline-earth syenites(31.5)

Phase 2 (d) Hornblende alkali syenite (15.0)

(e) Nepheline syenite (6.4)

The Lovozero massif, U.S.S.R. (Gerasimovskii and Lebedev, 1959) is different from the above complexes in that it completely consists of undersaturated rocks. The first intrusive phase consists of miaskitic nepheline syenites. The second and third phases are agpaitic and consist of lujavrites, foyaites, urtites and sodalite syenites. The bulk of the complex is made up of rocks of the second phase.

The above rock series differ from Marangudzi in that they are composed mostly of syenite and granite, basic rocks being present to a relatively small extent. The Okonjeje complex, S.W. Africa (Simpson, 1954) is more similar to Marangudzi in having a large amount of basic rock present. In the Marangudzi complex intermediate rocks between the gabbros and syenites have not been found. However, for Okonjeje Simpson describes two differentiation series from gabbro to syenite. One of these is tholeiitic and the other is alkaline.

Tholeiitic series: Gabbro - ferrogabbro - Syenite

Alkali series: Gabbro - essexite - pulaskite with late stage foyaites and tingvaites.

The Nuanetsi igneous province consists of a series of ring complexes to the N.W. of Marangudzi and was described by the Research Institute of African Geology, Leeds University. The complexes are made up of gabbro and granite with intermediate types being very rare. Nordmarkites are present to a limited extent but undersaturated rocks are missing.

The main variation within the rock series described above is in their state of SiO_2 saturation. It is interesting to compare the oxidation state of the iron and the alkali ratio for the different complexes. $\text{FeO}/\text{Fe}_2\text{O}_3$ and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios are given in Table 6.

The Marangudzi gabbros are more highly oxidised than those from Kûngnât and Okonjeje and are also more potash rich. They have similar $\text{FeO}/\text{Fe}_2\text{O}_3$ ratios to the Nuanetsi gabbros but are again higher in potash.

The Marangudzi essexite is less oxidised than those from Okonjeje, Oslo and Sandyk. Its $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio is similar to the essexite from Okonjeje, higher than that from Oslo and lower than the Sandyk essexite.

The Marangudzi quartz syenites are more highly oxidised than the augite syenites of the S.W. Greenland province and are similar to the Oslo and Okonjeje syenites. They are less oxidised than the Oslo nordmarkite and the Sandyk syenites. The Marangudzi quartz syenites have higher $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios than all the other rocks except the Sandyk syenites.

The Marangudzi nepheline syenites have similar $\text{FeO}/\text{Fe}_2\text{O}_3$ ratios to those for Okonjeje, Oslo and Sandyk. They have higher $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios than those from Okonjeje, Oslo and Lovozero but smaller ratios than the Sandyk syenites.

Table 6 : Comparison of Marangudzi with other complexes

	$\frac{\text{FeO}}{\text{Fe}_2\text{O}_3}$	$\frac{\text{K}_2\text{O}}{\text{Na}_2\text{O}}$		$\frac{\text{FeO}}{\text{Fe}_2\text{O}_3}$	$\frac{\text{K}_2\text{O}}{\text{Na}_2\text{O}}$
<u>Basic rocks</u>					
Gabbro R.8, Marangudzi	2.1	0.44	Eastern quartz syenite, Kungnat	3.9	1.0
Gabbro R.4, Marangudzi	2.4	0.34	Kit-sigsut syenite, Nunarssuit	3.7	0.84
Ringdyke gabbro, Kungnat	3.9	0.25	Ridge syenite, Okonjeje (Tholeiitic series)	1.5	0.95
Inner ridge gabbro, Okonjeje (Tholeiitic series)	6.6	0.18	Kjelasite, Oslo	1.9	0.42
Chilled core gabbro, Okonjeje (Alkali series)	9.3	0.17	Larvikite, Oslo	1.2	0.48
Nuanetsi gabbros	2.3	0.18	Nordmarkite, Oslo	0.7	0.58
	3.1	0.05	Alkaline-earth syenite, Sandyk	1.2	1.9
			Leucocratic earth syenite, Sandyk	0.6	3.9
			Hornblende alkaline syenite, Sandyk	1.6	3.0
Essexite E.26, Marangudzi	6.3	0.68		1.9	1.4
Andesine essexite, Okonjeje	3.4	0.75	Nuanetsi granites	1.1	1.4
Essexite, Oslo Province	1.9	0.35	<u>Nepheline syenites</u>		
Essexite, Sandyk Mountains	1.5	2.1	Pulaskite R.26, Marangudzi	2.6	1.5
			Foyaite R.2, Marangudzi	1.9	1.1
<u>Saturated syenites</u>			Juvite R.28, Marangudzi	2.6	1.9
R.177 Quartz syenite, Marangudzi	2.9	1.2	Pulaskite, Okonjeje	1.4	0.97
R.143 Quartz syenite, Marangudzi	1.2	1.1	Lardalite, Norway	1.2	0.39
R.439 Quartz syenite, Marangudzi	1.1	1.2	Pseudoleucite nepheline syenite, Sandyk Mountains	2.5	5.3
Augite syenite, Ilimaussaq	3.8	0.88	Massive nepheline syenite, Sandyk Mountains	1.1	5.3
Western quartz syenite, Kungnat	6.5	0.98	Miaskitic nepheline syenite, Lovozero	-	0.48

The Marangudzi and Sandyk massifs are similar to each other in their potash rich character and both complexes have pseudoleucite bearing rocks. I have shown that the Marangudzi rocks plot outside the low temperature trough in the system Ne - Ks - Qu and the same is true for the Sandyk rocks. The Kungnât syenites (Upton, 1960) and the Okonjeje undersaturated syenites (Simpson, 1954) plot inside this trough.

The Marangudzi syenites are generally more highly oxidised than the S.W. Greenland syenites but are similar to those of Okonjeje, Oslo and Sandyk. This must reflect the relatively high volatile content (e.g. H_2O , F, Cl) in the magma from which the Marangudzi syenites crystallised. This is confirmed by the presence of large amounts of modal amphibole in both the over and undersaturated rocks and sodalite in the latter.

C H A P T E R 4

CHEMISTRY OF THE MINERALS

In this chapter I will describe the chemical and optical mineralogy of feldspars, nephelines, pseudoleucites, amphiboles and magnetites from selected Marangudzi rocks. I can best describe the symbols used to identify the various minerals, and the rocks in which they are contained, by considering a hypothetical rock. Thus rock R.5 contains alkali feldspar F.5, plagioclase P.5, nepheline N.5, pseudoleucite PL.5, amphibole A.5 and magnetite M5. This system of notation is used throughout the thesis.

1. THE FELDSPARS

Alkali feldspar is the most abundant mineral in both the over and undersaturated rocks. It is invariably perthitic with the larger grains showing carlsbad twinning.

The alkali feldspars from the oversaturated rock types vary from crypto- to microperthites and are often clouded with alteration products. Those of the inner quartz syenites are usually the most coarsely exsolved with small plagioclases, showing albite twinning, set in a host of potash feldspar. Some of the larger grains in the outer quartz syenites have cores of albite with rims of a potash rich microperthite. Other feldspar grains in these rocks are similar in composition to the

potash feldspar rims described above. The porphyritic quartz syenites contain varying amounts of xenocrystic plagioclase as well as phenocrysts of microperthite. The plagioclase is zoned with cores of andesine and rims of albite. They often have rims of alkali feldspar. Presumably this zoning is due to reaction of plagioclase xenocrysts (derived from gabbro xenoliths) with alkali rich syenitic magma. Most of the feldspar in these rocks is a potash rich microperthite.

The alkali feldspars of the undersaturated rocks are generally more finely perthitic and less clouded than those of the oversaturated rocks. They often have cores of optically homogeneous material with rims of cryptoperthite. These feldspars give X-ray diffraction patterns showing complete exsolution; the optically homogeneous cores must therefore be X-ray perthite. There is little variation in perthite type between the rock types but microfoyaite R.15 has a completely cryptoperthitic feldspar. The juvite alkali feldspars are optically homogeneous but are rather clouded. Those of the phonolites seem to belong to the sanidine/anorthoclase series and some sections show baveno twinning.

The alkali feldspars of the over- and undersaturated rocks are typical of hypersolvus granites, syenites and nepheline syenites (Tuttle and Bowen, 1958).

Composition and optical properties Partial analyses and refractive indices of the feldspars are given in Table 7 , and the weight % of Or, Ab, An, Cn has been recalculated to 100%. When the weights % of the various oxides are calculated as feldspar molecules, the totals vary from 98.9 to 103.0 % and only two total more than 102%. This must indicate the purity of separation and relative accuracy of the analyses. In the discussion below, the Cn molecule will be considered with An.

Feldspars from the oversaturated rocks vary in composition from Or_{55.8} An_{1.4} (F.141) to Or_{49.2} An_{3.3} (F.439). The composition of F.21 is noteworthy in that it has Cn_{0.7} . As would be expected, there is little variation in R.I. Rees (1960) determined 2V for F.177 as 69.2° and this falls within the range of orthoclase cryptoperthites (Tuttle, 1952).

Feldspars from the undersaturated rocks vary from Or_{63.7} An_{3.1} (F.76) to Or_{55.9} An_{1.2} (F.15). F.28 has Or_{93.7} and this composition is typical of a juvite alkali feldspar. The generally higher Cn content of these feldspars relative to the oversaturated rock feldspars should be noted. The pulaskite alkali feldspars usually have the highest Or and An contents and that of microfoyaite R.15 has the lowest content of these molecules. This reflects the order in which these rocks crystallised. F.28 has a low R.I. compared to the other feldspars which show little variation. Rees (1960) determined 2V for F.76 as 59.5°

Table 7 : Analyses of feldspars.

	F21	F439	F141	F177	F26	F31	F76	F2	F20	F15	F28	P26
Na ₂ O	4.83	5.62	4.99	5.56	3.98	4.30	4.00	4.51	4.13	5.16	0.46	6.97
K ₂ O	9.29	8.34	9.38	8.59	10.65	10.37	10.97	10.23	10.56	9.58	16.31	1.01
CaO	0.75	0.64	0.29	0.27	0.76	0.60	0.49	0.52	0.51	0.25	0.38	7.03
BaO	0.28	0.06	0.03	0.01	0.94	0.19	0.29	0.15	0.41	0.00	0.29	0.11
Ab	40.8	47.5	42.7	47.6	32.8	35.8	33.2	37.4	34.5	42.9	3.8	59.0
Or	54.8	49.2	55.8	50.0	61.3	60.7	63.7	59.7	62.0	55.9	93.7	6.0
An	3.7	3.2	1.4	1.4	3.7	3.0	2.4	2.5	2.5	1.2	1.8	34.8
Cn	0.7	0.1	-	-	2.2	0.5	0.7	0.4	1.0	-	0.7	0.2
<i>B</i>	1.530	1.530	1.529	1.528	1.530	1.529	1.529	1.529	1.529	1.530	1.527	1.548

and this again falls within the range of orthoclase cryptoperthites.

Plagioclase The pulaskites have co-exisiting alkali feldspar and plagioclase of oligoclase-andesine composition. Plagioclase P.26 from R.26 has been separated and analysed (Table 7). Its composition is $An_{35} Ab_{59} Or_6$ and this agrees well with the composition indicated for its R.I. (Chayes , 1952) which is $An_{32} Ab_{68}$. The early formed foyaite R.17 and biotite foyaite also contain plagioclases of oligoclase-andesine composition while the early formed juvite R.730 contains untwinned plagioclase.

Barth (1956) constructed working curves from which, he suggested, the equilibrium temperature of co-exisiting alkali feldspar and plagioclase could be read if their compositions were known. Using these curves the temperature indicated for R.26 is approximately $850^{\circ}C$. This rock also contains nepheline and this will, of course, affect the distribution of Na_2O between the feldspars. The precise significance of this temperature is therefore unknown.

The system An - Ab - Or

Tuttle and Bowen (1958) discussed hypothetical phase relations within the system An - Ab - Or and delineated the cotectic curve separating the field of primary plagioclase crystallisation from that of primary alkali feldspar crystallisation. They also plotted the trace of intersection of the solidus and

solvus surfaces. This trace represents the extent of solid solution between plagioclase and alkali feldspars. Maximum solid solution will be shown by feldspars from trachytes and smaller amounts of solid solution by feldspars from rhyolites and phonolites (as liquidus and solidus temperatures are decreased by the presence of quartz and nepheline). The presence of water vapour under pressure also lowers the solidus and liquidus temperatures and therefore rocks crystallised under plutonic conditions should show less solid solution between co-existing plagioclase and alkali feldspar than those crystallised under volcanic conditions. Yoder, Stewart and Smith (1957) determined the system An - Ab - Or at a water pressure of 5000 bars and found that the solvus/solidus intersection reached the join Ab - Or, i.e. the solvus and alkali feldspar solidus intersect at this pressure. They were able to determine the position of the cotectic curve and the shape of the liquidus surface; the leucite field was, of course, completely suppressed at this pressure. Carmichael (1963) pointed out that although the cotectic curve closely approached the Ab - Or join, it could not intersect it.

Tuttle and Bowen (1958) and Turner and Veerhogen (1960) have described the crystallisation of feldspars under volcanic and plutonic conditions and I will only discuss the crystallisation of relevant compositions. In Figure 8, XYZ represents the intersection of the solidus and solvus surfaces for high solid solution between plagioclase and alkali feldspar (volcanic

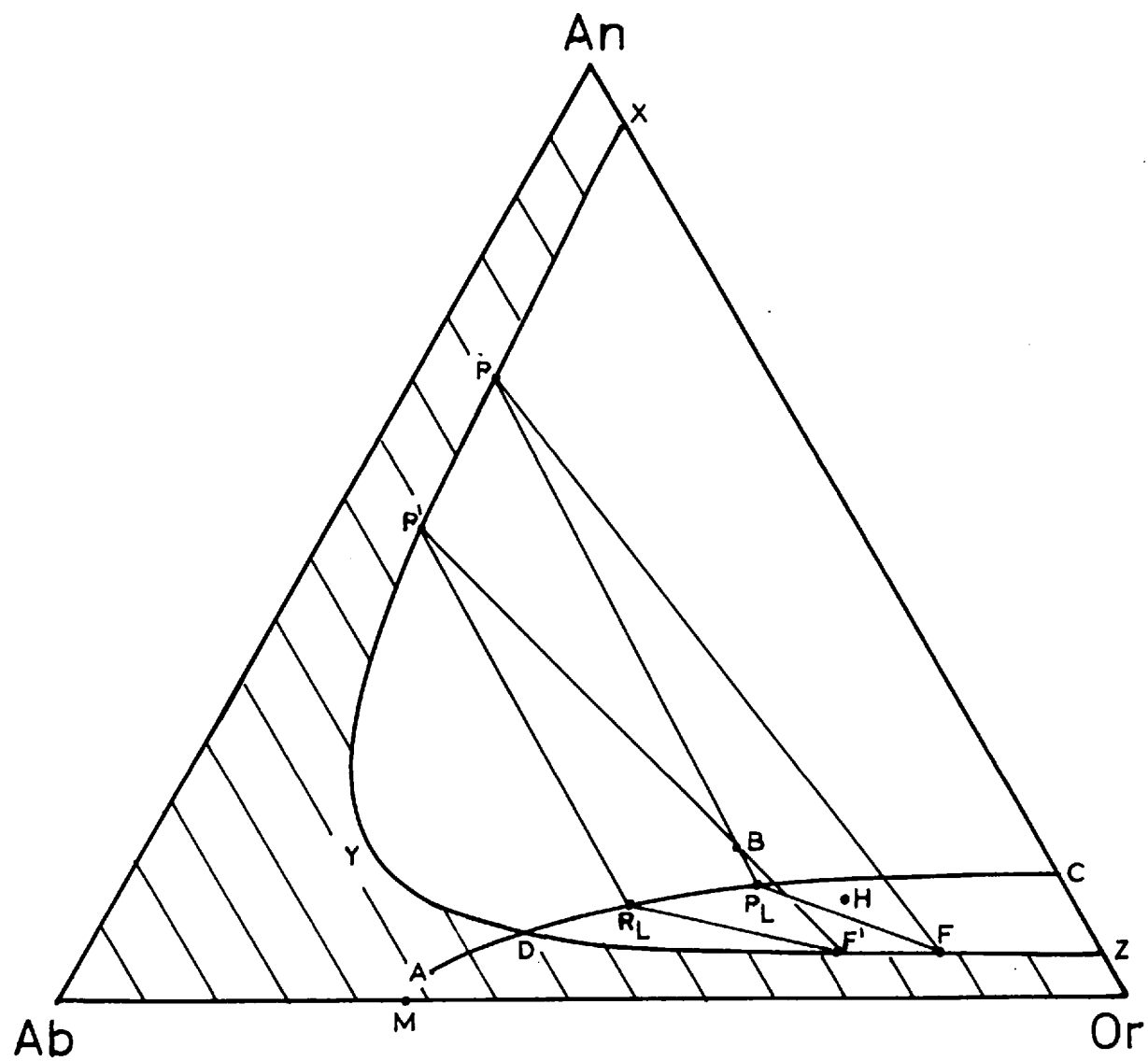


Figure 8

(after Bowen and Tuttle 1958)

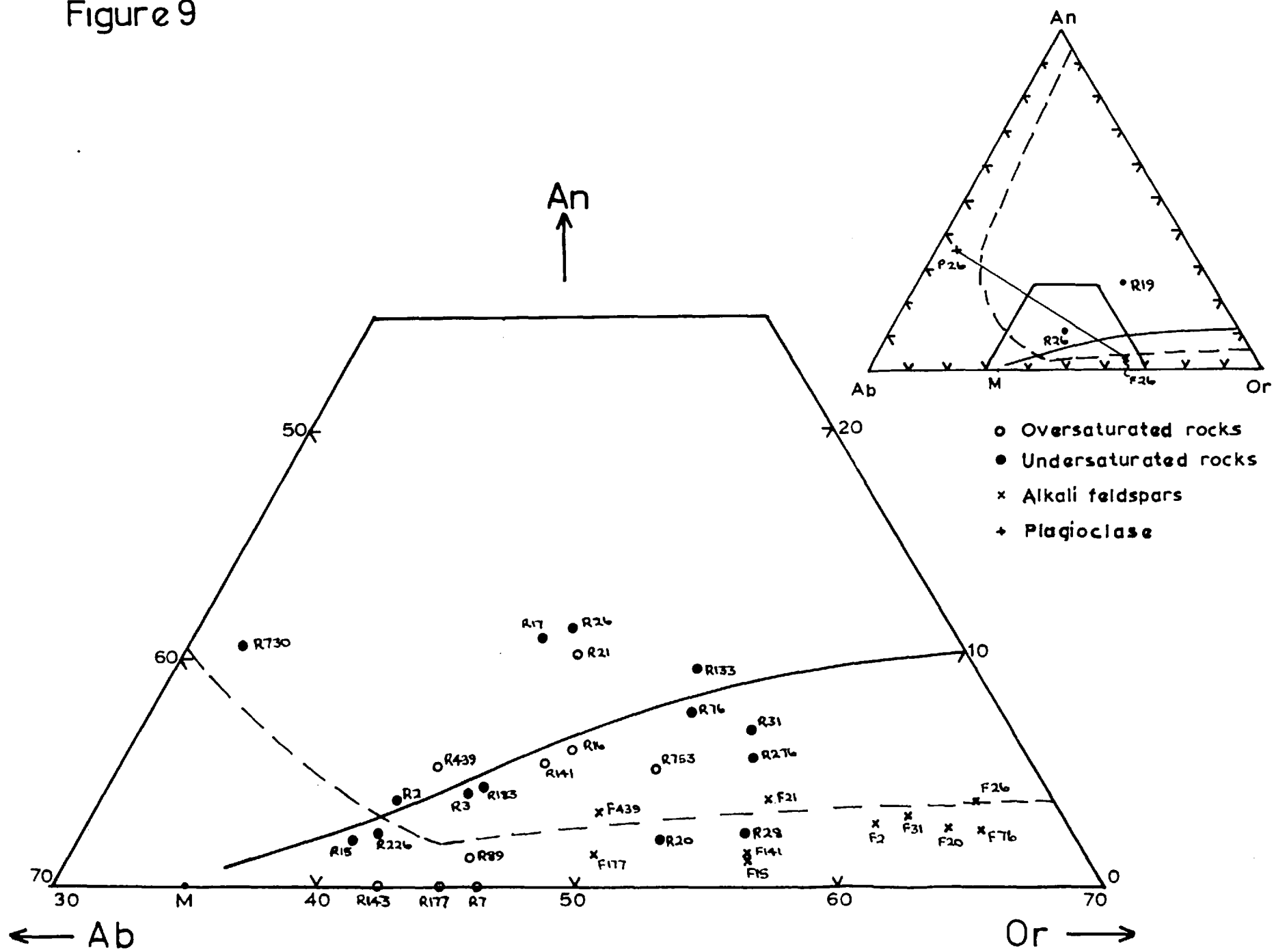
conditions) and AC the cotectic curve. The field of leucite has been neglected. Consider a composition B; the first phase to crystallise would be a lime rich plagioclase P and the liquid would move in a curved path towards the cotectic curve intersecting it at P_L at which point a potash rich alkali feldspar of composition F would crystallise. With further cooling under equilibrium conditions the liquid would move down the cotectic and the feldspars along XYZ towards Y. At a point R_L the liquid would disappear and the two feldspars P' and F' would be in equilibrium. FFP_L and $P'F'R_L$ are three-phase triangles. If the composition B crystallised under conditions of fractionation and the plagioclase did not react with the liquid, it would become zoned as the liquid moved down the cotectic curve. At some point between D and A the liquid would leave the cotectic and enter the alkali feldspar field moving in a curved path towards the alkali feldspar minimum M. The liquid would complete its crystallisation by precipitating a single alkali feldspar and crystallisation under these conditions would produce alkali feldspar grains with cores of zoned plagioclase.

A composition H would be similar to B except that alkali feldspar would crystallise first being joined by plagioclase when the liquid reached the cotectic. Compositions in the shaded area would only crystallise one feldspar under equilibrium conditions.

Carmichael (1960, 1963) analysed the co-existing feldspars and groundmasses of oversaturated rocks. He recalculated the groundmass normative constituents An, Ab, Or to 100 and plotted these values in the ternary feldspar system. This is equivalent to projecting compositions lying within the quaternary system An - Ab - Or - Qu onto the plane An - Ab - Or. The Marangudzi oversaturated rocks have been plotted in a similar manner. However, R.7 and R.177 contain trace amounts of normative Ac but this has been neglected and the rocks plotted on the join Ab - Or. The undersaturated rocks plot within the undersaturated volume of the system An - Ne - Ks - Qu and these have been projected onto the An - Ab - Or plane by adding sufficient SiO_2 to saturate normative Ne and Lc. Normative Ab, Or and An were then recalculated to 100. It was necessary to do this because if normative Ne was neglected the alkali ratio for the rocks would have been wrong by the amount of soda that had been allotted to Ne. In any case nepheline is invariably of later crystallisation than alkali feldspar and plagioclase.

The Marangudzi rocks and feldspars have been plotted in Figure 9, on which are shown the cotectic at 5000 bars (Yoder et al, 1957) and the hypothetical solidus-solvus intersection at 1000 bars H_2O pressure (Turner and Veerhogen, 1960). This latter pressure has been chosen as in Chapter 3 I suggested that the nepheline syenites crystallised at some

Figure 9



pressure just above 1000 bars. However, it is important to remember that Bowen and Tuttle (1958) found that the alkali feldspar solidus and solvus did not intersect at 4000 bars whereas Yoder et al (1957) found that they did intersect at 5000 bars. This means that the trace of intersection of the solidus and solvus surfaces in the system An - Ab - Or only intersects the alkali feldspar join at some pressure between 4000 and 5000 bars. The leucite^{field} has been neglected because at 1000 bars it only extends as far as Ab₃₀ on the alkali feldspar join and will not interfere with the compositions plotted.

The tie-line between co-exisiting plagioclase and alkali feldspar is drawn in (inset of Figure 9) and the bulk rock plots on the alkali rich side of this line. This may be due to distortion in the projection. Rocks R.26 and R.17 fall within the field of primary plagioclase crystallisation and they both contain plagioclase of andesine composition although the bulk of feldspar is alkali feldspar. Some of the larger alkali feldspars have cores of zoned plagioclase and the origin of these is most likely due to fractional crystallisation as described above. R.19 (inset of Figure 9) contains a considerable amount of modal plagioclase and R.730 has untwinned plagioclase. R.31 and R.76 have co-exisiting plagioclase and alkali feldspar with the former much less abundant than the latter. The two feldspars usually occur as discrete grains and only occasionally do the alkali feldspars include plagioclases; this is consistent with their

plotted positions. R.16, R.21 and R.439 have varying amounts of xenocrystic plagioclase and this explains their relatively An rich plot in comparison to the other oversaturated rocks. Although R.141 has a small amount of An, the other analysed outer quartz syenites R.7 and R.177 contain small amounts of Ac and have been plotted on the Ab - Or join. The cores of albite in the larger alkali feldspars in these rocks clearly cannot be explained in a similar way to the plagioclase cores of R.17 and R.26 and are most likely products of exsolution. The microperthitic margins to these albite cores seem to indicate two stages of growth with a sufficient time between these stages for exsolution of the original alkali feldspars to have taken place. The other plotted rock types contain no modal plagioclase and most of them plot in positions consistent with this. However, R.133 plots within the plagioclase field even though it has no plagioclase. R.276 also plots in a position which suggests the original liquid should have crystallised plagioclase. R.133 and R.276 contain fairly high modal amounts of hastingsite and hastingsite plus diopside respectively; this may explain the anomalously high An content of the norm.

The alkali feldspars and plagioclase P.26 plot quite near the hypothetical limit of feldspar solid solution at 1000 bars H_2O pressure.

Undersaturated rocks R.31, R.76, R.183, R.3, R.2, R.226 and R.15 fall in a fairly narrow band, roughly parallel to the cotectic curve, in the direction of falling temperature as indicated by the isotherms (Yoder et al, 1957). This seems to reflect the order of formation of rock series pulaskite - foyaite - microfoyaite. Foyaite R.20 falls well towards the potash rich apex from this band.

2 THE NEPHELINES

The structure of nepheline is based on a tridymite type of framework, containing 32 oxygens per unit cell in which approximately half the Si atoms are replaced by Al making a total of 16 atoms (Buerger, 1954 and Buerger, Klein and Donnay, 1954). The electrical neutrality is maintained by the presence of alkali atoms (and Ca to a smaller extent). Because of the rotational distortion of the framework, the alkali sites are of two different sizes, a smaller and a larger, in the ratio 6:2 making a total of 8 per unit cell. The larger has 9-fold oxygen co-ordination and tends to contain K atoms, whereas the smaller has 8-fold oxygen co-ordination and tends to contain Na atoms. The distribution of Ca atoms between the two cavities is uncertain.

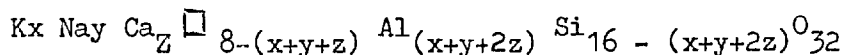
I have used the term nepheline to describe the natural mineral and synthetic solid solutions. Pure Na nepheline

(Na Al SiO₄) is denoted Ne, and pure kalsilite (K Al SiO₄) is denoted Ks. The compositions of various natural and synthetic nepheline solid solutions with no excess SiO₂ are described in terms of % of Ne or Ks, whereas those containing excess SiO₂ are described in terms of Ne, Ks and Qu.

Smith and Sahama (1954), Tuttle and Smith (1957,1958) and Donnay, Schairer and Donnay (1959) determined lattice parameters for nephelines in the system Ne-Ks. Smith and Sahama measured 2 θ for the (20.2) and (21.0) nepheline reflections while the other authors determined the parameters a, c and cell volume $V (= a^2 c)$. When they plotted these parameters in the system Ne-Ks all parameters showed a systematic variation. With increase in % Ks 2 θ (20.2) and (21.0) decrease while a, c and $a^2 c$ increase. However, the plots of all these parameters show a change of slope at a nepheline composition of Ne₇₅Ks₂₅ i.e. a Na:K ratio of 3:1. The various authors correlated this discontinuity with the presence (in Na rich nephelines) of Na atoms in the larger sites and (in K rich nephelines) of K atoms in the smaller sites. Hamilton and MacKenzie (1960) measured 2 θ (20.2) and (21.0) for nephelines containing excess SiO₂, i.e. nephelines falling in the ternary system Ne - Ks - Qu. These were crystallised at 700°C and at 1000 bars H₂O pressure. Although nephelines are referred to as containing excess SiO₂ it is more convenient to describe them as having a deficiency in the cation sites. This deficiency is usually referred to

as omission solid solution with the vacant sites designated by □ (Donnay et al, 1959). Hamilton and MacKenzie(1960) showed that the discontinuity of lattice parameters persists in nephelines containing excess SiO₂ and they suggested that the structural break occurs when the six smaller alkali sites are filled by Na atoms and the two larger sites by K atoms and vacancies.

The nepheline formula The sum of Si and Al never departs significantly from the ideal of 16. The resultant negative charge, owing to the replacement of Al for Si, is balanced by the presence of alkali atoms (and Ca). The number of Al atoms should therefore equal the number of valencies carried by the alkali atoms plus Ca, i.e. $Al = \sum R$ where $\sum R = Na + K + 2Ca$. Donnay et al (1959) gave the general nepheline formula as:-



Tuttle and Smith (1958) described the existence of a miscibility gap, at low temperatures, in the system Ne-Ks and suggested that the composition Na₃KAl₄Si₄O₃₂ (Buerger's ideal nepheline formula) is unique and at low temperatures is a compound.

Chemistry of nepheline Donnay et al (1959) and Deer, Howie and Zussman (1963) have compiled lists totalling 40 analysed nephelines. Most of these contain Ca and Fe³⁺ but some also

contain minor amounts of Ti, Mn and Mg. In calculating the formulae Fe^{3+} was assumed to substitute for Si and Ti, Mn and Mg for alkali atoms (and Ca). The total number of atoms in tetrahedral co-ordination averages 16.00 and varies by not more than ± 0.12 . All the nephelines contain deficiencies in alkali atoms plus Ca and these vacancies vary from 0.02 to 1.06 atoms. One nepheline (Bannister; 1931) contains 0.91 atoms of Ca and this causes a very high value of 1.43 atoms for $\square$. Potash rich nephelines generally contain smaller numbers of vacancies than soda rich types and Hamilton and MacKenzie (1960) consider that this indicates the vacancies are only present in the larger K sites (their Fig. 6).

Two nephelines from Marangudzi have been analysed and the analyses and other data are given in Table 8-. In comparison to other analysed nephelines they have higher SiO_2 and lower Al_2O_3 . The sum of Si, Al and Fe^{3+} for N.2 is 15.970 atoms and for N.20 is 15.941 atoms. The number of vacancies is 0.994 atoms in N.2 and 0.881 in N.20. The sum of Al, Fe^{3+} atoms should equal the sum of Na, K and 2 Ca (i.e. ΣR). Atoms of $\text{Al} + \text{Fe}^{3+}$ for N.2 total 7.174 and for N.20 are 7.172 whereas ΣR for N.2 is 7.287 and for N.20 is 7.423 atoms. In both nephelines there is an excess of alkalis plus Ca over $\text{Al} + \text{Fe}^{3+}$ as allowed in the structural formula. This suggests an error in the analyses giving either high SiO_2 , low Al_2O_3 or high alkalis and Ca. The gravimetric determination of SiO_2 would tend to be low rather than high and vice-versa for Al_2O_3 ; therefore any error would tend to exaggerate the

Table 8 : Marangudzi Nepheline Analyses

	N.2	N.2 [†]	N.20	N.20 [†]	
SiO ₂	46.31	45.73	46.30	45.72	
Al ₂ O ₃	30.95	31.30	31.15	31.51	Co-ordinates in system
Fe ₂ O ₃	0.51	0.52	0.37	0.38	Ne-Ks-Qu(weight %)
CaO	1.34	1.36	1.46	1.48	N.2 Ne _{71.1} Ks _{19.9} Qu _{9.0}
MgO	*		*		N.20 Ne _{72.3} Ks _{19.6} Qu _{8.1}
Na ₂ O	14.10	14.40	14.42	14.78	
K ₂ O	5.68	5.54	5.66	5.46	
H ₂ O [±]	0.44		0.34		
Total	99.33		99.70		
Σ	1.536		1.536		
ω	1.540		1.540		

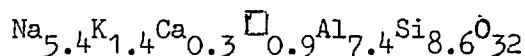
Number of ions on the basis of 32 oxygens

Si	8.796	8.769
Al	7.098	7.117
Fe ³⁺	0.076	0.055
Na	5.367	5.479
K	1.358	1.336
Ca	0.281	0.304
Si+Al+Fe ³⁺	15.970	15.941
Al+Fe ³⁺	7.174	7.172
ΣR	7.287	7.423
ΣR-(Al+Fe ³⁺)	+0.113	+0.251
□	0.994	0.881

[†] Analysis corrected for 3% alkali feldspar.

difference between $\text{Al}+\text{Fe}^{3+}$ and ΣR . Both nephelines were analysed in duplicate for SiO_2 and Al_2O_3 ; in triplicate for alkalis and CaO and MgO were checked quantitatively by a spectrographic method. SiO_2 , Al_2O_3 , Na_2O and K_2O were reproduced with ⁱⁿthe normal limits of the analytical methods. CaO seems to be slightly low rather than high and MgO was not detected (i.e. below 0.05%). Alkali feldspar as contaminant was looked for optically and was found to be less than 3% in both cases. X-ray diffraction traces showed no feldspar peaks which suggests that feldspar is less than 5%. The analyses in Table 8 have been corrected for 3% of alkali feldspar. This discrepancy between $\text{Al}+\text{Fe}^{3+}$ and ΣR seems to be quite common and other analysed nephelines show differences from -0.38 to +0.42.

The analysed Marangudzi nephelines are of very similar compositions but owing to the inexplicable analytical error noted above they vary slightly from the general formula given by Donnay et al (1959). Assuming the error to be in the Al/Si ratio their average formula would be :



I have already mentioned that Hamilton and MacKenzie (1960) suggested that the vacancies in the nepheline structure were limited to the two K sites. Barth (1963) suggested that $(\text{Na}+\text{Ca})$ occupy the six smaller sites while $(\text{K}+\square)$ occupy the two larger sites. This relationship is clearly not obtained in the Marangudzi nephelines as $\text{Na}+\text{Ca}$ is only 5.7 atoms while $\text{K}+\square$ totals 2.3 atoms. Other analysed soda poor nephelines which have $\text{Na}+\text{Ca} < 6$ and $\text{K}+\square > 2$ have a relatively small number of vacancies, i.e. usually

less than 0.3 atoms. It is impossible to say whether the vacancies in the Marangudzi nephelines are distributed between the two lattice sites or whether they are concentrated in the larger sites. The latter would necessitate K atoms entering the smaller sites.

Factors influencing the lattice parameters of nepheline

Donnay et al (1959) described a high temperature pure Na nepheline~~s~~ as having different cell dimensions to those of low temperature pure Na nephelines. The latter showed no variation in cell dimensions with variation in temperature of crystallisation. Edgar (1963) crystallised pure Na nepheline and 'ideal' nepheline ($\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$) at 1000 bars H_2O pressure and at various temperatures. He showed that, for both compositions, there was no sensible variation in cell dimensions.

Donnay et al (1959) studied the solid solutions series: Ne- CaAl_2O_4 , Ne-An, Ne-Ab and Ne-Ks. Of these only the first and last showed any variation of cell dimensions with change in composition. The second and third series showed no variation in lattice parameters which approximated to those of the quenched high temperature pure Na nepheline. Edgar (1963) studied the solid solution series: Ne-An- H_2O , Ne-Ab- H_2O and $\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_8$ -An- H_2O at 700°C and 1000 bars pressure and found a little variation in lattice parameters between Ne₁₀₀ and Ne₉₅ but no variation at lower Ne concentrations. However, Hamilton and MacKenzie (1960) showed that there was a small but significant change in lattice

parameters caused by omission solid solution in pure Na nepheline and suggested that this difference increases with increasing K content.

Determination of nepheline composition from lattice parameters

I have shown that the lattice parameters of nephelines in the system Ne-Ks vary systematically and several authors have used these variations to determine the composition of natural nephelines by comparison with synthetic and analysed natural nephelines. Smith and Sahama (1954) plotted the variation of 2θ (20.2) and (21.0) against $K/(K + Na + Ca)$ (atomic %) and showed that natural nephelines were displaced slightly from synthetic nephelines in the direction of higher K content. Smith and Tuttle (1957) and Donnay et al (1959) plotted the variation of a, c and cell volume V against the number of K atoms and found a reasonable agreement between natural and synthetic nephelines. Hamilton and MacKenzie (1960) crystallised nephelines, of composition along the join $Ne_{90}Ks_{10} - Ne_{66}Ks_{34}Qu_0$ and measured their reflections 2θ (20.2) and (21.0). They found that X-ray data for nephelines with no excess SiO_2 should not be used to determine the composition of nephelines containing excess SiO_2 and this includes most natural nephelines. They found reasonable agreement between the analysed compositions of natural nephelines and those determined from their X-ray results. Smith and Sahama (1954) and Hamilton and MacKenzie (1960) found that the (20.2) reflection gave better results than the (21.0) reflection but were not able to explain this anomaly.

The 2θ reflections (20.2) and (21.0) were measured for both nephelines N.2 and N.20 and a, c and V were determined for N.20 . The X-ray method used for the determination of 2θ was very similar to that used by Hamilton and MacKenzie (1960). The parameters a, c and V were calculated by the method of Donnay et al (1959) but the measurements of 2θ for the six peaks were made on only one scan of nepheline N.20. The cell parameters are given in Table 9 along with the estimated and analysed nepheline compositions. The ratio $K/K + Na + Ca$ was estimated using the working curves of Smith and Sahama (1954) . Atoms of K were determined, from the cell volume, using the working curve of Donnay et al (1959). The compositions in the system Ne-Ks-Qu were estimated using Hamilton and MacKenzie's (1960) working curves. Figure 10 is similar to Hamilton and MacKenzie's Figure 4B. The straight lines join the compositions obtained for N.2 and N.20 from the X-ray determinative graphs of Smith and Sahama (1954) and Hamilton and MacKenzie (1960). The extension of this line for (20.2) (solid line Fig. 10) passes very close to the analysed compositions of the nephelines. The (21.0) reflection (dashed line Fig. 10) gives much inferior results and this was also noted by Hamilton and MacKenzie.

None of these X-ray methods can give any real indication of the excess SiO_2 present in the nepheline as well as the Ne-Ks ratio. It therefore seems inescapable that for the full description nephelines they must be analysed chemically.

Table 9 : Composition of nepheline from X-ray data.

			X-ray data and estimated compositions		Analysed compositions of nephelines	
			N.2	N.20	N.2	N.20
20 (average of six traces)	21.0		27.269	27.266		
	20.2		29.690	29.684		
		a Å	--	9.987		
		c Å	--	8.370		
		a ² c = V Å ³	--	722.9		
		c/a	--	0.838		
1) Composition as K/K + Na + Ca (atomic %)						
	21.0		13	13	19.5	18.8
	20.2		15	17		
2) Number of K atoms						
		a ² c = V	--	1.2	1.36	1.34
3) Composition as Ne - Ks - Qu (weight %)						
	21.0	Ne	79.0	79.5	71.1	72.3
		Ks	15.4	14.5	19.9	19.6
		Qu	6.0	6.0	9.0	8.1
	20.2	Ne	77.0	76.0		
		Ks	17.5	18.5		
		Qu	5.5	5.5		

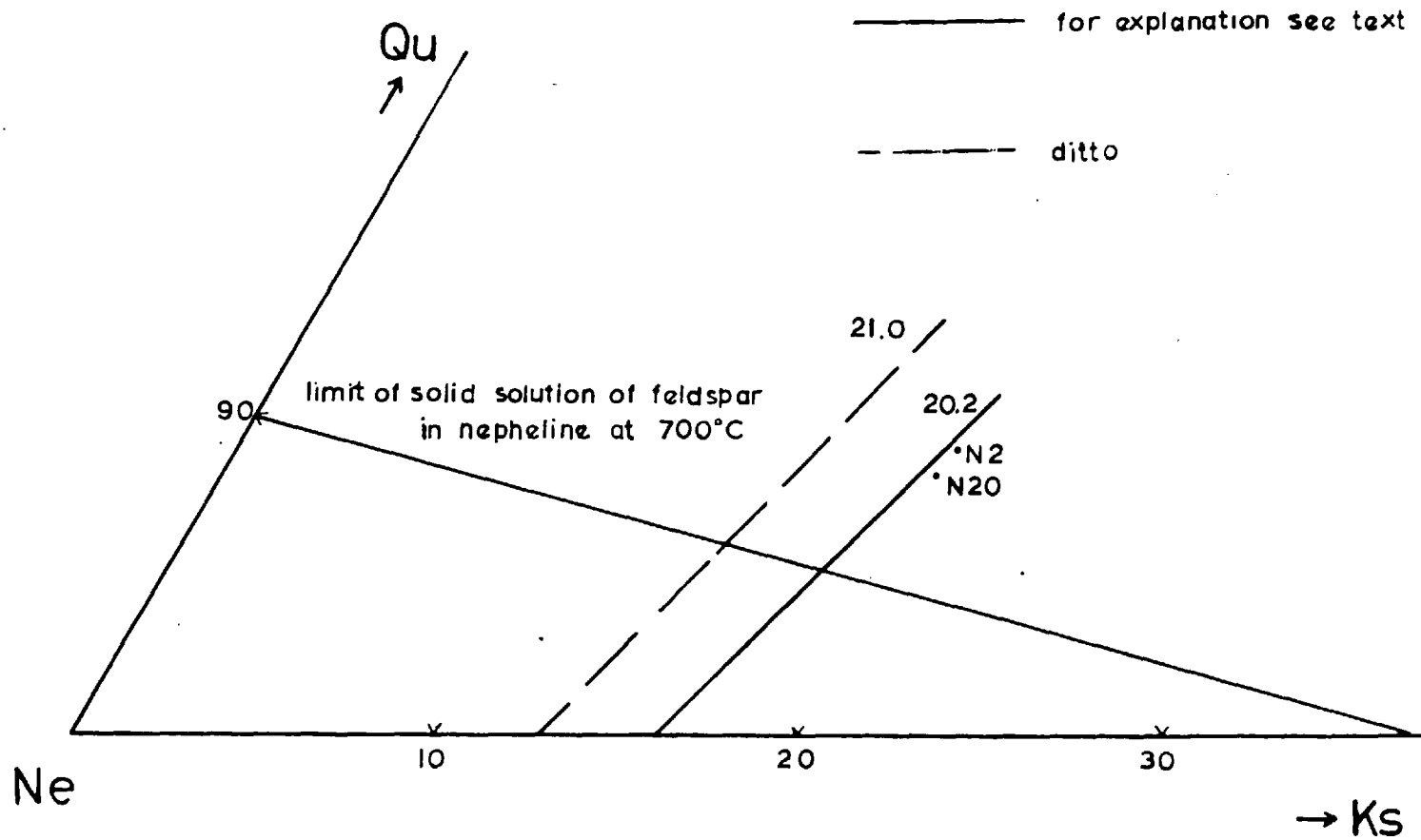


Figure 10

Nepheline-feldspar parageneses

Tuttle and Bowen (1958) classified granites, syenites and nepheline syenites with respect to the variable solid solution of alkali feldspars with temperature. They defined hypersolvus types as containing feldspars consisting of homogeneous solid solutions between albite and orthoclase, i.e. quenched high temperature forms. Subsolvus types contain feldspars in advanced stages of exsolution. Hypersolvus igneous rocks have feldspars which are either homogeneous or finely perthitic (X-ray or cryptoperthites) whereas subsolvus recrystallised or metamorphic rocks have coarser grained perthites or even discrete albite and microcline.

Morozewicz (1928) suggested that the average composition of natural nephelines was $Ne_{75}Ks_{21}Qu_4$ while Buerger gave his ideal nepheline composition as $Ne_{73}Ks_{27}$. Miyashiro (1951), Tilley (1953a, 1953b, 1954, 1956, 1957) and Tilley and Gittins (1961) have shown that the composition of nepheline is dependent on the thermal history of the host rock. Hypersolvus nepheline syenites contain nephelines whose composition is dependent on the bulk composition of the rock and which are in equilibrium with alkali feldspar of either the sanidine-anorthoclase, or the X-ray - cryptoperthite series. Subsolvus nepheline syenites contain nephelines whose compositions are independent of the bulk rock composition and are restricted to the Morozewicz-Buerger convergence field (Tilley 1954). The latter nephelines are in equilibrium with coarse perthites or completely exsolved albite and microcline, e.g. nepheline gneisses. Tilley

correlated the slopes of nepheline-feldspar tie lines with the two types of nepheline syenites. In Figure 11 AXB is the tie-line for a typical igneous assemblage where the alkali feldspar is a fine perthite and the nepheline falls outside the M-B field on the side of higher SiO_2 and Na_2O . CXD is the tie line for a metamorphic or plutonic assemblage, of the same bulk rock composition, where the alkali feldspar is a coarse perthite and the nepheline falls within the M-B convergence field. Tilley suggests that with slow cooling under plutonic conditions (i.e. extensive subsolidus reaction and recrystallisation) the nepheline of composition A will continuously react with the co-existing alkali feldspar B, becoming less silica and soda rich. If equilibrium is maintained the final nepheline composition will be C and the alkali feldspar D. The effect of this reaction is to cause the tie-lines to revolve about the bulk rock composition X. The slope of nepheline-feldspar tie-lines should therefore indicate the mode of origin of the nepheline syenite as being either igneous or metamorphic. Hamilton (1961) has suggested that when nepheline and feldspar are crystallising together on the liquidus they can exchange atoms of Si and Na. However, with subsolidus reaction the nepheline can only exchange alkali atoms with the feldspar and would maintain its Si/Al ratio. He suggested that the Si/Al ratio would only change when the nepheline was recrystallised and based this view on the absence of exsolved feldspar from plutonic rock and low temperature synthetic nephelines.

Figure 11

M = Nepheli
B = ditto c

Qu

Ab

Or

Ne

Ks

D

B

X

A

M*

C

B = ditto of Buerger.

(after Tilley, 1954)

Marangudzi nepheline syenites are typically hypersolvus and the nepheline-feldspar tie-lines for R.2 and R.20 have typically igneous trends (Figure 12). In Figure 12, N.2, R.2, F.2 and N.20, R.20 and F.20 are the tie-lines for Marangudzi foyaites R.2 and R.20. XYZ is the tie-line for a lardalite, Norway (Tilley, 1957) and QPN the tie-line for a pyroxene-nepheline syenite from Gooderham, Ontario (Tilley and Gittins, 1961). The data for these rocks are given in Table 10. The tie-lines all have similar trends even though the rocks are of widely differing compositions. The lardalite and pyroxene-nepheline syenite fall in the low temperature trough of the system Ne-Ks-Qu while the Marangudzi foyaites fall on the potash rich side of the trough. The Marangudzi foyaites have modal hastingsite which contains a certain proportion of felsic molecules. When this amount is subtracted from the bulk rock composition, the plotted position of the rock falls nearer the nepheline-feldspar tie-line (Figure 12).

Nepheline as a geological thermometer

Hamilton and MacKenzie (1960) and Hamilton (1961) studied the system Ne-Ks-Qu-H₂O at 1000 bars pressure and determined the limit of solid solution of feldspar in nepheline at 775°, 700° and 500° C. They suggested that these field boundaries indicate the possible compositions of nephelines in equilibrium with alkali feldspar at the various temperatures and showed that the higher the crystallisation temperature of the nepheline the higher would be its content of excess SiO₂. Thus if a natural

Figure 12

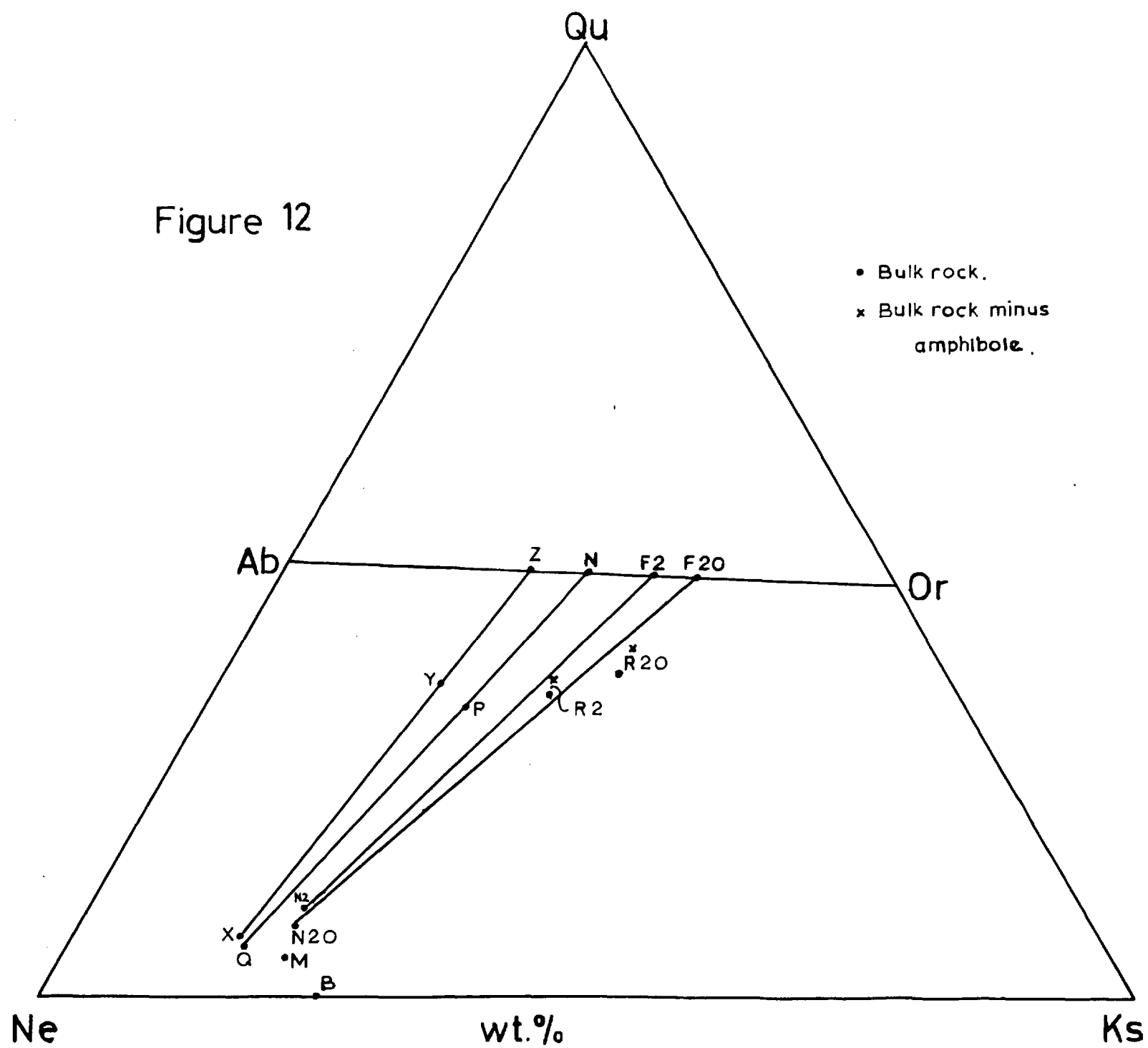


Table 10 : Data for rocks and co-existing nephelines and alkali feldspars

	Rock Composition			Nepheline Composition			Feldspar Composition	
	Ne	Ks	Qu	Ne	Ks	Qu	Ab	Or
1	38.3	30.2	31.5	71.1	19.9	9.0	38.7	61.3
2	37.0	30.0	33.0					
3	29.7	35.5	34.8	72.3	19.6	8.1	35.9	64.1
4	27.4	36.0	36.7					
5	46.8	26.4	32.8	78.2	15.2	6.6	60.4	39.6
6	45.8	23.5	30.7	77.5	17.3	5.2	50.3	49.7

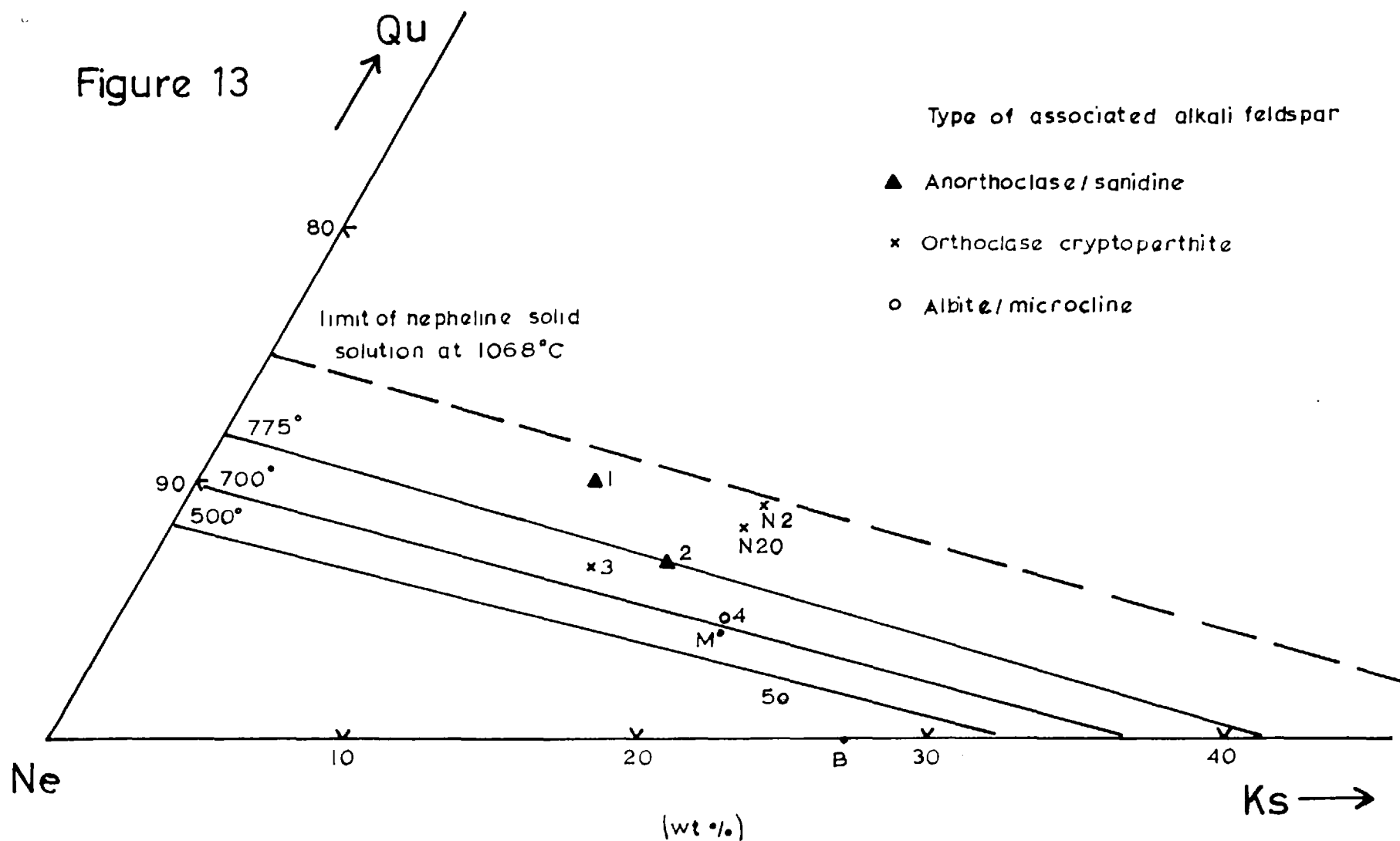
1. Foyaite R.2, Marangudzi (this work).
2. Bulk rock R.2. minus modal amphibole.
3. Foyaite R.20, Marangudzi (this work).
4. Bulk rock R.20. minus modal amphibole.
5. Lardalite, Norway (Tilley and Gittins 1961).
6. Pyroxene-nepheline syenite, Ontario (Tilley and Gittins 1961).

nepheline has been analysed and its composition recalculated in terms of Ne-Ks-Qu the temperature of its crystallisation can be estimated relative to these field boundaries. In the case of plutonic rocks which have suffered subsolidus reaction or recrystallisation misleading results will be obtained. The amount of subsolidus reaction or recrystallisation will be indicated by the type of alkali feldspar co-existing with the nepheline. Rocks with either sanidine/anorthoclase, orthoclase cryptoperthite, orthoclase microperthite or microcline/albite have suffered increasing amounts of subsolidus reaction. The content of excess SiO_2 in the co-existing nephelines would therefore give increasingly unreliable crystallisation temperatures.

Figure 13 shows the three determined field boundaries which have been drawn as straight lines to simplify relations. Also included is the approximate limit of nepheline solid solution at 1068°C . This is drawn in from the data of Greig and Barth (1938) and Tuttle and Smith (1958). Figure 13 is similar to Hamilton's (1960) Figure 2 and shows the plotted compositions of the Marangudzi nephelines and several other nephelines quoted by Hamilton. Table 11 gives the key to the nepheline samples shown in Figure 13 as well as the compositions of the nephelines and their suggested temperatures of crystallisation (Hamilton, 1961).

Hamilton did not give crystallisation temperatures for nephelines 4 and 5 as they occur in rocks which have suffered much

Figure 13



(after Hamilton 1961)

Table 11 : Data for rocks, nephelines and feldspars.

		Rock Composition			Nepheline Composition			Estimated crystallisation temperature °C
		Ne	Ks	Qu	Ne	Ks	Qu	
1	-	-	-	-	76.5	13.5	10.0	900
2.	FEAE 198	56.1	20.7	23.2	75.6	17.7	6.7	790
3	K114	46.8	20.4	32.8	78.3	15.1	6.6	750
4	-	45.8	23.1	31.1	74.7	20.9	4.4	-
5	E2	60.7	9.3	30.0	74.4	24.1	1.5	-
6	N2				71.1	19.9	9.0	950
7	N20				72.3	19.6	8.1	900

1. Phonolite, Kenya (Bowen and Ellested 1936).
2. Phonolite, Kenya (Tilley 1956).
3. Lardalite, Norway (Tilley and Gittins 1961).
4. Trachytoidal foyaite, Mariupol (Tilley 1954).
5. Nepheline syenite, Transvaal (Tilley 1953a).
6. Foyaite R2, Marangudzi (this work).
7. Foyaite R20, Marangudzi (this work).

(after Hamilton 1961)

subsolidus reaction. He suggested that the crystallisation temperatures for the phonolite nephelines (numbers 1 and 2) were realistic estimates of their liquidus temperatures. However, that for the lardalite nepheline (number 3) seems to be rather high considering the rock type and its associated feldspar. He suggested that this anomalous result might be due to the subsolidus reaction of alkali feldspar with nepheline, the latter becoming relatively enriched in K while its Si/Al ratio remains constant (see above). The Marangudzi nephelines also give high values for their crystallisation temperatures considering the rock types and associated alkali feldspars.

It is interesting to note that the nephelines of coarse grained Marangudzi foyaite R.2 and R.20 have compositions typical of quenched lava nephelines. This must be evidence of there having been little subsolidus reaction in the rocks and is substantiated by the co-existing feldspars having cores of X-ray perthite and margins of cryptoperthite.

3 THE PSEUDOLEUCITES

Pseudoleucite consists of an intergrowth of nepheline and alkali feldspar and seems to be formed by the alteration of primary leucite. In the Marangudzi complex pseudoleucites are found in the nepheline syenites (especially the juvites) and phonolites. Those in the nepheline syenites often lack any

crystal shape and occur in coarse grained groundmasses whilst those in the phonolites frequently show good crystal shape and occur in very fine grained groundmasses (Gifford, 1961). The pseudoleucites from both rock types vary from $\frac{1}{2}$ cm. to 10 cm. diameter. Those in the nepheline syenites are comparatively unaltered while those in the phonolites are often considerably altered to secondary analcite and zeolites. This is surprising when their relative crystal shapes are considered.

Table 12 shows the complete analysis of one, and the partial analysis of several Marangudzi pseudoleucites along with other analysed examples. Fudali (1963) studied the pseudoleucite BpM4 and found that it contained no secondary minerals; the analysis of this pseudoleucite (Zies and Chayes, 1960) is given in Table 12. The ratio $\text{Na}_2\text{O}/\text{K}_2\text{O}$ in BpM4 is taken to indicate the alkali ratio of an unaltered pseudoleucite. The phonolite pseudoleucites have much higher $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios than the juvite pseudoleucites and this substantiates that the former are much altered. The latter have similar alkali ratios to BpM4.

Origin of pseudoleucite

Bowen (1928) suggested the existence of a reaction point
Ne - Ks - Qu
in the ternary system / At this point any leucite present
would react with the liquid, forming alkali feldspar and nepheline,
until either the liquid or the leucite was used up. He was able
to confirm the existence of this invariant point experimentally

Table 12 : Analyses of pseudoleucites

	1	2	3	4	5	6	7
SiO ₂	57.42	56.9	53.36				
Al ₂ O ₃	21.85	22.6	25.41				
Fe ₂ O ₃	1.70	0.6	0.75				
MnO	0.03	-	-				
MgO	0.07	-	0.31				
CaO	0.19	1.3	0.83				
Na ₂ O	4.78	3.9	8.25	7.56	3.71	3.27	4.46
K ₂ O	13.40	10.8	9.45	9.84	13.29	13.53	12.98
TiO ₂	0.24	-	0.09				
H ₂ O ±	0.30	3.5	1.9				
BaO	0.28	-	-				
Total	100.26	99.7	100.63				

1. Pseudoleucite BpM4, Bearpaw Mountains, Montana (Zies & Chayes 1960)
2. .. Headed Dyke, Highwood Mountains, Montana (Larsen and Buie, 1938).
3. .. P.L.22, Phonolite, Marangudzi.
4. .. P.L.10, ...
5. .. P.L.28, Juvite ..
6. .. P.L.30
7. .. P.L.276

(Bowen and Schairer, 1935) and Bowen and Ellestad (1937) suggested that natural pseudoleucites owe their origin to this reaction. Larsen and Buie (1938) concluded that pseudoleucite was formed by the unmixing of a potash rich analcite. Fudali (1963) concluded that the subsolidus breakdown of leucite was responsible for the formation of pseudoleucite. He described the cooling of compositions in the system $\text{NaAlSi}_2\text{O}_6$ - KAlSi_2O_6 at 1000 bars H_2O pressure and showed that leucite solid solutions altered to nepheline and feldspar intergrowths by subsolidus reaction at various temperatures below 800°C . The temperature of breakdown varied with the composition of the leucite with soda rich types being less stable than potash rich types and altering at higher temperatures. He took samples of unaltered pseudoleucite and held them above 1000°C (1 atm. pressure) completely crystallising them to leucite solid solutions. He also held samples of fresh leucite at temperatures below 650°C (1000 bars pressure) and found some alteration to nepheline and feldspar.

Considering Fudali's conclusions it seems possible that the Marangudzi pseudoleucites were formed by the subsolidus alteration of primary leucite.

Chemistry of leucite and analcite

The Marangudzi pseudoleucites were analysed for Sr and Ba and the analyses are given in the appropriate section of Chapter 5 (Table 22). They were found to contain smaller concentrations of Sr and Ba than the rocks in which they are contained, which must

mean that the groundmasses contain even higher Sr and Ba. Zies and Chayes (1960) found a similar relationship for a pseudoleucite bearing tinguaitite. I have also determined Sr and Ba for phenocrystic fine leucites and pseudoleucites, and their/grained groundmasses, from lavas chosen from the collection of Imperial College Geology Department. The leucites were found to have lower Sr and Ba concentrations than their groundmasses. All these analyses are given in Chapter 5, Table 22 and their petrological significance is discussed in Chapter 6. It is sufficient at this stage to state that leucites and pseudoleucites contain less Sr and Ba than the liquids from which they crystallised.

It is interesting to consider further why leucite does not accept much Sr and Ba into its lattice. Potassium rich minerals generally concentrate Sr and Ba relative to K and the main carriers of Sr and Ba in the Marangudzi rocks are the alkali feldspars which contain up to $10\frac{1}{2}\%$ K_2O . R. Berlin (personal communication) has analysed the alkali feldspar phenocrysts of trachytes and kenytes and found that Sr and Ba were much enriched in the feldspars relative to the groundmasses (liquids). Leucites generally contain up to 20% K_2O and the comparative lack of Sr and Ba is difficult to reconcile with their high K_2O content. The problem therefore seems to be a structural one. Deer, Howie and Zussman (1963) have summarised the structures of leucite, analcite and pollucite. Leucite ($KAlSi_2O_6$) is tetragonal below $625^\circ C$ and cubic above this temperature. Its structure is based on a (Si, Al) - O framework

similar to that of analcite ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) and pollucite ($\text{CsAlSi}_2\text{O}_6$). The unit cell framework has cavities of two different sizes. There are sixteen larger sites (W sites) which have 12-fold co-ordination, these contain H_2O in analcite and K in K analcite ($\text{KAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$), Cs in pollucite and K in cubic leucite. There are twenty-four smaller sites (S sites) of which only sixteen are occupied and these have 6-fold co-ordination. The S sites are occupied by Na in analcite, K in K analcite and are vacant in leucite and pollucite. The cell edge of cubic leucite, analcite, K analcite and pollucite are respectively 13.4, 13.7, 13.8 and 13.6 Å. Natural leucites generally contain less than 2% Na_2O and less than 1% CaO but the position of Ca in the lattice is uncertain. Natural analcites also contain only small concentrations of CaO. The Ca analogue wairikite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$) has been found naturally but there seems to be little solid solution between the end members.

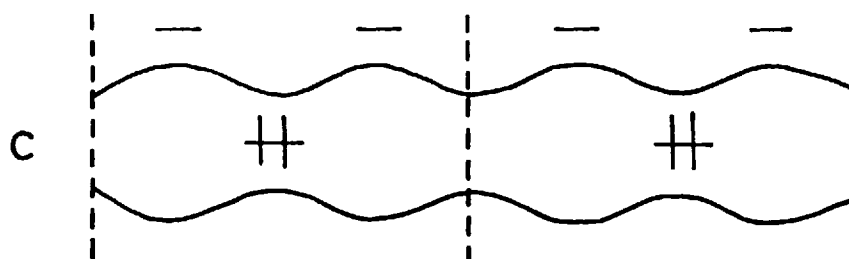
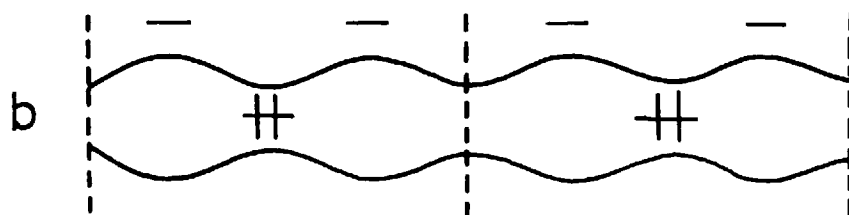
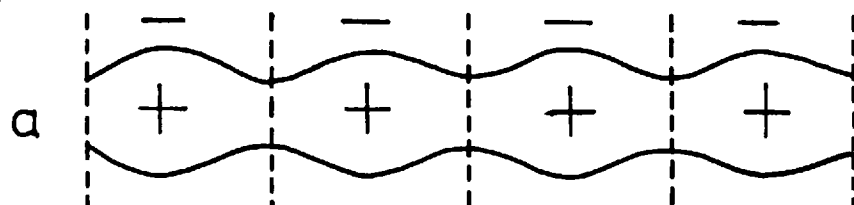
Barrer (1950) prepared leucite from analcite and vice-versa by ion exchange at low temperature (200°C). He also found that in synthetic analcites there is free interchange between Na ions and K, NH_4 , Ag, Tl and Rb ions but only slight exchange with Li, Cs, Mg, Ca and Ba ions. Cs ions are locked in the pollucite structure and the mineral cannot be prepared by ion-exchange with analcite; it can only be prepared by direct synthesis. Barrer used the concept of ion-sieve effect (which allows Rb to diffuse in the analcite structure but not Cs) to explain why Ca and Ba rich analcites are difficult to obtain. In the analcite

structure the interstitial channels have periodic constrictions (Fig. 14a) which are sufficiently narrow to prevent diffusion of Cs ions. Divalent cations cannot occupy positions at the constrictions because of steric reasons and their presence in only half of the sites normally occupied by univalent cations would lead to local disturbance of cationic and anionic charge (Fig. 14b).

Neither of these configurations is very stable and therefore exchange of univalent and divalent cations would be limited in extent. Barrer (1950) suggested that in chabazite and mordenite the constrictions are less marked and there would be room for the divalent cations to occupy intermediate positions in the channels (Fig. 14c). These relationships are in good agreement with natural minerals. Analcite contains little Ca whereas chabazite and mordenite contain large concentrations of Ca as well as Na and K. Reichert and Erdélyi (1935) reported the presence of Sr and Ba in chabazites; one sample contained 7.3% CaO, 1.55% Na₂O, 0.17% K₂O, 0.47% SrO and 0.17% BaO. Barrer and Denny (1961) found that Ca analcite was easier to form at low temperature than K analcite, the Sr analogue was prepared metastably at 350°C and Ba analcite was not obtained. Rb analcite was formed at 190°C and it is interesting to note that quite large concentrations of Rb occur in the analysed pseudoleucites and leucites (Chapter 5, Table 19).

Owing to the similar structures of analcite and cubic leucite similar arguments to above might explain the comparative

Figure 14



+ Univalent cation

++ Divalent cation

(after Barrer, 1950)

lack of Ca, Sr and Ba in leucites. Even though the ion-exchange experiments with analcite were carried out at temperatures considerably below the crystallisation temperature of leucite it is possible that the ease of entry of elements into the leucite lattice can be compared to that for the analcite lattice at low temperature. The absolute amounts of various elements entering the leucite lattice at high temperature will most likely differ greatly from those entering low temperature analcite but the order and ease of entry should be similar.

The replacement of Rb, Cs, Ca, Sr and Ba for K in leucite could be studied experimentally and it would be interesting to correlate the ionic replacements in leucite at high temperature (and pressure) with those in analcite and K analcite at low temperature (and pressure).

Nepheline shows a similar distribution of Sr and Ba to leucite. The analysed Marangudzi nephelines contain low concentrations of these elements; N.2 has 160 ppm Sr and 280 ppm Ba while N.20 has 160 ppm Sr and 240 ppm Ba. I thought originally that this reflected the late crystallisation of the nepheline, ie it is the last mineral to form. However, Oftedal (1963) analysed several nephelines and found that Sr was always less than 200 ppm and Ba less than 20 ppm. Some of these nephelines had clearly crystallised before the co-existing alkali feldspar which contained Sr. Oftedal concluded that Sr was low in nepheline because of

crystal chemical reasons. He suggested that if Ca or Sr replaced Na in nepheline vacancies would be introduced into the structure. Under these circumstances the nepheline structure must be sensitive to the size of the substituting ion so that the relatively large Sr (and Ba) is hardly admitted while the smaller Ca is accepted. A similar type of argument could also be used to explain the comparative lack of Sr and Ba in leucites.

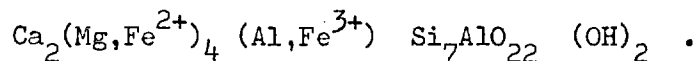
4 THE AMPHIBOLES

The general formula for amphiboles can be expressed:

$A_{O-1}X_2Y_5Z_8O_{22}(OH)_2$ where $A=Na,K$; $X = Ca,Na,Mn,Mg,Fe^{2+}$;
 $Y = Mg,Fe^{2+},Fe^{3+},Al,Mn,Ti$; $Z = Si,Al,Ti$. (OH) may be wholly or partly replaced by F and Cl. Structural work has shown that the A,X,Y and Z sites have respectively, tenfold, six or eightfold, sixfold and fourfold co-ordinations.

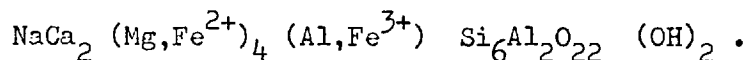
Kunitz (1930) divided the amphiboles into several series on the basis of isomorphous substitutions of the types $Mg = Fe^{2+}$, $NaAl = Ca,Mg$ and $NaSi = CaAl$ and suggested various 'end member' compositions. Sundius (1946) suggested a twofold scheme of isomorphous substitution: in the tremolite molecule $Ca_2Mg_5Si_8O_{22}(OH)_2$; or its ferrous analogue actinolite $Ca_2Fe^{2+}_5Si_8O_{22}(OH)_2$. The substitutions suggested were (i) occupation of vacant A sites by Na,K and/or replacement of Ca by Na,K, and (ii) substitution of Al,Al for $Si(MgFe^{2+})$. The Marangudzi amphiboles are hastingsites and I will only discuss the derivation of Ca rich amphiboles. By

a replacement of type (ii) Sundius derived the formula for common hornblende:



By combining replacements of types (i) and (ii) e.g.

$(\text{Mg}, \text{Fe}^{2+})\text{Si}_2 = \text{Na}(\text{Al}, \text{Fe}^{3+})_3$ he derived the formula for the pargasite-ferrohastingsite series:



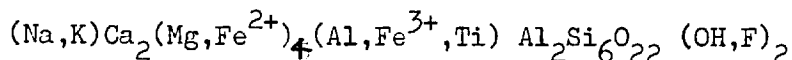
Replacement of Si by Al is limited to approximately two atoms for per formula unit.

Billings (1928) subdivided the hastingsite group on the basis of molecular proportion of FeO and MgO. Magnesiohastingsite has $\text{FeO}/\text{MgO} < \frac{1}{2}$, femahastingsite has a ratio $> \frac{1}{2}$ and ferrohastingsite has $\text{FeO}/\text{MgO} > 2$. Borley (1963) subdivided hastingsites with respect to the atomic ratio $\text{Fe}^{2+}/\text{Fe}^{2+} + \text{Mg}$. Magnesiohastingsite, femahastingsite and ferrohastingsite have values for this ratio in the ranges 0-35, 35-65 and 65-100 respectively. Borley's classification places the boundary between fema- and ferrohastingsites at a slightly lower Fe^{2+} content than Billings's.

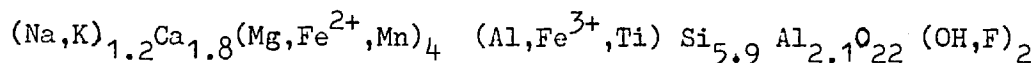
The Marangudzi amphiboles have relatively high Mn contents and this has been included with Fe^{2+} to give the ratio $\text{Fe}^{2+} + \text{Mn}/\text{Fe}^{2+} + \text{Mn} + \text{Mg}$. This ratio has values from 59.0 to 88.2 (Table 15) and, using Borley's classification, the Marangudzi amphiboles range from fema- to ferrohastingsites.

The chemical compositions of many, so called, barkeveekites and hastingsites are very similar and the main difference between them is that of colour. Hastingsites have green pleochroism while barkeveekites have brown pleochroism. This classification is rather confusing and I will refer to the Marangudzi amphiboles as hastingsites, even though some of them have brown pleochroism.

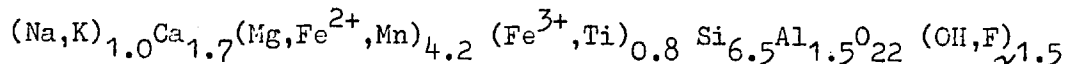
Classification of the Marangudzi amphiboles is based upon the general hastingsite formula:



The amphiboles from the undersaturated rocks approximate to the formula:



and those from the oversaturated rocks can be represented by:



Chemistry of the amphiboles

Twelve amphiboles have been analysed, eight from undersaturated rocks (A.2, A.15, A.20, A.26, A.28, A.31, A.76 and A.131) and four from oversaturated rocks (A.21, A.141, A.177 and A.439). The chemical analyses, cell formulae and other data are given in Tables 13, 14 and 15a. Owing to the lack of precision and accuracy in the determination of H_2O^+ and F, I have calculated the cell formulae for seven of the amphiboles to 23 oxygen atoms. The difference between calculating the same amphibole analysis to $24(\text{O}, \text{OH}, \text{F})$ or to $23(\text{O})$ is not significant and analyses which have

Table 13: Analyses and optical properties of Marangudzi amphiboles.

	Undersaturated rock amphiboles					Oversaturated rock amphiboles							
	A2*	A15*	A20*	A26†	A28†	A31†	A76*	A131*	A21†	A141†	A177†	A439†	
SiO ₂	37.34	36.80	36.73	36.91	36.44	37.78	37.48	37.08	40.55	39.66	40.29	39.89	SiO ₂
TiO ₂	1.12	0.96	1.56	1.95	2.04	3.04	2.63	0.89	1.66	1.98	1.83	1.70	TiO ₂
Al ₂ O ₃	10.92	10.15	12.08	13.31	13.58	11.17	11.74	11.77	7.90	7.52	7.01	8.74	Al ₂ O ₃
Fe ₂ O ₃	7.08	7.58	5.69	6.31	5.03	5.54	5.21	5.82	5.67	5.18	5.52	4.71	Fe ₂ O ₃
FeO	20.40	23.74	21.43	17.94	17.32	19.50	19.16	22.02	19.75	27.16	27.19	21.38	FeO
MnO	0.90	1.57	0.90	0.63	0.34	0.63	0.78	1.33	0.70	0.81	0.80	0.61	MnO
MgO	4.30	1.95	3.73	5.62	6.89	5.35	5.58	3.46	6.94	2.22	2.19	6.60	MgO
CaO	10.90	10.22	10.78	11.09	11.90	11.02	11.27	10.94	11.00	9.43	9.60	9.72	CaO
Na ₂ O	2.87	2.94	2.68	2.47	1.76	2.29	2.25	2.54	2.10	2.16	2.19	1.94	Na ₂ O
K ₂ O	2.00	1.88	2.36	2.21	2.46	2.08	2.15	2.07	1.54	1.43	1.40	1.42	K ₂ O
H ₂ O+	1.03	0.98	1.06	0.44	0.45	0.51	0.82	0.87	0.40	0.64	0.94	0.65	H ₂ O+
H ₂ O-	0.02	0.05	0.02	-	-	-	0.04	0.05	-	-	-	-	H ₂ O-
F	1.51	2.06	1.57	2.0	1.8	1.9	1.84	1.94	2.5	2.2	1.7	2.9	F
Cl	0.10	0.05	0.08	-	-	-	0.16	0.14	-	-	-	-	Cl
	100.53	100.93	100.67	100.88	100.01	100.81	101.11	100.92	100.71	100.39	100.66	100.26	
Less O-F, Cl	0.65	0.86	0.68	0.8	0.8	0.8	0.81	.85	1.0	0.9	0.7	1.1	Less O=F, Cl
Total	99.88	100.07	99.99	100.08	99.31	100.01	100.30	100.07	99.71	99.49	99.96	99.16	Total
α	1.701	1.710	1.692	1.696	1.702	1.696	1.700	-	1.689	1.708	1.706	1.692	α
Pleochroism													
X	pale yellow-green	pale yellow	pale yellow	pale yellow	pale brown	pale brown	pale brown	-	pale yellow	pale yellow	pale yellow	pale yellow	X
Y	yellow-green	yellow-green	yellow-green	brown-green	brown	green-brown	green-brown	-	yellow-green	yellow-green	yellow-green	yellow-green	Y
Z	dark green	dark green	dark green	dark brown-green	dark brown	very dark brown	dark brown	-	dark brown-green	dark green	dark green	dark olive-green	Z

* Analyst I.S.E. Carmichael (Borley and Frost 1963)

† Analyst C.M.B. Henderson

Table 14 : Formulae of Marangudzi amphiboles.

	A2 [†]	A15 [†]	A20 [†]	A26 [*]	A28 [*]	A31 [*]	A76 [†]	A131 [†]	A21 [*]	A141 [*]	A177 [*]	A439 [*]	
Si	5.99	6.01	5.89	5.78	5.72	5.94	5.92	5.97	6.38	6.46	6.53	6.35	Si
Al	2.01	1.96	2.11	2.22	2.28	2.06	2.08	2.03	1.47	1.44	1.34	1.64	Al
Ti	-	0.03	-	-	-	-	-	-	0.15	0.10	0.13	0.01	Ti
Z	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	Z
Al	0.05	-	0.17	0.23	0.22	0.01	0.10	0.20	-	-	-	-	Al
Ti	0.14	0.09	0.19	0.23	0.24	0.36	0.31	0.11	0.04	0.14	0.10	0.19	Ti
Fe ³⁺	0.85	0.92	0.69	0.74	0.59	0.66	0.63	0.70	0.67	0.64	0.67	0.56	Fe ³⁺
	1.03	1.01	1.05	1.20	1.05	1.03	1.04	1.01	0.71	0.78	0.77	0.75	
Fe ²⁺	2.74	3.24	2.87	2.35	2.27	2.56	2.53	2.96	2.60	3.68	3.69	2.68	Fe ²⁺
Mn	0.13	0.22	0.13	0.08	0.05	0.08	0.10	0.18	0.06	-	0.03	-	Mn
Mg	1.03	0.47	0.89	0.31	1.61	1.25	1.31	0.83	1.63	0.54	0.51	1.57	Mg
Na	0.07	0.06	0.06	0.06	0.02	-	0.02	0.02	-	-	-	-	Na
	3.97	3.99	3.95	3.80	3.95	3.89	3.96	3.99	4.29	4.22	4.23	4.25	
Y	5.00	5.00	5.00	5.00	5.00	4.92	5.00	5.00	5.00	5.00	5.00	5.00	Y
Ca	1.87	1.79	1.85	1.86	2.00	1.86	1.91	1.89	1.85	1.64	1.67	1.66	Ca
Na	0.82	0.86	0.77	0.70	0.51	0.70	0.66	0.77	0.64	0.68	0.69	0.60	Na
K	0.41	0.39	0.48	0.44	0.49	0.42	0.44	0.43	0.31	0.30	0.29	0.29	K
Mn	-	-	-	-	-	-	-	-	0.03	0.11	0.08	0.08	Mn
Fe ²⁺	-	-	-	-	-	-	-	-	-	0.02	-	0.17	Fe ²⁺
AX	3.10	3.04	3.10	3.00	3.00	2.98	3.01	3.09	2.83	2.75	2.73	2.80	AX
OH	1.10	1.06	1.14				0.87	0.93					OH
F	0.77	1.06	0.79				0.91	0.99					F
Cl	0.02	0.01	0.02				0.04	0.04					Cl
OH,F,Cl	1.89	2.13	1.95				1.82	1.96					OH,F,Cl

† Formula calculated to 24(C,OH,F,Cl); * Formula calculated to 23(b)

Table 15a : Data for amphiboles

	A2	A15	A20	A26	A28	A31	A76	A131	A21	A141	A177	A439
$\frac{\text{Fe}^{2+} + \text{Mn} \times 100}{\text{Fe}^{2+} + \text{Mn} + \text{Mg}}$	73.5	88.0	77.2	65.0	59.0	67.9	66.8	79.1	62.3	87.7	88.2	65.2
$\frac{\text{FeO}}{\text{MgO}}$ (mole %)	2.66	6.83	3.24	1.79	1.41	2.04	1.93	3.58	1.60	6.90	7.24	1.82
$\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}}$	3.2	3.5	4.1	3.2	3.8	3.9	4.1	4.3	3.9	5.8	5.5	5.0
$\frac{\text{Fe}^{2+}}{\text{Mn}}$	22.1	15.0	23.0	28.0	50.4	30.6	24.4	16.1	28.2	33.3	33.5	34.7
$\frac{\text{Fe}^{2+} \times 100}{R^\dagger}$	55	65	58	48	45	52	51	59	52	74	74	54

† R = all elements in Y group.

Table 15b : Norms of amphiboles.

	A2	A15	A20	A26	A28	A31	A76	A131	A21	A141	A177	A439
Or	5.3	11.1	-	6.1	-	12.2	8.3	7.2	8.9	8.3	8.3	8.3
Lc	5.0	-	12.5	5.2	7.0	-	3.5	3.9	-	-	-	-
Ab	-	2.1	-	-	Ks 3.2	1.0	-	-	13.1	17.0	15.5	16.2
Ne	13.4	12.2	12.5	11.4	8.0	9.9	10.2	11.4	2.6	0.7	1.6	-
An	10.8	8.9	13.9	18.6	22.9	14.2	15.6	15.0	7.8	6.7	5.2	11.1
Di	27.6	24.1	24.2	18.5	19.8	22.4	22.6	21.4	24.1	20.8	26.3	13.4
Ol	21.2	23.6	23.0	22.8	23.9	21.9	22.7	26.0	26.3	29.1	27.2	29.9
Hy	-	-	-	-	-	-	-	-	-	-	-	3.4
Il	2.1	1.8	3.0	3.7	3.8	5.8	5.0	1.7	3.2	3.8	3.5	3.2
Mn	10.2	11.1	8.4	9.1	7.2	8.1	7.7	8.3	8.1	7.7	8.0	7.0
Fl	3.1	4.1	3.3	4.0	3.7	3.9	3.9	4.1	5.1	4.5	3.5	5.9

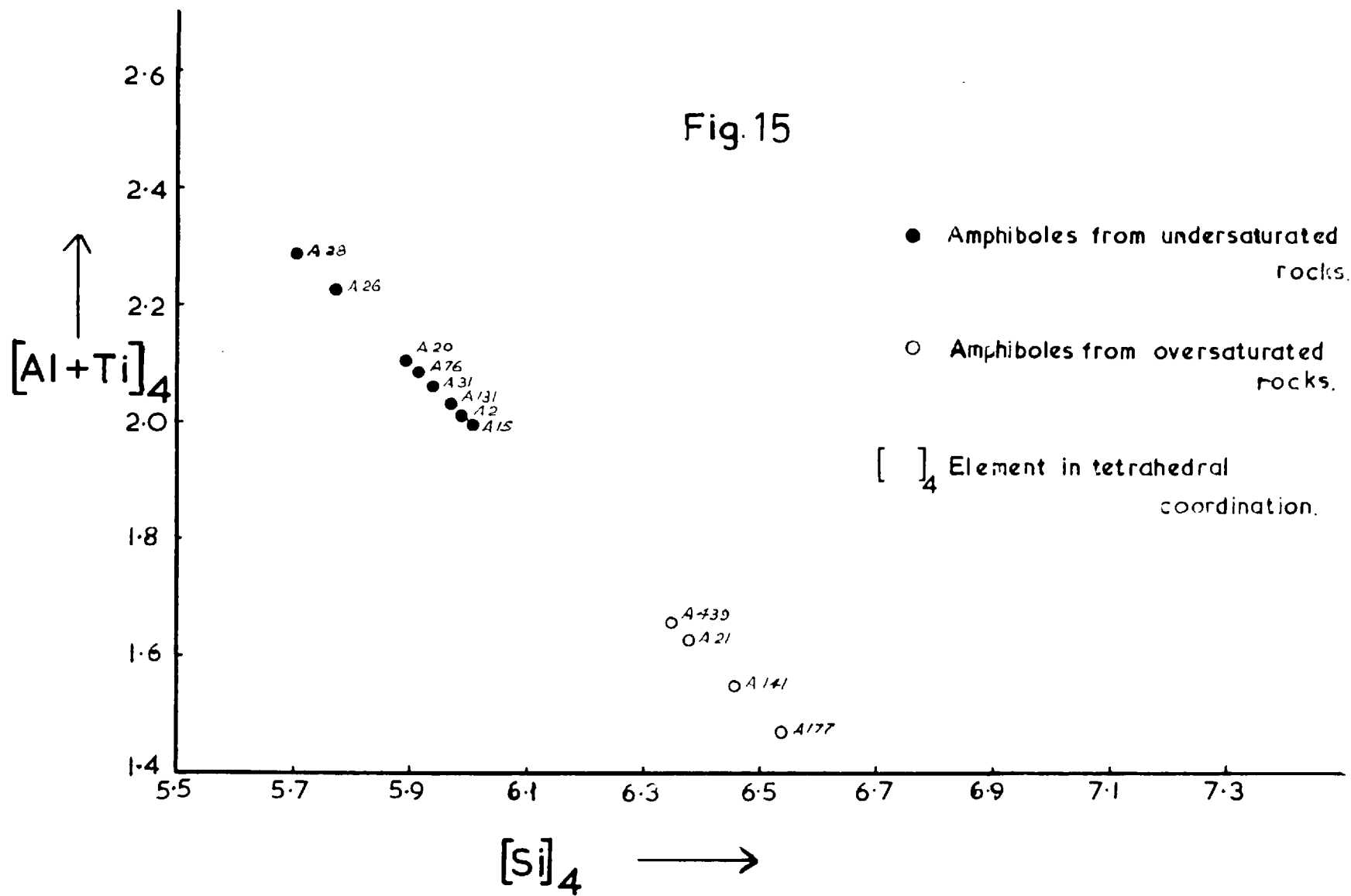
been calculated by the two different methods can be compared directly.

The chemical data show that there is a distinct difference between amphiboles from the over- and undersaturated rocks and I will discuss the two groups separately.

The Z group contains the tetrahedrally co-ordinated ions Si^{4+} (0.42 A°), Al^{3+} (0.51) and Ti^{4+} (0.68). In the undersaturated rock amphiboles Si increases from 5.72 (A.28) to 6.01 (A.15). A.15 is the only undersaturated rock amphibole that has $\text{Si} + [\text{Al}]_4$ less than eight atoms and this deficiency is made good with Ti (0.03 atoms). The oversaturated rock amphiboles have higher Si and lower Al than the above types and in all cases Ti has been added to make a total of eight atoms. Si increases from 6.35 (A.439) to 6.53 atoms (A.177), Al decreases from 1.64 (A.439) to 1.34 atoms (A.177) and Ti varies from 0.01 (A.439) to 0.16 atoms (A.21). Figure 15 shows the relative proportion of Si to Al+Ti in the Z group and exemplifies the difference between amphiboles from over and undersaturated rocks.

The Y group contains the ions Fe^{2+} (0.74 Å°), Mg^{2+} (0.66), Mn^{2+} (0.80), Fe^{3+} (0.64), Al and Ti all in 6-fold co-ordination. This group contains a total of five atoms (as required by the ideal hastingsite formula). When the above elements total less than five and where there is an excess over three atoms in the X group, Na atoms are added to make good this deficiency. Na is chosen

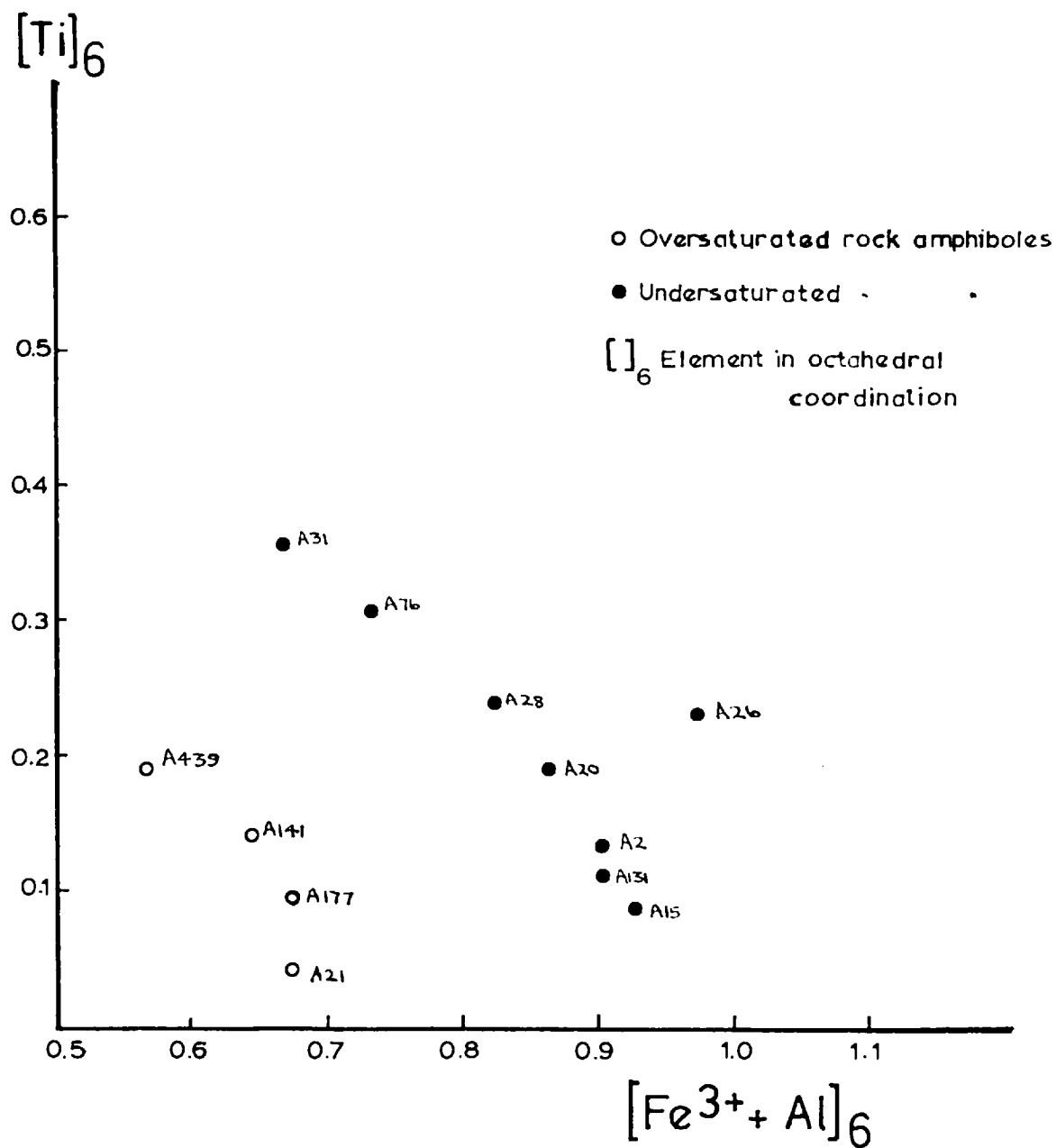
Fig.15



rather than Ca as it has a smaller value for the radius ratio $r_{\text{oxygen}} : r_{\text{cation}}$ and would be more likely to occur in 6-fold co-ordination. The ideal hastingsite formula has four atoms of $(\text{Fe}^{2+}, \text{Mg}, \text{Mn})$ and one atom of $(\text{Fe}^{3+}, \text{Al}, \text{Ti})$ and I will discuss the results with reference to this.

After addition of Na, atoms in the Y group total five for all undersaturated rock amphiboles except A.26 (4.99) and A.31(4.92) . Fe^{2+} and its substituents vary from 3.74 in A.26 to 3.98 atoms in A.131. All the undersaturated rock amphiboles except A.15 contain some Al in 6-fold co-ordination and this amount varies from 0.01 in A.31 to 0.23 atoms in A.26. Ti varies from 0.08 atoms in A.15 to 0.36 atoms in A.31. $[\text{Ti}]_6$ and $[\text{Al} + \text{Fe}^{3+}]_6$ show a regular inverse relationship (Figure 16). for all samples except A.26. Amphibole A.26 is peculiar in that it has $(\text{Fe}^{3+}, \text{Al}, \text{Ti})$ totalling 1.20 atoms and $(\text{Fe}^{2+}, \text{Mg}, \text{Mn})$ totalling 3.74 atoms. These totals are considerably higher and lower respectively than those for the other undersaturated rock amphiboles. Fe^{3+} increases from 0.59 atoms in A.28 to 0.92 in A.15 and there seems to be a direct relationship with Fe^{2+} as the ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ stays relatively constant (Table 15). A.26 is again seen to be odd in that its $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio is lower than that for the amphiboles from similar rock types . The chemical determination of total iron and FeO for A.26 were carried in duplicate and the results were repeated within the usual limits of error. Fe^{2+} increases from 2.27 atoms in A.28 to 3.24 in A.15 ^{and Mg} /decreases sympathetically

Figure 16



from 1.61 to 0.47 atoms. Mn is subordinate in amount and increases with increasing Fe^{2+} but at a more rapid rate. The Fe^{2+}/Mn ratio therefore decreases with increasing Fe^{2+} (Table 15a).

The oversaturated rock amphiboles all contain more than five atoms of Y group elements and this excess has been added to the X group as Mn and Fe^{2+} . Mn is added first as it would be more likely to occur in 8-fold co-ordination (Mn has a higher radius ratio than Fe^{2+}). Fe^{3+} and its substituents vary from 0.71 atoms in A.21 to 0.78 in A.141, this is considerably less than the theoretical total of one atom. $[\text{Ti}]_6$ varies from 0.04 atoms in A.21 to 0.19 in A.439 and again shows an inverse relationship with $(\text{Al} + \text{Fe}^{3+})_6$ (Fig. 16). Fe^{3+} varies from 0.56 atoms in A.439 to 0.67 in A.21 and A.177. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio shows that there is little increase of Fe^{3+} with increasing Fe^{2+} . Fe^{2+} and its substituents vary from 4.22 atoms in A.141 to 4.29 atoms in A.21, this is more than the theoretical four atoms. Total Fe^{2+} (in both X and Y groups) increases from 2.60 atoms in A.21 to 3.70 atoms in A.141 and Mg decreases sympathetically from 1.63 atoms in A.21 to 0.51 atoms in A.177. Total Mn increases slightly from 0.08 atoms in A.439 to 0.11 atoms in A.141 and A.177 and the Fe^{2+} (Mn ratio remains almost constant (Table 15a).

The AX group contains the larger cations Ca^{2+} (0.99 Å), Na^+ (0.97), K^+ (1.33) and small amounts of Mn and Fe^{2+} , all in

8- or 10-fold co-ordination. The theoretical formula requires three atoms in this group, two of which should be Ca atoms.

In the undersaturated rock amphiboles the total number of atoms (after addition of Na to the Y group) varies from 3.00 in A.26 to 3.11 in A.20. There is some small correlation between Ca and (Na,K) content. Ca increases from 1.79 atoms in A.15 to 2.00 in A.28 and alkalis decrease from 1.31 atoms in A.15 to 1.02 in A.28. A.28 is the only amphibole with similar contents of Na and K (0.53 and 0.49 atoms respectively). In all the other undersaturated rock amphiboles Na exceeds K by up to 2:1.

In the oversaturated rock amphiboles the total number of atoms is always less than three even after excess Mn and Fe^{2+} from the Y group has been added. The total varies from 2.72 atoms in A.21 to 2.67 atoms in A.177 and total alkalis remain almost constant. A.21 contains higher Ca than the other oversaturated rock amphiboles. The Na/K ratio is higher in the over- than in the undersaturated rock amphiboles and is always greater than 2. Total atoms of Mn and Fe^{2+} vary from 0.03 in A.21 to 0.25 in A.439.

The (OH) group contains OH^- , F^- and Cl^- ions. Five amphiboles (on which H_2O^+ was determined precisely) were calculated to 24 (O,OH,F,Cl) and the number of atoms in this group varies from 1.82 in A.76 to 2.13 in A.15. In the undersaturated rock amphiboles

the F content varies from 1.5 (weight %) in A.2 to 2.1 % in A.15. In the oversaturated rock amphiboles F is of a generally higher tenure and varies from 1.7% in A.177 to 2.9% in A.439.

The two most important ionic substitutions in this group of amphiboles are (i) $\text{Fe}^{2+} = \text{Mg}$ and (ii) $\text{Al} = \text{Si}$.

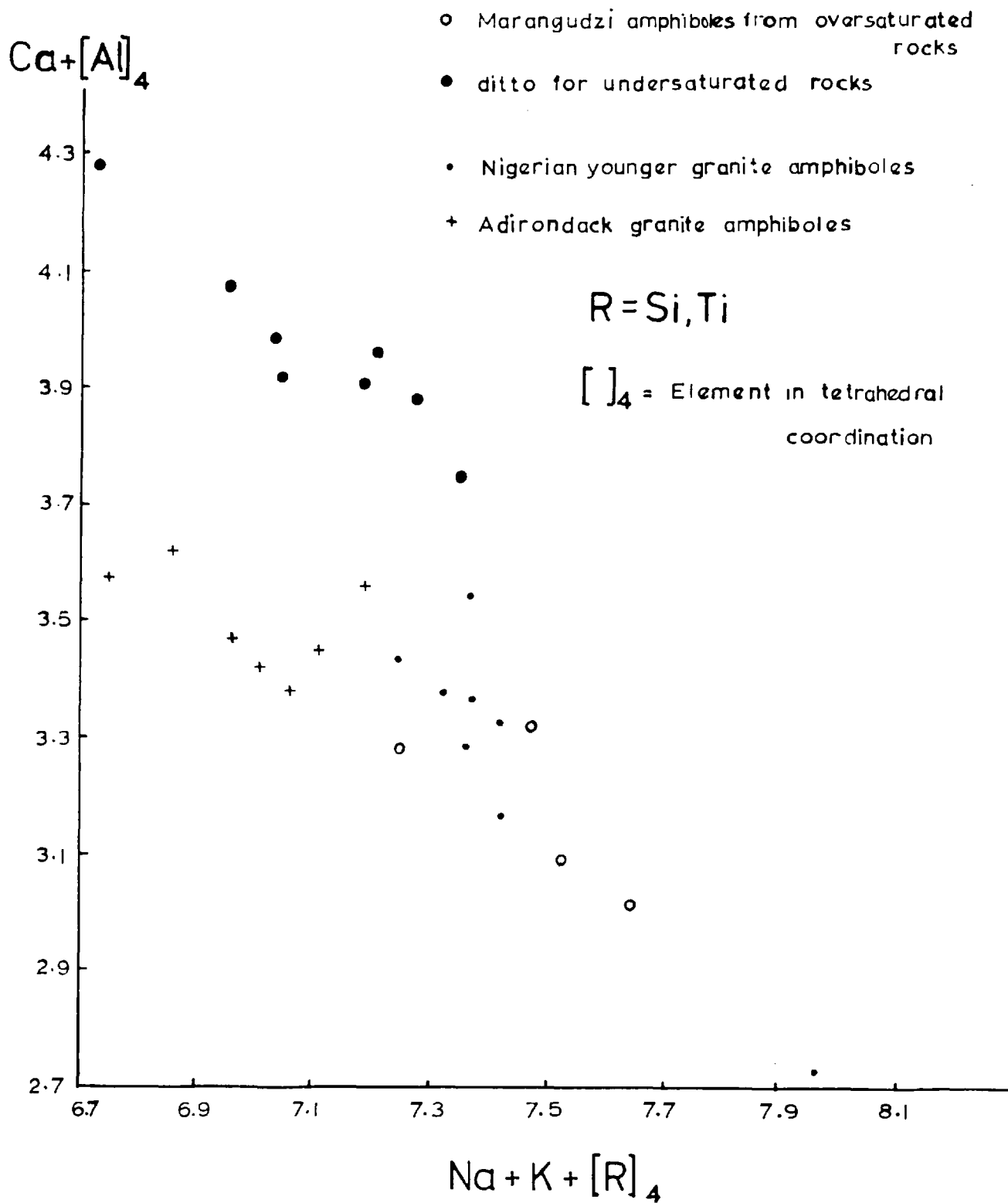
(i) The substitution of Fe^{2+} for Mg can be represented by a function of the type $\text{Fe}^{2+} + \text{Mn} / \text{Fe}^{2+} + \text{Mn} + \text{Mg}$, this indicates the amount of iron enrichment in the amphiboles and will be denoted I.E.

Assuming there to be iron enrichment with differentiation, amphiboles crystallised from early formed liquids would have smaller values for I.E. than those crystallised from progressively formed later liquids. In the undersaturated rocks amphiboles I.E. increases from 59.0 in A.28 to 88.0 in A.15. In the oversaturated rock amphiboles I.E. increases from 62.3 in A.21 to 88.2 in A.177 (Table 15).

The substitution of Fe^{2+} for Mg has been used to classify the hastingsite group of amphiboles (Billings, 1928; Borley, 1963). A differentiated series of hastingsites should show variation from magnesio- to fema- to ferrohastingsites. The Marangudzi amphiboles range from fema- to ferrohastingsites.

(ii) The substitution of Al for Si has been combined with the less important one of Ca for alkalis and Figure 17 shows the variation of $\text{Ca} + [\text{Al}]_4$ with $\text{Na} + \text{K} + \text{Si}$. The undersaturated rock

Figure 17

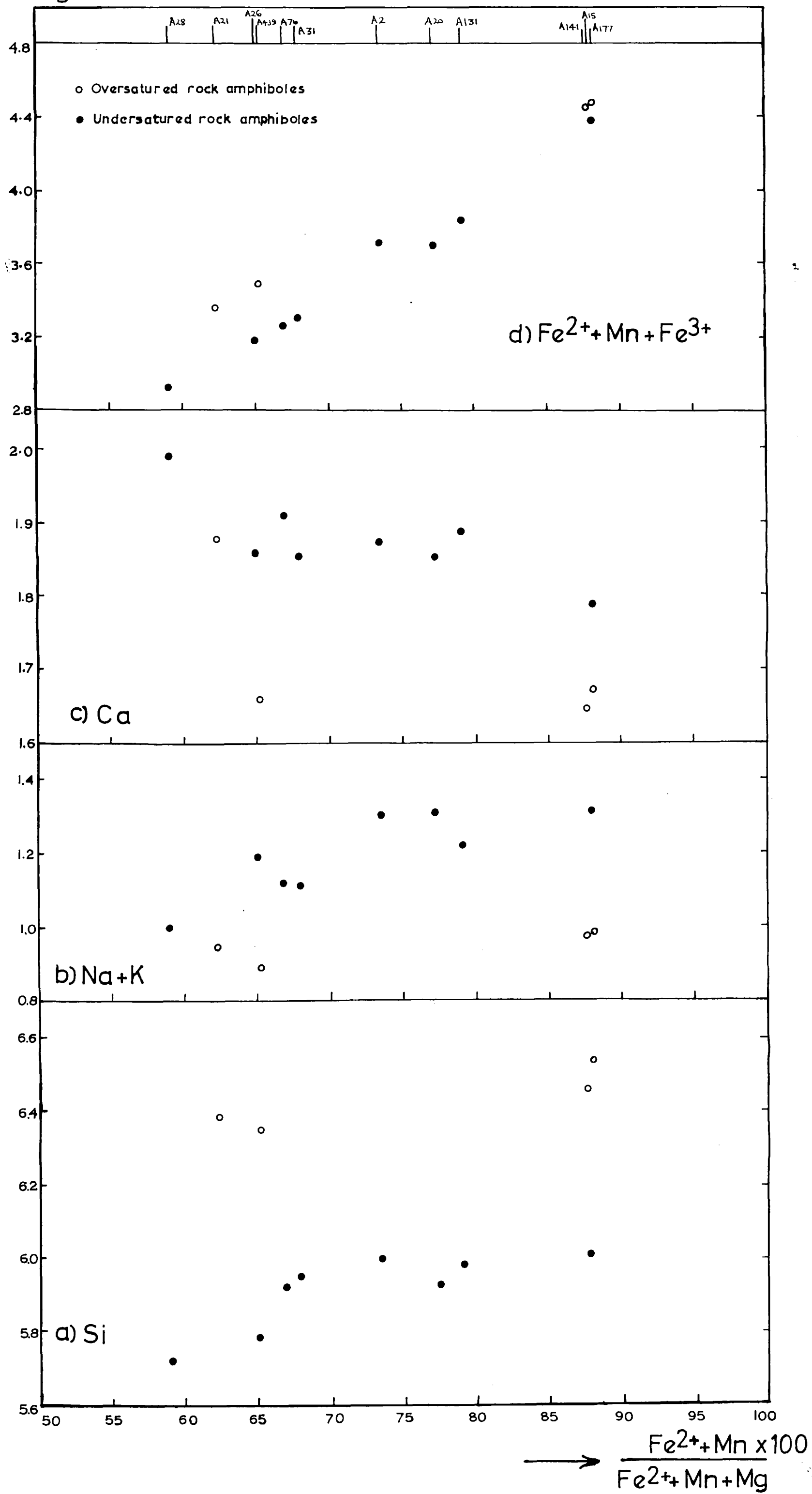


hastingsites are displaced upwards from the oversaturated rock hastingsites owing to their higher Al contents. Hastingsites from the alkaline Nigerian younger granites (Borley, 1963) and the calc-alkaline Adirondack granites (Buddington and Leonard, 1953) are included for comparison.

Atomic variations are best shown by plotting atoms of element against I.E. Figures 18a, b, c and d show the variation of Si, (Na+K) , Ca and ($\text{Fe}^{2+} + \text{Mn} + \text{Fe}^{3+}$) respectively. These plots show the striking differences between the amphiboles from the two rock types. In the undersaturated rock amphiboles Si seems to increase slightly with increasing I.E. (i.e. with differentiation), (Na+K) shows a similar relationship but Ca decreases. The oversaturated rock amphiboles contain slightly higher ($\text{Fe}^{2+} + \text{Mn} + \text{Fe}^{3+}$) than the undersaturated rock amphiboles (Fig . 18d).

Other series of genetically related hastingsites have been described from Adirondack granites (Buddington and Leonard, 1953) and from Nigerian younger granites (Borley and Frost, 1963). Marangudzi undersaturated rock hastingsites contain lower SiO_2 , higher Al_2O_3 , higher total alkalis and slightly higher CaO than hastingsites from the Adirondacks and Nigeria. Marangudzi oversaturated rock hastingsites are very similar in composition to those from Nigeria but contain slightly higher SiO_2 and lower Al_2O_3 than those from the Adirondacks. I.E. varies over similar ranges in the three series of hastingsites.

Figure 18



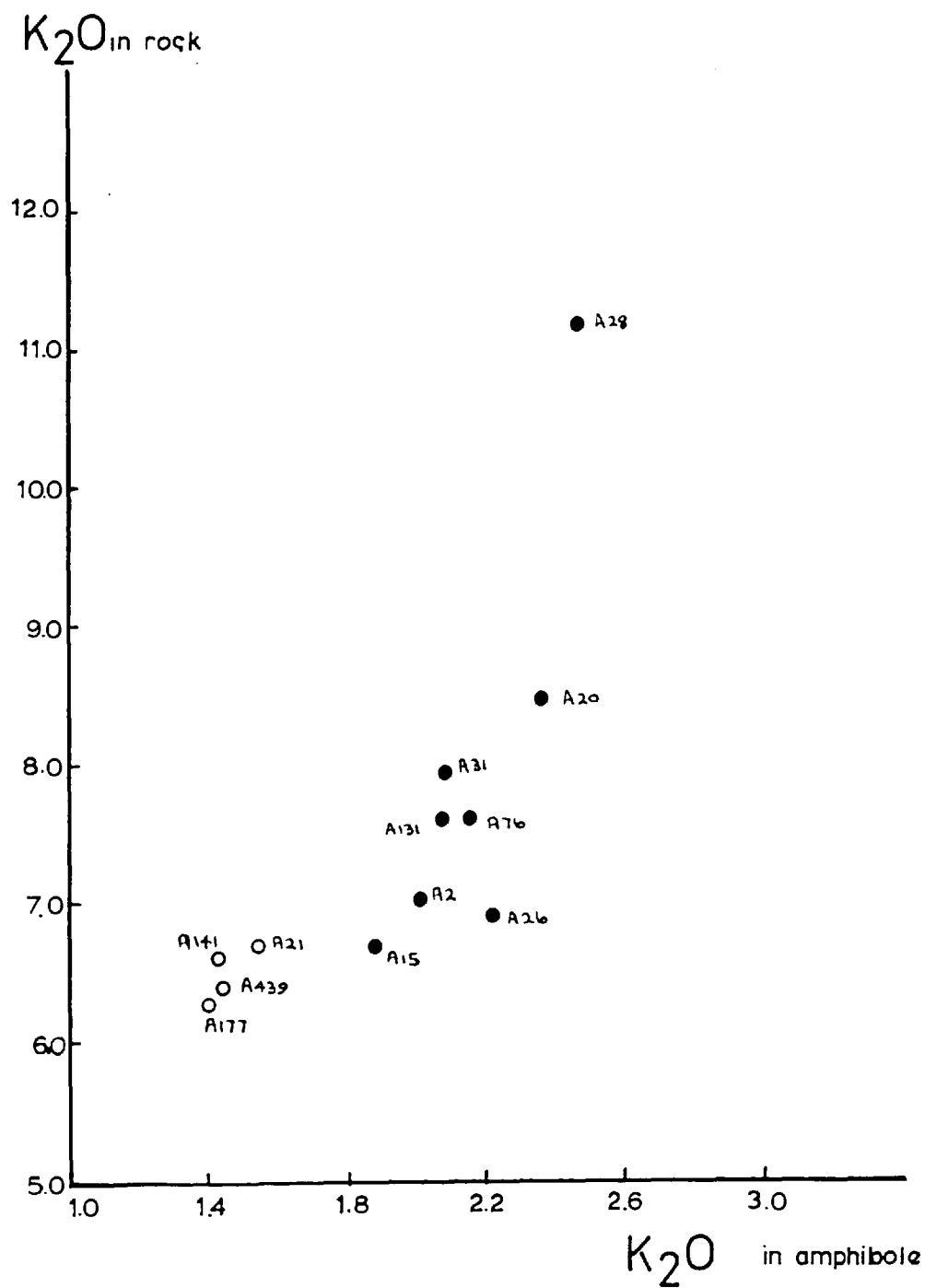
Petrological considerations

I have shown that there is a significant difference between the over- and undersaturated rock amphiboles from Marangudzi. The amphiboles from the undersaturated rocks have lower SiO_2 , higher Al_2O_3 , higher $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ and slightly higher CaO than those from the oversaturated rocks. The chemical compositions of the amphiboles therefore reflect the composition of the liquids from which they crystallised. Figure 19 shows that as the K_2O content of the rock increases, so does the K_2O of its contained amphibole. A.28 has the highest K_2O and it is significant that rock R.28 is very rich in K_2O and contains pseudoleucites.

Iron enrichment in a differentiated series of mafic minerals has been well established in, for example, Skaergaard pyroxenes. It should be possible to use the values for $\text{Fe}^{2+} + \text{Mn}/\text{Fe}^{2+} + \text{Mn} + \text{Mg}$ (I.E) shown by a genetically connected series of amphiboles, as a guide to the order of formation of the rocks in which they are contained. The value of I.E. for any particular ferromagnesium mineral will, to ascertain extent, depend on whether it co-exists with another ferromagnesium mineral. De Vore (1957) discussed the chemical composition of the co-existing pairs of minerals; Ca pyroxene-hornblende and hornblende-biotite. He referred to the ratio $\text{Mg}/\text{Mg} + \text{Fe}^{2+}$ and found similar values for this in both pairs of co-existing minerals.

Early crystallisation of an ore mineral would affect the composition of a mafic mineral of later crystallisation. The latter

Figure 19



would tend to be more enriched in Mg than it would have been if the ore mineral had not crystallised.

The Marangudzi amphiboles A.28, A.31 and A.76 co-exist with varying amounts of pyroxene belonging to the diopside - hedenbergite series. A.28 and A.439 co-exist with small amounts of biotite. It is unlikely that there would be much difference in iron-magnesium ratio for the co-exisiting minerals and there should be little error in directly comparing the I.E. values for amphiboles from different rock types. The modal amount of magnetite in the Marangudzi rocks is small and does not vary much. Magnetite is therefore unlikely to affect the I.E. of the amphiboles to any great extent.

Iron enrichment shown in the Adirondack and Nigerian hastingsites has been correlated with the relative positions of the parent rocks in a series of genetically related rocks. The same can be done for the Marangudzi amphiboles. I have shown that pulaskite-foyaite-microfoyaite is a differentiated rock series. The amphiboles these rocks contain show increasing values for I.E. from 65.0 (A.26) to 88.0 (A.15), and this is in good agreement with other chemical data. The pseudoleucite bearing dyke R.131 contains an amphibole A.131 which is clearly a late formed type (I.E.= 79.1). Juvite R.28 contains an amphibole A.28 which has the lowest value for I.E (59.0) and must be an early formed type even though the rock is of late intrusion.

In the series pulaskite-foyaite-microfoyaite the amphiboles show a decrease in TiO_2 from 3.04% (A.31) to 0.96% (A.15). Juvite amphibole A.28 has 2.04% TiO_2 and this is extra evidence that it is an early formed type.

Comparison of optical properties and chemical composition

I have given the refractive indices and colours of pleochroism for the Marangudzi amphiboles, in Table 13.

Borley (1963) plotted the refractive indices of various hastingsites and barkevekites against $\text{Fe}^{2+} + \text{Mn}/\text{Fe}^{2+} + \text{Mn} + \text{Mg}$ (I.E.) and found that there was a large range in I.E. for any particular value for refractive index. A similar result is found for the Marangudzi amphiboles, however, those with the highest values for I.E. tend to have the highest refractive indices.

The amphiboles from the pulaskites (A.26, A.31 and A.76) and juvite (A.28) are pleochroic in shades of brown while those from the foyaites and microfoyaite are pleochroic in shades of green. It is significant that the amphiboles with brown pleochroism have the highest TiO_2 contents and those with green pleochroism have the lowest TiO_2 contents. Some sections of A.31 are coloured a very dark brown and this amphibole has the highest TiO_2 of 3.04%.

5 THE ORE MINERALS

Gifford (1961) carried out a brief survey on the ore minerals contained in the Marangudzi rocks and his results are summarised here. The gabbros contain titaniferous magnetite as subhedral to anhedral grains. Exsolution lamellae of ilmenite and ulvöspinel are present and some samples are slightly altered to martite (secondary hematite). The oversaturated rocks contain titaniferous magnetite and ilmenite. The ilmenite is present as exsolution lamellae in the magnetite, as intergrowths with the magnetite and as discrete grains. Ulvöspinel is not seen but some alteration to martite is reported. The undersaturated rocks contain titaniferous magnetite which has exsolution lamellae of ilmenite and may show alteration to martite.

Three magnetites from the undersaturated rocks have been analysed; M.76 from pulaskite R.26, M.2 from foyaite R.2 and M.15 from microfoyaite R.15. In R.76 the magnetite is seen almost exclusively as inclusions in the amphibole and pyroxene or in association with aggregates of amphibole. The presence of magnetite in R.2 and R.15 is similar to above except that rather more exists as discrete grains. In R.15 the magnetite is seen as grains interstitial to well formed perthite grains. Unfortunately it was not possible to prepare polished sections of these minerals.

Chemical composition of magnetite. Deer, Howie and Zussman (1963) give the theoretical formulae of magnetite as

$\text{FeO} \cdot \text{Fe}_2\text{O}_3$ this is equivalent to 31.03 FeO, 68.97 Fe_2O_3 weight %. Small amounts of Al can substitute for Fe^{3+} and small amounts of Ca, Mg and Mn can replace Fe^{2+} . There is continuous solid solution between magnetite and ilmenite ($\text{FeO} \cdot \text{TiO}_2$) and magnetite and ulvöspinel ($2\text{FeO} \cdot \text{TiO}_2$). There is also solid solution between magnetite and maghemite ($\gamma\text{Fe}_2\text{O}_3$) and for natural compositions between these end-members the sum of the cations (calculated to 32 oxygens) will be less than the ideal of 24 which exists for pure magnetite. The end member maghemite has 21.33. Maghemite is often formed by oxidation of magnetite and Basta (1959) showed the existence of titaniferous maghemite formed by the oxidation of titaniferous magnetite. Buddington, Fahey and Vlisdis (1955) suggested that the concentration of TiO_2 in magnetite was a function of crystallisation temperature and that the higher the temperature the greater the TiO_2 content. They found that a magnetite from a hornblende microperthite granite from the Adirondacks had about 10% excess Fe_2O_3 but X-ray photographs showed no hematite lines.

The analyses and formula (calculated to 32 oxygens) of the Marangudzi magnetites are given in Table 16. They have comparatively high Fe_2O_3 (up to 72½% in M.15) and because of this the sum of the cations is less than 24. M.76 has 23.378, M.2 has 23.440 and M.15 has 23.322 cations for 32 oxygens. TiO_2 is up to 8½%, MgO and CaO are near 1% and CaO averages ½% .

Table 16 : Analyses and formulae of Marangudzi magnetites.

	M76	M2	M15
TiO ₂	8.56	3.63	2.53
Fe ₂ O ₃	60.35	68.98	72.65
FeO	28.48	25.09	22.49
MnO	1.25	0.90	1.03
MgO	1.19	1.04	1.07
CaO	0.43	0.61	0.69
Total	100.26	100.25	100.46

Formula calculated for 32 oxygens.

Ti	1.905	0.814	0.565
Fe ³⁺	13.446	15.483	16.225
	<u>15.351</u>	<u>16.297</u>	<u>16.790</u>
Fe ²⁺	7.052	6.258	5.583
Mn	0.313	0.228	0.258
Mg	0.525	0.462	0.472
Ca	0.137	0.195	0.219
	<u>8.027</u>	<u>7.143</u>	<u>6.532</u>
Total	23.378	23.440	23.322

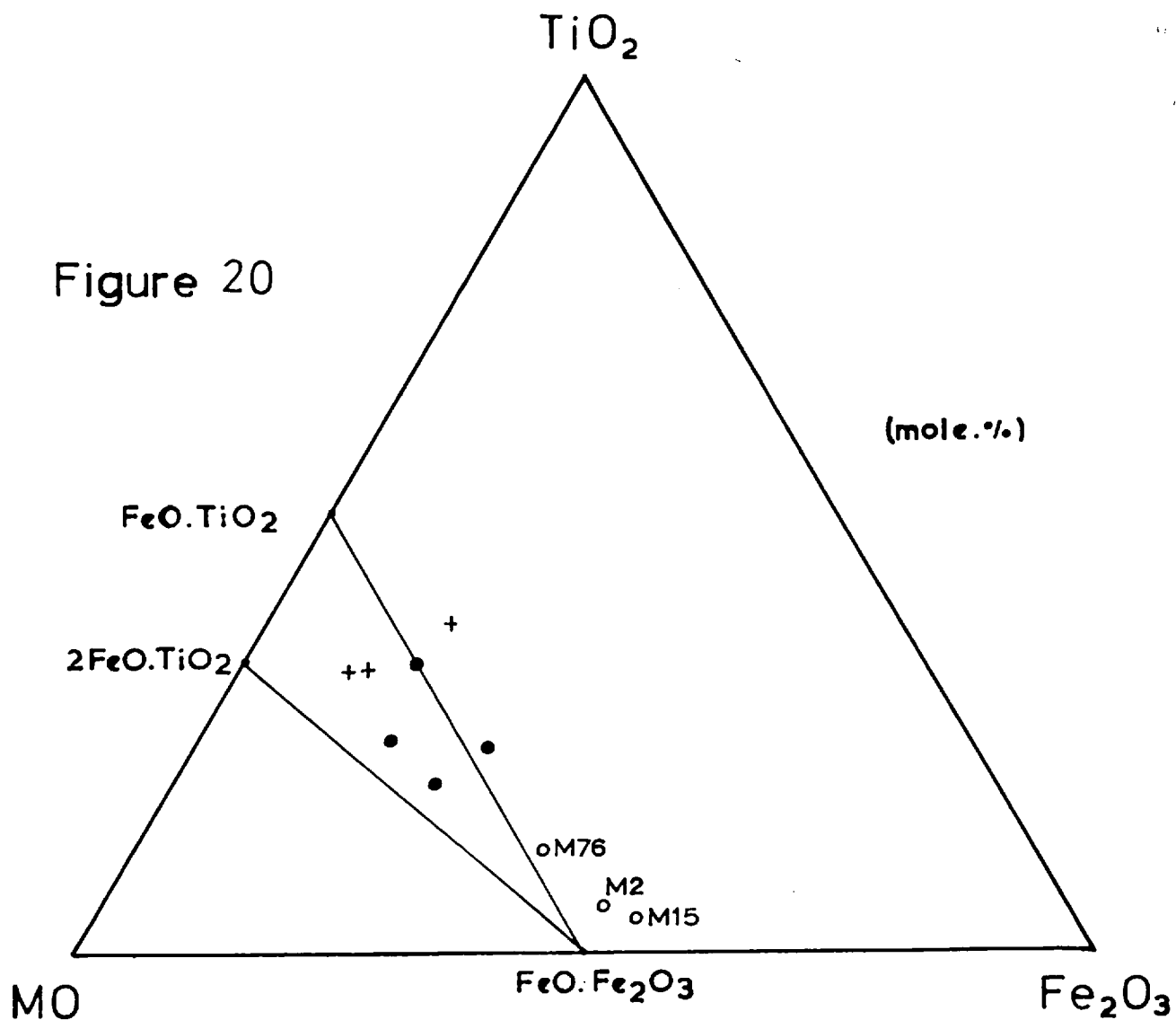
Molecular proportions

TiO ₂	11.4	5.2	3.7
Fe ₂ O ₃	40.4	49.3	53.3
MO	48.2	45.5	43.0

$$MO = FeO + MnO + MgO + CaO$$

The magnetites have been plotted in Figure 20 where MO includes FeO, MgO, MnO and CaO and they fall inside the magnetite, hematite, ilmenite field. Titanomagnetites from Skaergaard (Vincent and Phillips, 1954) and Black Jack Sill (Wilkinson, 1959) have been included for comparison. The magnetite from the earliest formed rock R.76 has the highest TiO_2 and the lowest Fe_2O_3 while that from the latest formed rock R.15 has the lowest TiO_2 and the highest Fe_2O_3 . There seems to be a decrease of TiO_2 with differentiation (falling temperature) and this might be expected bearing in mind the conclusions of Buddington et al (1955). X-ray photographs of the magnetites were taken and all showed ilmenite reflections. The ilmenite lines in M.76 were much stronger than those in M.2 and M.15 in which they were of similar strength. This would be expected bearing in mind the chemical analyses. This ilmenite is presumably present as exsolution lamellae. M.76 and M.2 show hematite reflections but in M.15 these are barely detectable, this is surprising as M.15 has the highest Fe_2O_3 content. As polished sections were not available it is uncertain whether the excess Fe_2O_3 is present as exsolved hematite (M.76 and M.2), in the magnetite lattice (M.15) or as very finely divided alteration products which might not show up on the X-ray photos. Gifford (1961) reported that the magnetites usually show some alteration to martite and it therefore seems likely that M.2. and M.76 have exsolution lamellae of hematite as well as a little secondary hematite while M.15 has high Fe_2O_3 in the lattice and a little martite as alteration product. The magnetites plot

Figure 20



- Marangudzi .
- Skaergaard .
- + Black Jack Sill .

(Fig. 20) just on the hematite rich side of the join magnetite-ilmenite and their composition before secondary oxidation must have fallen very near this join. M.76 crystallised as a titaniferous-magnetite but M.2 and M.15 must have been almost pure magnetite.

Basta (1957) determined the cell edge of a pure magnetite as $8.396 \text{ \AA}$ and the cell edge of each of the three analysed magnetites is $8.39 \text{ \AA}$.

Petrological considerations Wilkinson (1959) analysed titanomagnetites from the Black Jack differentiated teschenite sill and found that with falling temperature (differentiation) the magnetites showed an increase in Fe_2O_3 , a slight increase in TiO_2 and a decrease in FeO . It seems likely that the Marangudzi magnetites also show this increase in Fe_2O_3 with differentiation. The richness of volatiles in the Marangudzi rocks (H_2O , F, Cl) would guarantee that iron would exist in a high oxidation state and this is substantiated by the relatively high Fe_2O_3 in the rocks, amphiboles and magnetites.

Distribution of TiO_2 between amphibole and magnetite Veerhogen (1962) discussed the distribution of Ti between pyroxene and magnetite and suggested that the solubility of Ti in amphiboles would be similar to that in pyroxenes. Veerhogen suggested that Ti can only enter the pyroxene structure at high temperature and the higher the temperature the greater the solubility of Ti.

Thermodynamical considerations led him to conclude that Ti would enter silicates rather than magnetite under conditions of relatively high partial pressure of oxygen. Finally, in undersaturated melts (low silica activity) a greater solubility of Ti in the silicate phase would be expected.

The Marangudzi rocks crystallised under highly oxidising conditions owing to their high volatile content. Because of this the hastingsites contain high Ti relative to the magnetites and this is in accordance with Veerhogen's suggestions. The Fe^{3+}/Ti ratios for the co-exisiting amphiboles and magnetites are given:-

	Amphibole	Magnetite
R.76	2.0	7.1
R.2	6.1	19.1
R.15	7.7	28.8

The hastingsites are enriched in Ti relative to the magnetites by a factor of greater than three.

The % of the total TiO_2 in the rock carried by the amphiboles is given below:

Oversaturated rock amphiboles		Undersaturated rock amphiboles			
A.21	88	A.2	87	A.26	95
A.439	61½	A.15	80	A.31	79
A.141	59	A.26	97	A.76	77½
A.177	58				

In the oversaturated rocks R.141, R.177 and R.439 the proportion of the total TiO_2 carried by the amphibole varies from 58 to 61½ but in R.21 it is 88%. R.21 varies from the other oversaturated rocks in that although it has modal quartz it has normative nepheline and is clearly less saturated than the other types. In the nepheline syenites the amount of TiO_2 carried by the amphiboles varies from 77½ to 97% . Amphiboles A.31 and A.76 have the lowest proportion of TiO_2 and also co-exist with pyroxene. The pyroxene will presumably contain some TiO_2 and the total proportion of TiO_2 carried by the silicate minerals will be higher than that for the amphibole alone.

These data seem to substantiate Veerhogen's (1962) conclusion that the silicate minerals of undersaturated rocks have higher solubilities of Ti than those in oversaturated rocks. It is significant that the oversaturated rocks contain discrete grains of ilmenite as well as exsolution lamellae in the magnetites (Gifford, 1961). It is immaterial whether the discrete ilmenite crystallised separately or whether it had been in solid solution in the magnetite and subsequently exsolved. The important point is that in the Marangudzi oversaturated rocks, TiO_2 seems to enter the ore minerals more readily than it does in the undersaturated rocks.

C H A P T E R 5

TRACE ELEMENT GEOCHEMISTRY

In this Chapter I will discuss the geochemistry of various trace elements in the Marangudzi complex. The analytical methods used to determine these elements are summarised in the appendix.

1 THE ALKALI ELEMENTS

Lithium The chemical properties of Li are more similar to those of Mg than to the other alkali elements. Owing to the similar ionic radii of Li^+ and Mg^{2+} (0.68 and 0.66 Å) Li shows diadochic substitution for Mg in some ferromagnesian minerals. Strock (1936) showed the strong enrichment of Li in micas (rather less so in pyroxenes and amphiboles) and suggested a diadochy of the type $2\text{Mg}^{2+} = \text{Li}^+ + \text{Fe}^{3+}$. Li tends to accumulate in the magma and is enriched in the latest products of differentiation. Because of this accumulation the Li/Mg ratio increases with differentiation. Horstman (1957) has suggested that in Mg poor rocks Li substitutes for Fe^{2+} and in these rocks the $\text{Li}/(\text{Mg} + \text{Fe}^{2+})$ ratio should be more applicable than Li/Mg. Rankama and Sahama (1950) and Goldschmidt (1954) gave data for Li which suggest its concentration in granites relative to nepheline syenites. Turekian and Wedepohl (1961) recommend the abundances; basalts 17, high Ca granites 24, low Ca granites 40 and syenites 28 ppm Li.

Gerassimovskii and Lebedev (1959) analysed rocks from the Lovozero massif and found enrichment of Li with differentiation. The early miaskites have an average of 32 ppm and the late agpaïtes an average of 78 ppm Li. Zlobin and Lebedev (1960) analysed plumasitic, potash rich rocks from Sandyk and found an increase from 18 ppm in the early alkaline gabbroids to 31 ppm Li in the late formed nepheline syenites. Stavrov and Znamenskii (1961) and Svechnikova and Kalenchuk (1962) stressed the relationship between Li and F and the latter authors showed that late stage aplites, which had lost most of their volatiles during crystallisation, were impoverished in Li and F. Burnham and Jahns (1961) found enrichment of Li and F in the aqueous phases of synthetic and natural pegmatite melts relative to the condensed phases.

Strock (1936) analysed rocks from the Oslo province and found that the Li/Mg ratio varied over a similar range in the over- and undersaturated rock series. The values were:-

	Li ppm	Li/Mg		Li ppm	Li/Mg
Essexite	17	80	Kjelasite	-	-
Larvikite	22	240	Nordmarkite	8	210
Lardalite	37	380	Granitite	-	2000
Ditroite	1150	7000			

Simpson (1954) found up to 400 ppm Li in a foyaite from Okonjeje. The Li content of the Kûngnât syenites (Upton, 1960) is usually in the range 5-10 ppm but the Ilimaussaq (Hamilton, 1964) augite

syenites have higher Li (up to 60 ppm).

Most of the Li in silicate rocks is carried by the mafic minerals and Sen, Nockolds and Allen (1959) found enrichment of Li in late stage hornblendes from the Southern Californian batholith. Wager and Mitchell (1951) and Wilkinson (1959) found enrichment of Li in late stage olivines and pyroxenes from Skaergaard and the Black Jack teschenite sill respectively.

Li concentration, Li/Mg ratio and $\text{Li}/\text{Mg}+\text{Fe}^{2+}$ ratio for Marangudzi rocks are given in Table 17.

The gabbros contain very similar Li concentrations and average $1\frac{1}{2}$ ppm but dolerite R.25 and alkali basic rocks E.26 and R.32 have higher Li contents. The oversaturated rocks vary from 2 to 12 ppm Li with the outer quartz syenites showing little variation from 9 ppm. Li/Mg varies from 40 in R.16 to 640 in R.89. The inner quartz syenites contain very low Mg and it may be more significant to compare the $\text{Li}/\text{Mg}+\text{Fe}^{2+}$ ratio for the oversaturated rocks. The outer quartz syenites average 26 for $\text{Li}/\text{Mg}+\text{Fe}^{2+}$ while the inner quartz syenites average 15 and seem to be older rock types. The porphyritic quartz syenites show a greater range in values from 7.7 in R.16 to 52 in R.439 and the latter seems to be the youngest of this rock type.

The nepheline syenites have Li from 2 to 12 ppm and the phonolites are highest with up to 30 ppm. The rock series

Table 17 : Distribution of Li

	Li ppm	$\frac{\text{Li}}{\text{Mg}} \times 10^5$	$\frac{\text{Li} \times 10^5}{\text{Mg} + \text{Fe}^{2+}}$		Li ppm	$\frac{\text{Li}}{\text{Mg}} \times 10^5$	$\frac{\text{Li} \times 10^5}{\text{Mg} + \text{Fe}^{2+}}$
R.4	1 $\frac{1}{2}$	4.2	2.3	R.1	6	-	-
R.8	1 $\frac{1}{2}$	3.6	2.0	R.2	6 $\frac{1}{2}$	88	15
R.75	2	-	-	R.3	4 $\frac{1}{2}$	130	20
R.100	1 $\frac{1}{2}$	-	-	R.17	7	44	12
R.266	1 $\frac{1}{2}$	-	-	R.20	5 $\frac{1}{2}$	100	13
				R.183	5 $\frac{1}{2}$	120	16
R.25	11	-	-	R.226	-	-	-
R.50	2	-	-				
				R.14	12	-	-
E.26	7	8.9	5.2	R.15	11	550	42
R.32	8	9.7	5.8	R.133	7 $\frac{1}{2}$	97	19
R.89	4 $\frac{1}{2}$	640	15	R.19	4 $\frac{1}{2}$	20	7 $\frac{1}{2}$
R.103	7	-	-	R.174	2 $\frac{1}{2}$	-	-
R.143	4	310	15				
				R.28	3 $\frac{1}{2}$	76	19
R.7	8	270	25	R.30	2	-	-
R.118	9	-	-	R.276	4	52	16
R.141	9	300	25				
R.177	9	300	27	R.10	16	530	145
				R.22	20	460	80
R.16	2	40	7.7	R.24	22	-	-
R.21	4 $\frac{1}{2}$	45	12	R.53	30	-	-
R.439	12	200	52	R.128	9	-	-
				R.129	19	-	-
T.14	1	-	-				
				R.420	5	120	25
R.26	5	45	11	R.441	4 $\frac{1}{2}$	-	-
R.31	7	91	17				

biotite foyaite-microfoyaite shows an increase of Li from $2\frac{1}{2}$ to 12 ppm. The pulaskites and foyaites have similar concentrations of approximately 6 ppm. The juvites have comparatively low Li, averaging 3 ppm. Bearing in mind the fact that Li is concentrated in the volatile phase, it is significant that the quenched phonolites contain the highest Li concentrations. The biotite foyaite-microfoyaite series shows an increase in Li/Mg from 20 in R.19 to 550 in R.15 and this is in good agreement with the order of formation as suggested from major element evidence. The plagioclase rich foyaite R.17 has a Li/Mg ratio of 44 and is clearly an earlier rock type than the other foyaites while microfoyaite R.133 has a Li/Mg of 97 and is earlier than microfoyaite R.15. The juvites have low values for the ratio and seem to be early formed rocks even though they are of late intrusion. The phonolites have high Li/Mg and must be late formed types. $\text{Li}/\text{Mg}+\text{Fe}^{2+}$ shows similar relationships to Li/Mg.

The level of Li concentration in the over- and undersaturated rocks from Marangudzi is similar and this is in contrast to the contention that Li is higher in granites than in nepheline syenites (Rankama and Sahama 1950, Goldschmidt 1954). In comparison to the Lovozero and Sandyk intrusions the Marangudzi complex is very poor in Li but has similar concentration to the Kûngnât syenites.

Rubidium. The most distinctive feature of the geochemistry of Rb is its coherence with K during the major part of the magmatic process. Rb and K have similar valencies, ionisation potentials and electronegativities. Owing to the smaller size of K^+ relative to Rb^+ (1.33 and 1.47 Å respectively) the latter is enriched in the liquid with differentiation. Rankama and Sahama (1950) and Goldschmidt (1954) gave data showing that Rb is higher in granites than in nepheline syenites. Turekian and Wedepohl (1961) recommend the abundances; basalt 30, high Ca granites 110, low Ca granites 170 and syenites 110 ppm Rb. Alkali feldspar is generally the main Rb carrier but micas concentrate Rb and have lower K/Rb ratios than feldspars. This must be because the relatively large Rb ion is more able to enter the large 12-coordinated sites in micas than the smaller sites in alkali feldspars.

Ahrens, Pinson and Kearns (1952) analysed a selection of igneous rocks for K and Rb and found that during the major part of magmatic activity K/Rb remained virtually constant and it was only in the late stage rocks (aprites and pegmatites) that K/Rb decreased. Nockolds and Allen (1953, 1954 and 1956) found that K/Rb was constant for a given rock series. Taylor, Emeleus and Exley (1956) found that the normal K/Rb ratio for a selection of igneous rocks was 240 but that New Zealand rhyolites, St. Austell granites and Mourne granites showed relative enrichment of Rb and have K/Rb as low as 49. They suggested that these rocks were very late stage and thought it was significant that there were no

pegmatites associated with any of the complexes. Demin and Khitarov (1957) reported a decrease of K/Rb from 187 to 120 with differentiation in granites of the Malay Laba massif. Tauson and Stavrov (1957) analysed granitoids from Susamyr and found enrichment of Rb in the later rock types. Early diorites have 70 ppm and late leucocratic granites have 250 ppm Rb. Gerasimoviskii and Lebedev (1959) and Volkov and Savinova (1959) analysed Lovozero undersaturated rocks and found only slight enrichment of Rb with differentiation. The latter authors reported an average Rb concentration for the massif of 210 ppm and a range in K/Rb from 280 to 170. Zlobin and Lebedev (1960) studied the potash rich rocks from Sandyk and found that with differentiation K and Rb increased and Na remained constant. The average Rb concentrations, for the first to last magmatic phases, increase from 240 to 950 ppm and the K/Rb ratios decrease from 185 to 102. They suggested that the potash rich character of these rocks was reflected in their high Rb content. Finally, they reported that the main Rb carrier was the alkali feldspar but biotites concentrated the Rb and have up to 3500 ppm. Volkov and Savinova (1961) compared the variation of K/Rb in acid and alkali magmas. They suggested that Rb follows K in both magma types but that accumulation of K and Rb with differentiation only occurs in acid and potash rich alkali magmas (e.g. Sandyk). Soda rich alkali magmas show little variation in K/Rb and K and Rb do not accumulate with differentiation to any great extent (e.g. Lovozero). Butler, Bowden and Smith (1962) analysed Nigerian Younger granites

and found an increase of Rb from 120 to 1400 ppm and a decrease in K/Rb from 330 to 25. In the Liruei complex K/Rb decreased progressively with the time of emplacement but in Amo the ratio varied irregularly. Taylor and Heier (1958) and Heier and Taylor (1959a) analysed the alkali feldspars from Norwegian gneisses, granites and pegmatites and found K/Rb ratios from 300 to 34.

Rb concentrations and K/Rb ratios for Marangudzi rocks are given in Table 18.

Gabbros R.8 and R.266 have K/Rb ratios of 240 and 380 and plagioclases of composition $_{65}A_{65}$ and $_{83}A_{83}$ respectively. It is interesting to note that the rock with the more calcic plagioclase has the higher K/Rb.

The oversaturated rocks have Rb varying from 100 to 240 ppm but K does not vary much from 5%. The inner quartz syenites are impoverished in Rb relative to K and K/Rb ratios vary from 330 to 580. The outer quartz syenites have lower K/Rb ratios averaging 250 and seem to be younger rocks than the inner quartz syenites. The porphyritic quartz syenites average 230 for K/Rb and the granite R.753 has a K/Rb of 200.

The undersaturated rocks have higher Rb and range from 150 to 670 ppm while K/Rb varies from 420 to 130. The biotite foyaites R.19 has a comparatively low K/Rb of 220 and this is explained by its high modal biotite. The pulaskites and foyaites

Table 18 : K and Rb in Marangudzi rocks

	K	Rb	K/Rb		K	Rb	K/Rb
R4	0.5	*	-	R26	5.7	200	280
R8	0.6	25	240	R31	6.6	190	350
R75	0.4	*	-	R76	6.4	150	420
R100	0.3	*	-				
R266	0.3	8	380	R1	6.5	200	320
				R2	5.9	150	390
R25	0.9	52	170	R3	6.9	200	340
R50	0.4	*	-	R17	5.4	150	360
				R20	7.1	190	370
E26	1.4	95	150	R183	6.6	160	420
R32	3.1	170	180	R226	6.7	230	290
R89	5.6	130	430	R14	5.9	300	200
R103	5.8	100	580	R15	5.7	320	180
R143	4.9	150	330	R133	6.8	220	310
R7	5.5	220	250	R28	9.3	550	170
R118	5.2	180	290	R30	7.2	390	180
R141	5.7	180	310	R276	8.7	670	130
R177	5.2	220	240	R730	5.1	160	320
R16	5.0	210	240	R10	6.2	210	300
R21	5.5	240	230	R22	6.4	170	380
R439	5.3	230	230	R24	6.8	170	390
				R53	5.7	220	260
R753	4.7	230	200	R128	7.5	360	210
T14	4.0	140	290	R129	5.0	170	290
				R131	6.8	210	320
R19	6.0	270	220				
R174	6.7	180	370	R420	7.9	190	420
				R441	9.9	280	350

are relatively poor in Rb compared with K and have K/Rb ratios from 280 to 420. Microfoyaite R.14 and R.15 are late formed rocks and have comparatively low K/Rb ratios (200 and 180 respectively) . Microfoyaite R.133 has a much higher ratio of 310 and this is further evidence that it is an older rock than R.14 and R.15. Juvites R.28, R.30 and R.276 have the highest Rb concentrations (550, 390 and 670 ppm) and the lowest K/Rb ratios (170, 180 and 130) while juvite R.730 has much lower Rb and a K/Rb of 320. Although the high Rb and low K/Rb ratios of R.28, R.30 and R.276 suggest that they may be late formed rocks, other evidence suggests the opposite. For example FeO/MgO , Li/Mg ratios are typical of comparatively early formed rocks. The phonolites have Rb from 170 to 360 ppm and K/Rb from 390 to 210.

The overall variation of K/Rb in these rocks is rather haphazard and has been represented in Figure 21.

The solid line refers to the K/Rb curve of Ahrens, Pinson and Kearns (1952) and the dashed lines to the normal limits of scatter. The Sandyk complex has similar potash to Marangudzi but has higher Rb. The Marangudzi oversaturated syenites have similar Rb and K/Rb to syenites from Kûgnât (Upton, 1960) and Ilimaussaq (Hamilton, 1964).

The concentrations of Rb and values for K/Rb in the alkali feldspars, nephelines and pseudoleucites from Marangudzi rocks are given in Table 19. Also included are data for leucites,

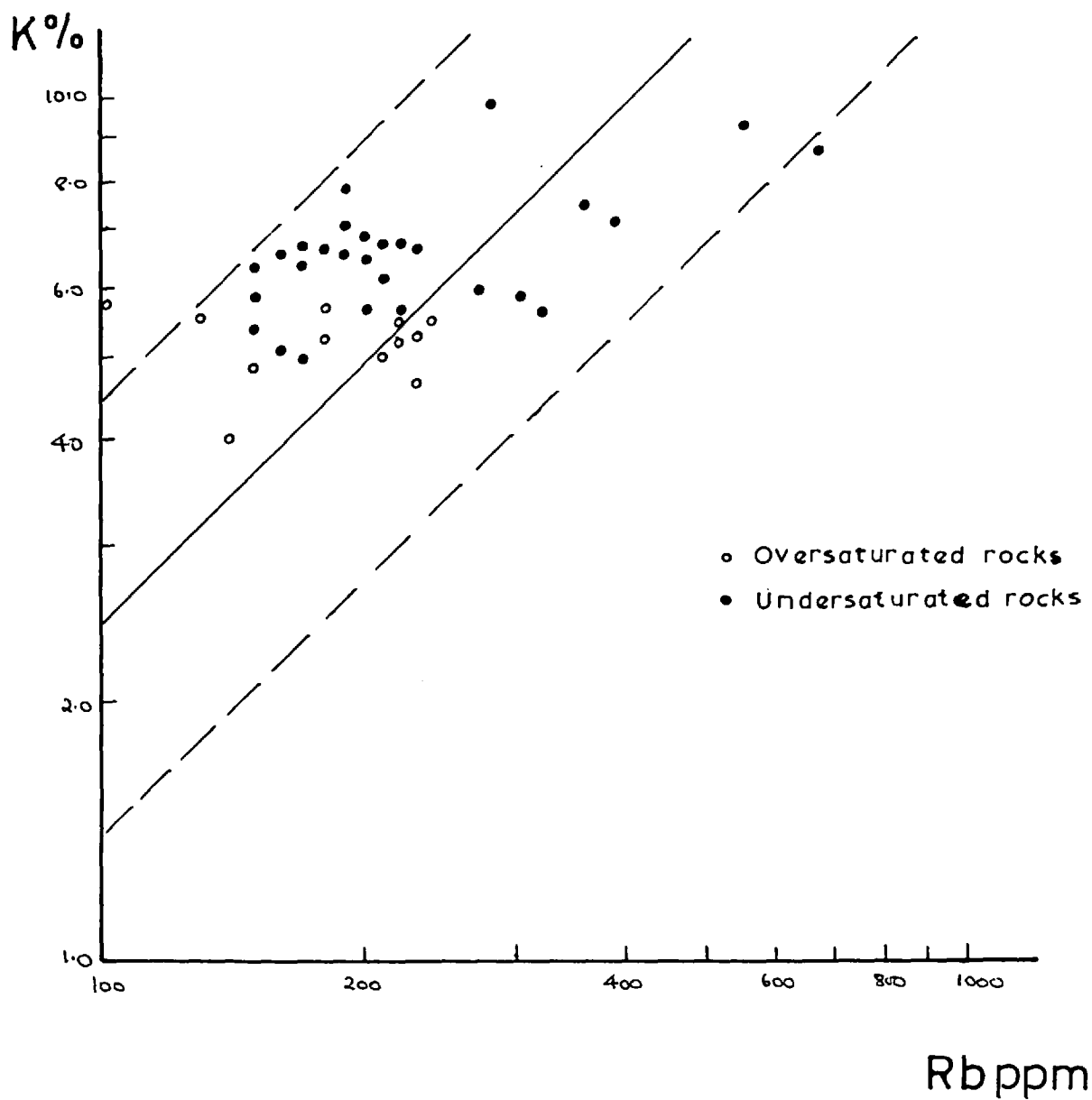


Figure 21

Table 19 : Rb and K/Rb in minerals.

	Rb	K/Rb		Rb	K/Rb	
F.21	420	180	P.L. 28	560	200	
F.439	340	200	R. 28	550	170	
			P.L. 30	590	190	
F.141	320	240	R. 30	390	180	
F.177	380	190	P.L.276	660	160	
			R.276	690	130	
F.26	350	250	P.L. 10	430	190	
F.31	280	310	R.10	210	380	
F.76	320	280	P.L.22	410	190	
			R.22	170	380	
F.2	210	400				
F.20	240	370	P.L.180	390	200	
			Groundmass	180	200	330
F.15	480	170	Leucite	3120	1530	100
			Groundmass	3120	360	180
F.28	520	260	Leucite	3141	1290	130
			Groundmass	3141	420	170
N.2	220	210	Leucite	4354	770	210
N.20	160	280	Groundmass	4354	110	440

180 - Tinguaitite, Serra da Tinguá, Brazil.

3120 - Leucitophyre, Monte-Cimini, Italy.

3141 - Leucitite, Capo-di-Bavo, Rome.

4354 - Mikenite, Bufumbira, Congo.

pseudoleucites and their groundmasses from volcanic rocks chosen from Imperial College Geology Department collection.

In the Marangudzi oversaturated rocks the alkali feldspars account for the bulk of the Rb but K/Rb in the feldspars is consistently lower than K/Rb in the rocks. Rb in the undersaturated rocks is shared between the alkali feldspars and nephelines. Nephelines N.2 and N.20 from foyaite R.2 and R.20 have lower K/Rb ratios than the co-existing alkali feldspars F.2 and F.20. K/Rb values are: N.2 210, F.2 400, R.2 390, and N.20 280, F.20 370, R.20 370. Sveshnikova and Kalenchuk (1962) gave analyses of a nepheline syenite and its co-existing nepheline and alkali feldspar. The nepheline has 370, the feldspar 370 and the rock 230 ppm Rb while the K/Rb ratios are respectively 135, 270 and 150. The ratio for the nepheline is again seen to be about half of that in the feldspar. In the Marangudzi foyaite alkali feldspar crystallised before the nepheline and the relatively high Rb of the latter might be explained by it mopping up the Rb which had accumulated during the crystallisation of the alkali feldspar. Feldspar F.15 has the lowest K/Rb ratio of 170 and this comes from the late formed microfoyaite R.15.

The pseudoleucites of the phonolites and juvites contain considerable amounts of Rb (Table 19). The juvite pseudoleucites have similar K/Rb ratios to those of the rocks. However, the phonolite pseudoleucites have K/Rb ratios lower than those of the

rocks by a factor of two (an average of 190 and 380 respectively). The pseudoleucite from Serra da Tingua and the fresh leucites analysed show a similar relationship for K/Rb relative to their groundmasses. This enrichment of Rb in leucite relative to the groundmass (liquid) suggests that Rb is accepted into the relatively large holes in the leucite lattice in preference to K. I have already discussed this in Chapter 4. I thought originally that the high Rb and low K/Rb in juvites R.28, R.30 and R.276 indicated their late formation. However, these rocks have large modal amounts of pseudoleucite and this might explain the high Rb and low K/Rb. The juvites may therefore have crystallised from comparatively early formed liquids and this is substantiated by the high FeO/MgO and Li/Mg ratios shown by the rocks.

Caesium Cs^+ has a much larger ionic radius ($1.67\text{\AA}$) than K^+ and Rb^+ and tends to be much enriched in residual liquids. The mineral pollucite ($\text{CsAlSi}_2\text{O}_6$) is found in pegmatites. Rankama and Sahama (1950) and Goldschmidt (1954) gave data showing that Cs is enriched in granites relative to nepheline syenites. Turekian and Wedepohl (1961) recommend the values; basalts 1.1, high Ca granite 2. , low Ca granite 4. and syenite 0.6 ppm Cs.

Rankama and Sahama (1950) showed that Cs is concentrated in micas relative to K bearing framework minerals and Goldschmidt (1954) reported over 200 ppm Cs in some leucites (isostructural with pollucite) but much smaller concentrations in K feldspars.

Sveshnikova and Kalenchuk (1962) found an average of 10 ppm Cs in nepheline syenites. Beus and Fabrikova (1961) reported an average of 5.5 ppm Cs for granites and stated that the bulk of the Cs was in the alkali feldspar. Only in rocks enriched in mica did the latter become a Cs carrier as well as a concentrator. Stavrov and Znamenskii (1961) analysed granitic rocks and stated that the affinity of Cs for K does not govern its behaviour in the magmatic process. They suggested that, as Cs and B both become enriched in late differentiates, they may exist in magmas as the complex fluoride CsBF_4 . It is interesting to note that the mineral avogradrite $(\text{K,Rb})\text{BF}_4$ has been reported from volcanic vents. Gerassimovskii and Lebedev (1960) found an increase in Cs with differentiation in the Lovozero rocks. The average concentration in the early stage miaskites is 0.8 ppm and that in the late stage agpaite is 2.2 ppm Cs. They also reported that there was no direct relationship between Cs content and K or Rb. Zlobin and Lebedev (1962) also reported an increase in Cs for the Sandyk massif. The early alkaline gabbroids have an average of 13 ppm and the late nepheline syenites an average of 38 ppm. They found a direct relationship of Cs with K and Rb, K/Cs decreased with differentiation and Rb/Cs remained almost constant. They also found that biotites had lower K/Cs ratios than co-existing alkali feldspars. Ahrens (1954) and DeLeon and Ahrens (1957) found a haphazard distribution of Cs in granites from New England and Yugoslavia. Butler and Thompson (1963) found a similar relationship in the Nigerian Younger Granites although the early

formed rocks tend to have the lower Cs and the latest formed rocks the highest. The range of Cs concentrations is from 0.6 to 9.6 ppm.

The Marangudzi rocks show a similarly haphazard distribution of Cs (Table 20).

The gabbros are low but the alkali basic rocks E.26 and R.32 have higher Cs contents of 3.2 and 3.3 ppm Cs respectively. The oversaturated rocks have a range from 0.4 (R.143) to 2.5 ppm Cs (R.439). As K and Rb are relatively constant in these rocks there is a large range of K/Cs (21,000 to 123,000) and Rb/Cs (92 to 380). In the undersaturated rocks there is a similarly erratic distribution of Cs from 0.5 (R.3) to 4.5 ppm Cs (R.14). It is noteworthy that R.14 is a late formed rock and has the highest Cs concentration. Juvites R.28 and R.30 have K in excess of 8% and also have comparatively high Cs (3.1 and 4.4 ppm respectively). The K/Cs ratio varies from 13,100 to 138,000 but is usually in the range 18,000 to 30,000. Rb/Cs varies from 67 to 400.

In comparison to the Lovozero and Sandyk massifs the Marangudzi rocks have similar K/Cs ratios to those of Lovozero (range of 13,000 to 62,000) but much larger ones than those of Sandyk (range of 2,100 to 3,800). Zlobin and Lebedev (1962) attributed the high Cs of the Sandyk rocks to their K rich character, the nepheline syenites having K up to 8% and K/Na ratios of up to 2. The Lovozero rocks are comparatively poor in K and invariably have less than 4½%. The Marangudzi rocks

Table 20 : Distribution of Cs

	Cs	$\frac{K}{Cs} \times 10^{-3}$	$\frac{Rb}{Cs}$		Cs	$\frac{K}{Cs}$	$\frac{Rb}{Cs}$
R8	0.3	20	85	R26	2.3	25	87
R266	0.2	15	40				
				R3	0.5	140	400
R29	1.0	9	52	R17	1.8	30	83
E26	3.2	4.4	30	R14	4.5	13	67
R32	2.3	14	74				
				R19	3.3	19	82
R143	0.4	125	380				
				R28	3.1	30	180
R118	1.3	40	140	R276	4.4	20	150
R177	0.9	58	240				
				R22	2.2	29	78
R16	1.1	45	190	R53	2.1	27	105
R439	2.5	21	92				

analysed for Cs contain up to 9.3% K and are usually in the range 5 to 7% K, however, they have similar K/Cs ratios to those of Lovozero. The Marangudzi complex differs from Sandyk in that although both complexes are rich in K, the latter has a much higher Cs content.

2 THE ALKALINE EARTH ELEMENTS

Strontium In early formed rocks Sr^{2+} ($1.18\overset{\circ}{\text{\AA}}$) replaces Ca^{2+} ($0.99\overset{\circ}{\text{\AA}}$) in minerals but as Ca decreases, and K increases, with differentiation the diadochy between Sr^{2+} and K^+ ($1.33\overset{\circ}{\text{\AA}}$) becomes increasingly important. Owing to its larger size Sr is not accepted into early Ca minerals. It accumulates in the liquid until potash feldspar crystallises at which point Sr is concentrated in the feldspar relative to K. Late stage rocks and pegmatites are impoverished in Sr. Noll (1934, quoted by Goldschmidt, 1954) showed that syenites and especially nepheline syenites are enriched in Sr relative to basic rocks and granites. Turekian and Wedepohl (1961) recommend the abundances: basalts 465, high Ca granites 440, low Ca granites 100 and syenites 200 ppm Sr.

In basic rocks the main Sr carrier is plagioclase. Turekian and Kulp (1956) and Butler and Skiba (1962) analysed plagioclases from Stillwater and Somalia and found an increase in Sr with decrease in An. In granites and syenites the main Sr carrier is potash feldspar and in undersaturated rocks some is carried in the feldspathoids. Noll (1934) found 4100 ppm Sr

in sanidine phenocrysts from the Drachenfels trachyte whereas the bulk rock had 680 ppm.

Sr is found replacing Ca in pyroxenes and amphiboles but it is too small an ion to enter the 12-coordinated sites in micas . Sr is also found in apatite and Wilkinson (1959) reported 4000 ppm in an apatite from the Black Jack teschenite sill.

Barium Ba^{2+} only replaces Ca^{2+} in plagioclase and other Ca minerals to a limited extent because of its larger ionic radius ($1.33 \text{ \AA}$ compared with $0.99 \text{ \AA}$) Ba shows a similar build up to Sr in the liquid until the crystallisation of potash feldspar. Ba is then concentrated in early feldspars relative to K and is typically low in late stage rocks and pegmatites. The similar sizes of Ba^{2+} and K^+ causes a close coherence between them and Ba enrichment occurs especially in K rich rocks. Von Engelhardt (1936 , quoted by Goldschmidt, 1954) found that Ba was enriched in syenites and nepheline syenites relative to basic rocks, diorites and granites. Turekian and Wedepohl (1961) recommend the average abundances: basalt 330, high Ca granites 420, low Ca granites 840 and syenites 1600 ppm Ba.

Small concentrations of Ba occur in the plagioclases of basic rocks but in syenites the main Ba carrier is alkali feldspar. Larsen et al (1941) found that some of the zoned alkali feldspars of the Highwood province have Ba rich cores and lower Ba concentrations in successive zones towards the rim.

Rankama and Sahama (1950) showed that Ba is enriched in micas relative to K. Sen et al (1959) analysed the co-existing plagioclase and alkali feldspar for a granodiorite from the S. Californian batholith. They found that the plagioclase had 430 ppm Sr and 170 ppm Ba while the alkali feldspar had 200 ppm Sr and 2500 ppm Ba.

Von Engelhardt (1936) analysed the soda rich rocks of the Oslo province for Ba. He reported the following concentrations: essexite 230, larvikite 2100, lardalite 1100, nordmarkite 1600 and granitite 130 ppm Ba. Simpson (1954) gave values for the Sr and Ba concentrations of the Okonjeje rocks:-

Alkali series			Tholeiitic series		
	Sr	Ba		Sr	Ba
Core gabbro	700	175	Gabbro	250	50
Essexite	1350	2000	Fenogabbro	700	2000
Pulaskite	500	3000	Ridge syenite	400	5000
Foyaite	1500	1000	Acid rock	500	1500

Gerassimovskii and Lebedev (1958) reported average Sr concentrations for the **three** main intrusive phases of the Lovozero complex as 2000, 820 and 1800 ppm Sr.

Upton (1960) found Ba concentrations of up to 9700 ppm in the Kungnät syenites but they were generally below 2000 ppm. Sr varied from 25 to 650 ppm. Hamilton (1964) found that the Ilimaussaq augite syenites have from 1000 to 5000 ppm Ba and 200 to 400 ppm Sr.

Heier and Taylor (1956 b) analysed alkali feldspars from Norwegian gneisses, granites and pegmatites and found that the alkali feldspars most enriched in Rb had the lowest Sr and Ba concentrations. They reported ranges from 3850 to 7000 ppm Ba and 770 to 1000 ppm Sr. Even though the absolute concentrations varied considerably they found that the Ba/Sr ratio stayed relatively constant and had a range from 3.1 to 14. They concluded that there was a close correlation between Sr and Ba in alkali feldspars. Taylor and Heier (1961) continued this work and suggested that the Ba/Rb ratio could be used as an index of differentiation. Ba^{2+} and Rb^{+} have similar ionic radii, electro-negativities and both form very ionic bonds. However, Ba^{2+} is concentrated relative to Rb^{+} in early K feldspar because of its divalent state. With differentiation Ba/Rb therefore decreases even though K/Rb remains constant. They also found that Ba/Sr decreases with differentiation as Ba-O is a more ionic bond than Sr-O leading to preferential enrichment of Ba in early crystallising alkali feldspar.

Analyses of the Marangudzi rocks and minerals for Sr and Ba are given in Table 21. Also given are Ba/Sr ratios for the rocks and minerals and Ba/Rb for the alkali feldspars .

The gabbros have Sr from 390 to 690 ppm and from 200 to 430 ppm Ba. It is interesting to note that R.266 and R.8 have plagioclases of composition An_{83} and An_{65} while the rocks have Sr concentrations of 390 and 670 ppm respectively. Alkali basic rocks E.26 and R.32 have much higher Sr and Ba concentrations.

Table 21 : Distribution of Sr and Ba in rocks, feldspars and nephelines.

	Sr	Ba	Ba/Sr		Sr	Ba	Ba/Sr		Sr	Ba	Ba/Sr	Ba/Rb
R4	620	200	0.3	R19	1950	1.3%	6.6	R24	1750	3550	2.0	
R8	670	350	0.5	R174	730	2850	5.0	R53	1650	4440	2.7	
R75	690	-	-					R128	440	990	2.2	
R100	400	-	-	R26	1150	5500	4.7	R129	2000	-	-	
R266	390	430	1.1	R31	400	1250	3.2					
				R76	400	1450	3.6	R131	500	940	1.9	
R25	580	810	1.4									
R50	140	-	-	R1	650	2150	3.3	R420	2050	3050	1.5	
				R2	380	920	2.4	R441	1550	-	-	
E26	370	740	2.0	R3	390	950	2.4					
R32	920	4600	5.0	R17	1350	7100	5.2	F21	500	2500	5.0	5.9
				R20	560	2400	4.2	F439	290	500	1.7	1.5
R89	40	340	8.5	R183	530	1250	2.4	F141	70	310	4.3	1.0
R103	120	1300	10.8	R226	100	120	1.2	F177	(30)	100	3.0	0.3
R143	<15	110	>7.3					F26	1600	8400	5.0	24.0
				R14	50	<100	<2.0	F31	590	1650	2.8	5.9
R7	30	160	5.3	R15	40	<100	<2.5	F76	710	2600	3.7	8.0
R118	25	135	5.3	R133	440	1300	3.0	F2	660	1350	2.0	6.4
R141	50	240	4.8					F20	720	3800	5.3	17.5
R177	20	100	5.0	R28	2000	6050	3.0	F15	(30)	50	1.7	0.1
				R30	1950	6300	3.2	F28	800	2600	3.2	5.0
R16	120	1250	10.5	R276	800	1450	2.4					
R21	420	2450	5.8	R730	4700	1.6%	3.4	P26	1250	990	0.8	-
R439	250	640	2.6									
				R10	2100	4400	2.1	N2	160	280	1.8	1.3
R753	80	1000	12.5	R22	1800	3600	2.0	N20	160	240	1.5	1.5

The inner and outer quartz syenites (main oversaturated ring rocks) invariably have Sr less than 50 ppm Sr and Ba less than 400 ppm. Inner quartz syenite R.103 has 120 ppm Sr and 1300 ppm Ba, however, all the analysed inner quartz syenites have Ba/Sr ratios near 10. The outer quartz syenites average 5.1 for Ba/Sr. The porphyritic quartz syenites have higher Sr and Ba than the other oversaturated rocks and R.21 is especially high with 420 ppm Sr and 2450 ppm Ba. Ba/Sr ratios vary from 5.8 in R.21 to 2.6 in R.439. The much higher Sr and Ba found in the porphyritic quartz syenites as compared with the main oversaturated ring rocks could be explained by the former rock type being more intimately related to the undersaturated rocks than to the main oversaturated ring rocks. I will discuss this further in Chapter 6.

The undersaturated rocks have much higher Sr and Ba concentrations than the bulk of the oversaturated rocks. There is a large decrease of Sr and Ba in the rock series biotite foyaite-microfoyaite (late stage foyaite). Biotite foyaite R.19 is exceptionally high with 1950 ppm Sr and 1.3% Ba while R.174 is lower with 730 ppm Sr and 2850 ppm Ba. The pulaskites have the ranges 400 to 1150 ppm Sr and 1250 to 5500 ppm Ba. Early formed foyaite R.17 has comparatively high Sr and Ba i.e. 1350 and 7100 ppm respectively. Other foyaites vary from 100 to 650 ppm Sr and from 120 to 2400 ppm Ba. R.226 is a late formed foyaite and has the lowest Sr and Ba. Microfoyaites R.14 and R.15 have less than 50 ppm Sr and less than 100 ppm Ba. Microfoyaite R.133 has 440 ppm Sr and 1310 ppm Ba and is clearly an earlier formed type than the other microfoyaite. Ba/Sr decreases from 6.6 in biotite foyaite R.19 to 1.2 in late stage foyaite R.226 and this

is in accordance with Taylor and Heier's (1961) suggestion that Ba/Sr decreases with differentiation. R.133 has a Ba/Sr ratio of 3.0 and this is extra evidence that it is an earlier rock than the other microfoyaite. Juvites R.28 and R.30 are of similar composition and have approximately 2000 ppm Sr and 6000 ppm Ba. R.276 is lower with 800 ppm Sr and 1400 ppm Ba while R.730 is exceptionally high with 4700 ppm Sr and 1.6 % Ba. This is confirmation that R.730 is an earlier formed juvite than the other analysed types. There is little variation in Ba/Sr but R.276 is rather lower than the others. The high Sr and Ba of the juvites suggests that although they are of late intrusion (post microfoyaite) they must have crystallised from comparatively early formed liquids. This is in good agreement with other chemical data that I have discussed previously. All the phonolites except R.128 have similar contents of Sr and Ba. The range is from 1650 to 2100 ppm Sr and 3550 to 4400 ppm Ba. R.128 is lower with 440 ppm Sr and 990 ppm Ba but Ba/Sr is similar for all the phonolites and varies from 2.0 to 2.7. Pseudoleucite dyke R.131 has 500 ppm Sr, 940 ppm Ba and a Ba/Sr ratio of 1.9. The high Sr and Ba concentrations of the phonolites may again be evidence that they are early formed liquids which are of late intrusion.

The most important fact about distribution of Sr and Ba in the Marangudzi complex is that the undersaturated rocks tend to have much higher contents of these elements than the oversaturated rocks. Any suggestion as to the petrogenesis of these rock types

must explain this phenomenon and I will discuss this further in Chapter 6.

In the Marangudzi syenites the main carriers of Sr and Ba are the alkali feldspars (Table 21). The concentrations of Sr and Ba in the feldspars is proportionately higher than in the rocks but the Ba/Sr ratios are similar.

Taylor and Heier (1961) recommended the use of the Ba/Rb ratio as an index of differentiation. The range in Ba/Rb for the oversaturated rock feldspars is from 5.9 (F.21) to 0.3 (F.177). In the undersaturated rocks the feldspar from the early formed pulaskite R.26 has the largest Ba/Rb of 24.0 and that from the late formed microfoyaite R.15 has the lowest ratio of 0.1.

Co-existing plagioclase and alkali feldspar from R.26 have respectively 1250 ppm Sr, 990 ppm Ba and 1600 ppm Sr, 8400 ppm Ba. The enrichment of Ba in the alkali feldspar is clear but the plagioclase contains lower Sr than the alkali feldspar, this is in contrast to the data of Sen et al (1959).

Nephelines N.2 and N.20 contain comparatively small concentrations of Sr and Ba and average 160 ppm Sr and 260 ppm Ba.

In the pseudoleucite section of Chapter 4 I stated that the Marangudzi pseudoleucites contain lower concentrations of Sr and Ba than the rocks in which they are contained. Sr and Ba must

therefore be concentrated in the groundmass. The analytical data leading to this conclusion are given in Table 22. Zies and Chayes (1960) have found a similar relationship for a pseudoleucite tinguaitite in which the pseudoleucite has 0.28% BaO and the groundmass 0.66% BaO. The Marangudzi pseudoleucites are rather altered and sometimes contain secondary analcite and zeolites, and I thought that this alteration might have been accompanied by leaching out of Sr and Ba. However, the pseudoleucite analysed by Zies and Chayes has also been studied by Fudali (1963) who found that it was completely unaltered. There can therefore have been no loss of Sr and Ba from this pseudoleucite. I have also analysed leucites, pseudoleucites and groundmasses (or bulk rocks) of volcanic rocks from various localities and the Sr and Ba data are given in Table 22. Sr and Ba concentrations in the leucites and pseudoleucites are again found to be considerably lower than in the groundmass or bulk rock. This means that the liquid, from which the leucites crystallised, must have been continuously enriched in Sr and Ba. I have discussed this phenomenon from a structural viewpoint in the pseudoleucite section of Chapter 4 and will consider its petrogenetical significance in Chapter 6.

3 GERMANIUM

Owing to the similar ionic radii of Si^{4+} and Ge^{4+} (0.42 and 0.53 Å respectively) most of the Ge in the lithosphere is camouflaged in silicate minerals. Goldschmidt (1954) has suggested that Ge is enriched in granitic rocks relative to basic

Table 22 : Sr and Ba in leucites, pseudoleucites and their groundmasses.

	Sr ppm	Ba ppm		Na ₂ O %	K ₂ O %	Sr ppm	Ba ppm
PL 28	2050	4000	PL 180	7.46	9.41	260	50
R28	2000	6050	R 180	8.09	7.91	250	50
PL 30	350	1450	Lc 1488	-	-	420	2250
R30	1950	6300	R 1488	-	-	1350	2800
PL 276	310	540	Lc 3120	1.49	18.66	300	710
R 276	800	1450	Gd 3120	3.42	7.96	2150	1950
PL 10	840	2300	Lc 3141	0.54	19.90	180	850
R 10	2100	4400	Gd 3141	2.01	8.88	1800	2050
PL 22	900	2650	Lc 4354	0.81	9.85	110	800
R 22	1800	3600	Gd 4354	5.21	5.82	1900	2150
PL 24	770	-	Lc 7044	-	-	1400	1300
R24	1750	-	R 7044	-	-	2400	2050
* PL	-	2500					
Gd	-	6000					

Lc = Leucite 180 - Tinguaita, Serra da Tinguá, Brazil.

Gd = Groundmass 1488 - Leucite Basanite, Vesuvius

* = Sample of Zies 3120 - Leucitophyre, Monte-Cimini, Italy

and Chayes (1960) 4354 - Mikenite, Bufumbira, Congo

7044 - Nosean leucitophyre, Eifel

3141 - Leucitite, Capo di Bovo, Rome

and undersaturated rocks. However, recent work by Onishi (1956) El Wardani (1957) and Burton, Culkin and Riley (1959) has shown that the abundance of Ge is similar for most rock types. Turekian and Wedepohl (1961) recommend the abundances: basalt 1.3 ppm, granites 1.3 ppm and syenites 1. ppm Ge.

Ringwood (1955 b) suggested that Ge occurs in silicate magmas as the complex ion GeO_4^{4-} . Because of the large size of this ion it is difficult for it to replace SiO_4^{4-} tetrahedra in minerals and Ge therefore becomes enriched in residual magmas.

Wickman (1943) has suggested that Ge preferentially substitutes for Si in minerals having the least linked SiO_4 tetrahedra. This has been broadly confirmed by El Wardani (1957), Burton et al (1959) and Harris (1954). The last author, in concluding that Ge substitutes preferentially in neso- and inosilicates, found a $\text{Ge/Si} \times 10^6$ atomic ratio of 1.69 for a pitchstone compared with ratios of 1.75 in the glass, about $7\frac{1}{2}$ for the olivine and clino-pyroxene and just below 1 in the quartz-feldspar mix.

The Russian school have produced Ge analyses on genetically connected rock series. Barkser, Mitskevich and Lazebnik (1961) have correlated the Ge content of rocks with the modal content of dark minerals but found that pegmatites tended to be higher than the parent granite (1.9 and 1.7 ppm Ge respectively). They considered that this substantiated Goldschmidt's idea of Ge enrichment in late differentiates. Lin, Morozov and Znamenskaya (1962) found an

increase of Ge with differentiation in a granite series even though the modal amount of mafic minerals decreased. The average Ge concentration for early formed diorites was 1.2 ppm and that for late formed alaskites was 1.9 ppm. The average $\text{Ge/Si} \times 10^6$ ratio was almost constant at 1.8. Tauson (1959, quoted by Lin et al, 1962) also reported enrichment of Ge in later, more silica rich, granites and $\text{Ge/Si} \times 10^6$ averaged 1.7 .

With differentiation there is usually a decrease in modal amount of mafic minerals as well as an increase in silica. As Ge tends to become enriched in mafic minerals their decrease in modal amount with differentiation tends to cancel out the increase of Ge with increase in Si. This explains why little variation of Ge is seen in differentiated series of rocks.

Ge concentrations in Marangudzi rocks and minerals are given in Table 23. There is little variation between the rock types but the oversaturated rocks generally have higher concentrations than the undersaturated rocks, this would be expected owing to their higher SiO_2 concentrations. The basic rocks have Ge from 0.9 to 1.2 ppm, the oversaturated rocks from 1.0 to 1.5 ppm and the undersaturated rocks from 0.4 to 1.1 ppm. Pulaskites, foyaite, microfoyaite and phonolites have almost constant Ge of 0.9 to 1.1 ppm; the biotite foyaite are lower with 0.6 and 0.8 ppm and the juvites are lower still with 0.4 and 0.5 ppm.

Table 23 : Ge in rocks and minerals

	Ge ppm	SiO ₂ %	$\frac{\text{Ge}}{\text{Si}} \times 10^6$ atom %		Ge ppm	SiO ₂ %	$\frac{\text{Ge}}{\text{Si}} \times 10^6$
R8	1.1	46.6	2.0	R14	1.1	-	-
R266	1.2	-	-	R15	1.1	57.2	1.6
R29	0.9	-	-				
				R28	0.4	51.5	0.65
E26	1.0	49.0	1.7	R276	0.5	51.2	0.82
R32	0.9	39.9	1.9				
				R10	0.9	51.1	1.5
R89	1.2	62.0	1.6	R22	1.1	50.6	1.8
R143	1.5	63.2	2.4	R128	0.9	-	-
R7	1.4	64.0	1.8	R420	0.9	46.0	1.6
R141	1.4	63.1	1.9				
R177	1.4	64.0	1.8	F2	0.8	(65)	(1.0)
				F15	1.0	-	-
R16	1.0	67.6	1.2	F20	1.0	-	-
R21	1.1	59.1	1.6				
R439	1.1	62.0	1.5	N2	0.6	46.3	1.1
R19	0.6	48.1	1.0	A21	2.0	40.6	4.1
R174	0.8	-	-	A439	1.9	39.9	4.0
				A141	2.7	39.7	5.7
R26	1.0	54.0	1.5	A177	3.5	40.3	7.3
R31	0.9	56.9	1.3				
				A2	2.3	37.3	5.2
R2	1.1	53.5	1.7	A15	3.3	36.8	9.0
R3	1.0	56.4	1.5	A20	2.2	36.7	6.0
R17	1.1	51.6	1.8	A26	2.1	36.9	4.8
R20	1.1	56.0	1.6	A28	2.2	36.4	6.0
R183	1.1	55.0	1.7	A31	2.5	37.8	5.5
				A76	2.2	37.5	4.9
				A131	1.4	37.1	3.2

In the oversaturated rocks $\text{Ge/Si} \times 10^6$ varies from 1.2 to 2.4 while in the undersaturated rocks the ratio varies from 0.65 to 1.8 .

The alkali feldspars have Ge from 0.8 to 1.0 ppm and F.2 has a Ge/Si ratio of 1.0 . The co-existing nepheline N.2 has a much lower Ge concentration of 0.6 ppm but a similar Ge/Si ratio of 1.1. The amphiboles contain much higher Ge and all except two have concentrations in excess of 2 ppm (A.131 and A.439 have 1.4 and 1.9 ppm respectively). $\text{Ge/Si} \times 10^6$ ratios are much higher than the rock, feldspar and nepheline values and vary from 3.2 to 9.0. Amphiboles from the oversaturated rocks vary from 1.9 to 3.5 ppm Ge and this compares with a range of 1.4 to 3.3 ppm in the undersaturated rock amphiboles . It is interesting to note that the amphibole from the late formed microfoyaite R.15 has the highest Ge concentration of the undersaturated rock amphiboles.

4 YTTRIUM

Rankama and Sahama (1950) state that because of the large size of Y^{3+} (0.92 Å) it does not replace Mg or Fe^{2+} in the minerals of basic rocks and becomes enriched in residual magmas. Turekian and Wedepohl (1961) recommend the abundances: basalts 21, high Ca granites 35, low Ca granites 40 and syenites 20 ppm Y. Nockolds and Allen (1954) found enrichment of Y with differentiation in alkali rock series and reported that late stage rocks had up to 60 ppm. Bowden (1961) found an increase of Y with differentiation

in Nigerian Younger granites. Early granites average 100 ppm Y and late formed riebeckite granites average 400 ppm.

Y is concentrated in apatite and sphene in which it substitutes for Ca. Wickman (1943) suggested a diadochy of the type $\text{CaTi} = \text{Y, Al}$ for the replacement of Y for Ca in apatite and Wilkinson (1959) reported 450 ppm Y in an apatite from the Black Jack sill. Y and the lanthanides form the independent minerals allanite and monazite which occur as accessory minerals in many igneous rocks. Goldschmidt (1954) suggested that small concentrations of Y replace Ca in pyroxenes and amphiboles. Wager and Mitchell (1951) found that Y was concentrated in pyroxenes of late formed rocks and Sen et al (1959) found similar relations in hornblendes from the S. Californian batholith. The range of concentration in these hornblendes was from 65 to 3000 ppm Y.

Concentrations of Y in Marangudzi rocks are given in Table 24. R.4 has 60 ppm Y and is the only gabbro with Y above sensitivity (40 ppm). Malignite R.32 has Y below 40 ppm but contains apatite with 150 ppm. The oversaturated rocks often have Y below sensitivity but the outer quartz syenites have from 40 to 50 ppm Y and contain accessory allanite. The undersaturated rocks usually have Y below sensitivity but late formed microfoyaite R.14 and R.15 have 60 ppm.

Marangudzi amphiboles were analysed for Y and Yb and the concentrations are given in Table 24. The oversaturated rock

Table 24 : Distribution of Y, Yb and Zr.

	Y	Zr		Y	Zr	Yb	I.E.
R4	60	50	R19	35	60		
R50	40	60	R174	40	100		
R32	x	210					
E26	55	150	R28	x	210		
			R30	x	200		
R89	x	80	R276	x	60		
R103	x	70	R730	x	190		
R143	40	490					
			R10	x	270		
R7	50	300	R22	x	230		
R118	50	630	R24	x	200		
R141	40	570	P53	x	160		
R177	45	300	R28	x	170		
			R129	x	360		
R16	x	310	R131	x	200		
R21	45	230					
R439	x	540	R420	85	720		
R753	x	240	R441	x	140		
R26	50	150	A21	240	440	25	62.3
R31	40	140	A439	320	450	35	65.2
R76	x	40	A141	380	190	40	87.7
			A177	520	130	65	88.2
R1	65	140					
R2	x	130	A28	60	240	5	59.0
R3	x	90	A26	130	610	10	65.0
R17	x	160	A76	125	480	10	66.8
R20	x	150	A31	160	890	13	67.9
R183	x	100	A2	110	620	13	73.5
R226	x	90	A20	150	680	13	77.2
			A131	130	-	13	79.1
R14	60	430	A15	145	1250	20	88.0
R15	60	340					
R133	40	150					

amphiboles show an increase from 240 to 520 ppm Y and 25 to 65 ppm Yb with increase in I.E. (see Table 24). The undersaturated rock amphiboles are less variable but the earliest amphibole (A.28) has the lowest Y (60 ppm) and Yb (5 ppm) and later formed types have higher contents. The latest formed amphibole A.15 has the highest Yb concentration of 20 ppm.

5 ZIRCONIUM

Zr forms a simple orthosilicate mineral zircon (ZrSiO_4) which consists of SiO_4^{4-} tetrahedra linked to Zr^{4+} ions (0.79 Å), Zr being in 8-fold co-ordination. Rankama and Sahama (1950) state that the zircon structure is unstable and cannot form during early stages of magmatic crystallisation and therefore Zr is enriched in the last rocks to crystallise. However, Ringwood (1955 b) has suggested that in silicate magmas Zr occurs as the complex ion ZrO_4^{4-} which is a larger ion than SiO_4^{4-} and is therefore enriched in residual magmas. Nockolds and Allen (1954) found that Zr increases in alkali rock series from the basic to the more acid types. Goldschmidt (1954) stressed that Zr was especially enriched in alkali magmas and Chao and Fleischer (1961) have suggested that Zr is more soluble in alkali than in tholeiitic magmas. They suggested that when the solubility of Zr was exceeded, zircon would crystallise. Turekian and Wedepohl (1961) recommend the abundances: basalt 140, high Ca granites 140, low Ca granites 175 and syenites 500ppm Zr.

Gerassimovskii, Tuzova and Shevaleevskii (1958) analysed rocks from the Lovozero massif and found that Zr was enriched in late

formed rocks. The early miaskites had an average of 1240 ppm and the late formed agpaites an average of 1.10% Zr. Gerasimovskii (1956) suggested that agpaitic nepheline syenites contain higher Zr than miaskitic types. Hamilton (1964) found Zr in excess of 1% in agpaites from Ilimaussaq but the normal augite syenite (plumasitic) has from 200 to 500 ppm Zr. The Kûgnât syenites (Upton, 1960) have variable Zr up to 2000 ppm.

Wager and Mitchell (1951) and Wilkinson (1959) found that Zr is concentrated in the clinopyroxenes of the Skaergaard and Black Jack intrusions. Borley (1963) reported up to 6500 ppm Zr in alkali amphiboles from the Nigerian Younger granites and allocated Zr to the tetrahedral group. Sen et al (1959) found up to 2500 ppm Zr in hornblendes from the calc-alkaline S. Californian batholith.

Zr concentrations in Marangudzi rocks and amphiboles are given in Table 24. The gabbros usually have Zr below sensitivity (40 ppm) but R.4 has 50 ppm. Alkali basic rocks E.26 and R.32 have higher Zr concentrations. Co-existing pyroxene and biotite from R.32 have respectively 200 and 50 ppm Zr. The oversaturated rocks contain accessory zircon and Zr is up to 630 ppm. Inner quartz syenites R.89 and R.103 have much lower Zr than the other oversaturated rocks and have 80 and 70 ppm respectively. The undersaturated rocks contain lower Zr than the oversaturated rocks and only microfoyaïtes R.14 and R.15 contain zircon. The pulaskites and foyaïtes have similar contents of Zr and vary from

90 to 160 ppm. The biotite foyaites and microfoyaite have respectively lower and higher concentrations than this. The rock series biotite foyaite-microfoyaite therefore shows an increase in Zr. R.276 has 60 ppm Zr and is much lower than the other juvites which average 200 ppm. The phonolites have Zr in the range 160 to 360 ppm and average about 250 ppm.

It is interesting to note that the quartz syenites have higher Zr than the nepheline syenites, bearing in mind Chao and Fleischer's (1961) conclusion regarding the relative solubility of Zr in alkali and tholeiitic magmas.

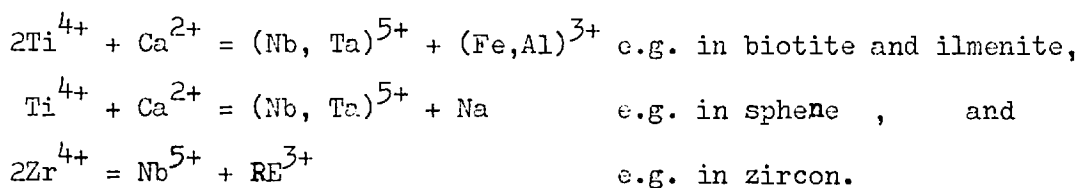
The oversaturated rock amphiboles have comparatively low Zr and most of the Zr in the rock is carried by accessory zircon. Amphiboles of the porphyritic quartz syenites have 450 ppm Zr while those from the outer quartz syenites are lower with less than 200 ppm. Amphiboles from the undersaturated rocks have generally higher Zr and range from 240 to 1250 ppm. Most of the Zr in these rocks is carried by the amphiboles except in R.15 which also has accessory zircon. Assuming the I.E. to represent the order of formation of the amphiboles, it is significant that the amphibole with the lowest I.E. has the lowest Zr concentration (A.28) and that with the highest value has the highest Zr (A.15).

6 NIOBIUM AND TANTALUM

The ionic radii of Nb^{5+} and Ta^{5+} are very similar (0.69 and 0.68 Å) and because of this there is close coherence between them

in magmatic processes. Rankama and Sahama (1950) have shown that Nb and Ta are concentrated in the residual liquids of magmatic differentiation, particularly so in the pegmatite phase. Ringwood (1955b) has suggested that Nb and Ta exist in silicate melts as the complex ions NbO_4^{3-} and TaO_4^{3-} . These are larger ions than SiO_4^{4-} , have different charges and are therefore enriched in residual liquids. Primary Nb and Ta minerals separate at a late stage especially during the pegmatite phase. Nb and Ta are especially enriched in alkali rocks. Rankama and Sahama showed that there is little variation of Nb/Ta ratio in various igneous rock types and gave an average value of 11.4. Turekian and Wedepohl (1961) recommend the abundances: basalts 19 ppm Nb, 1.1 ppm Ta; high Ca granites 20 ppm Nb, 3.6 ppm Ta; low Ca granites 21 ppm Nb, 4.2 ppm Ta and syenites 35 ppm Nb and 2.1 ppm Ta.

Es'kova (1959) analysed miaskitic nepheline syenites from the Vishneyvie Mountains and reported average concentrations of 250 ppm Nb and 21 ppm Ta. The Nb/Ta ratio varied from 6.9 to 11.3 and averaged 11.8. He found that ilmenite was the chief carrier and concentrator of Nb and Ta and held them in diadochic substitution for Ti. Nb and Ta were found replacing Zr in zircon to a limited extent. He suggested diadochic substitutions of the following types:



(RE = rare earth ion)

Gerassimovskii, Kakham, Rodionova and Venkina (1959) analysed rocks from the Lovozero complex and found from 90 to 1600 ppm Nb and from 6 to 330 ppm Ta. They found an accumulation of Nb and Ta with differentiation and the agpaites were especially enriched in these elements. Average contents for the massif are 700 ppm Nb, 40 ppm Ta and Nb/Ta of 12. They found no separation of Nb and Ta even during the pegmatitic phase, however, Gerassimovskii and Venkina (1960) reported separation of Nb and Ta during postmagmatic processes and showed coherence between Nb-Ti and Ta-Zr. Butler and Smith (1962) analysed Nigerian Younger granites and found ranges of concentration from 70 to 110 ppm Nb and 4.6 to 6.5 ppm Ta; Nb/Ta varied from 12 to 24. Hamilton (1964) analysed syenites from Ilimaussaq and found that the augite syenites have up to 18 ppm Nb, nordmarkites have from 7 to 50 ppm Nb but the agpaitic rocks have up to 1400 ppm.

Analyses of Marangudzi rocks for Nb and Ta are given in Table 25, also shown are Nb/Ta and Zr/Nb ratios. The gabbros have Nb < 15 ppm and Ta < 1 ppm but malignite R.32 is higher with 60 ppm Nb and 4.3 ppm Ta. The oversaturated rocks have Nb from 20 to 140 ppm and Ta 4.5 to 5.9 ppm. Nb/Ta varies from 15.6 to 23.7. In the undersaturated rocks the ranges are from 20 to 280 ppm Nb and 1.7 to 9.9 ppm Ta. Nb/Ta varies from 13.4 to 28.2. The biotite foyaites have less than 40 ppm Nb and this is consistent with their early formation. The pulaskites have 55 to 160 ppm Nb, 3.1 to 6.1 ppm Ta and Nb/Ta from 13.4 to 24.3. The foyaites have Nb from

Table 25 : Distribution of Nb and Ta

	Nb	Ta	Nb/Ta	Zr/Nb		Nb	Ta	Nb/Ta	Zr/Nb
R.4	<15	0.3	<50	-	R.19	40	-	-	2.5
R.8	<15	0.6	<25	-	R.174	25	-	-	2.4
R.25	25	1.1	23	-					
R.32	60	4.3	14	3.5	R.28	40	1.7	23.6	5.2
R.26	35	-	-	4.3	R.30	50	2.4	20.8	4.0
					R.276	20	-	-	3.0
R.89	20	-	-	-	R.730	-	-	-	-
R.103	-	-	-	-					
R.143	85	4.7	18.1	5.8	R.10	190	7.7	24.6	1.4
					R.22	150	6.6	22.8	1.5
R.7	110	5.3	20.8	2.7	R.24	140	6.7	21.0	1.4
R.118	90	5.3	17.0	7.0	R.53	95	-	-	1.7
R.141	90	-	-	6.3	R.128	110	-	-	1.5
R.177	100	5.3	19.0	3.0	R.129	210	-	-	1.7
					R.131	210	8.5	24.7	1.0
R.16	170	4.5	15.6	4.4					
R.21	130	5.9	22.0	2.3	R.420	680	-	-	1.1
R.439	140	5.9	23.7	3.9	R.441	75	-	-	1.9
R.753	120	-	-	2.0					
					A.21	690	29.8	23.2	
R.26	160	6.6	24.3	1.4	A.439	1000	43.6	23.2	
R.31	55	4.1	13.4	2.5	A.141	560	17.4	32.2	
R.76	60	3.4	17.6	0.7	A.177	540	18.6	29.1	
R.1	140	-	-	1.0	A.28	410	17.1	24.0	
R.2	200	8.5	23.6	0.7	A.26	560	26.8	20.9	
R.3	120	-	-	0.8	A.76	340	17.3	19.6	
R.17	280	9.9	28.2	0.6	A.31	420	22.9	18.3	
R.20	180	6.7	26.9	0.8	A.2	930	33.7	27.6	
R.183	150	6.3	23.8	0.7	A.20	860	35.6	24.2	
					A.131	-	48.8	-	
R.14	250	-	-	0.8	A.15	1450	37.7	38.6	
R.15	190	9.3	20.4	0.6					
R.133	170	-	-	0.9					

120 to 280 ppm, Ta 6.3 to 9.9 and Nb/Ta relatively constant from 23.6 to 28.2. The microfoyaïtes have from 170 to 250 ppm Nb, R.15 has 9.3 ppm Ta and Nb/Ta of 20.4. The juvites have Nb less than 50 ppm. R.28 and R.30 have 1.7 and 2.4 ppm Ta and Nb/Ta ratios of 23.6 and 20.8. The low Nb and Ta again suggests that they are early formed rocks. The phonolites have Nb from 95 to 210 ppm, Ta 6.6 to 7.7 ppm and relatively constant Nb/Ta from 21.0 to 24.6. Pseudoleucite dyke R.131 has 210 ppm Nb, 8.5 ppm Ta and Nb/Ta of 24.7.

Zr/Nb ratios in the oversaturated rocks vary from 2.0 to 7.0 but the ratio in the undersaturated rocks is generally lower and ranges from 0.6 to 5.2. The pulaskites have Zr/Nb from 0.7 to 2.5, the foyaïtes 0.6 to 1.0 and the microfoyaïtes vary from 0.6 to 0.9. The biotite foyaïtes are comparatively rich in Zr and have Zr/Nb ratios of 2.4 and 2.5 while the juvites have ratios from 3.0 to 5.2. The phonolites have relatively constant Zr/Nb from 1.4 to 1.7.

Analyses of Marangudzi amphiboles for Nb and Ta are given in Table 25. In the oversaturated rock amphiboles Nb is in the range 540 to 1000 ppm and Ta 17.4 to 43.6 ppm. Nb in the bulk rocks is mostly held in the amphiboles. Amphiboles A.21 and A.439 have similar Nb/Ta ratios to the bulk rocks but A.141 and A.177 have higher Nb/Ta ratios than the rocks. This must be due to some Ta being held in the accessory minerals (zircon and allanite). In the undersaturated rock amphiboles Nb varies from 340 to 1450 ppm

and Ta from 17.1 to 48.8 ppm . Nb in the bulk rocks is again mostly held in the amphiboles. Nb/Ta ratios in all the amphiboles except A.15 are similar to Nb/Ta in the corresponding rocks and Ta must also be mostly carried in the amphibole. However, A.15 has a Nb/Ta ratio of 38.6 while the rock R.15 has a ratio of 20.4. The remaining Ta must be held in accessory minerals (zircon).

7 VANADIUM, CHROMIUM, COBALT, NICKEL AND COPPER

Nockolds and Allen (1954) studied alkali rock series and found that Cr and Ni are enriched in basic rocks and show a rapid decrease with differentiation. Co is less enriched in basic rocks and stays fairly steady until the latest stages of differentiation at which point it falls off. V may increase slightly before decreasing in the latest formed rocks. Ringwood (1955 a) discussed the distribution of elements with respect to their ionic radii and electronegativities. He concluded that an element with a lower electronegativity would be incorporated into a crystal relative to an element with higher electronegativity. He suggested that diadochy between the following pairs of elements is controlled by the relative electronegativities of the cations; Na^+ for Cu^+ , Fe^{2+} for Cu^{2+} , V^{3+} for Fe^{3+} and Cr^{3+} for Fe^{3+} . The diadochies Ni^{2+} for Fe^{2+} and Co^{2+} for Fe^{2+} are controlled by ionic radii . Because of these diadochies Cu should be enriched, while V, Cr, Ni and Co should be impoverished, in residual liquids.

Wager and Mitchell (1951) analysed pyroxenes from the Skaergaard intrusion and found high Cr in the earliest pyroxene (3000 ppm). Later, more iron rich types had less than 1 ppm Cr. V entered the early pyroxenes and persisted to the middle of the differentiation series, Ni was present in the early pyroxenes but was not detected in the latest ones and Co was steady at 50 ppm but fell to 15 ppm in the most iron rich pyroxene. Cu rose to 1000 ppm in the ferrogabbro pyroxene but then fell sharply due to the crystallisation of a sulphide phase. Similar relations were seen for Co, Ni and Cu in olivines and Co, Ni, Cu, V and Cr in magnetites. Sen et al (1959) analysed hornblendes from the S. Californian batholith and found the concentration ranges; Cr 100 - 30 ppm, V 265 - 175 ppm, Ni 55 - 5 ppm, and Co 45 - 10 ppm. Cr, V, Ni and Co all decrease as the hornblende becomes more iron rich (i.e. with differentiation).

The analyses of the Marangudzi amphiboles for these elements are shown in Table 26. In the table the amphiboles are arranged in order of increasing I.E. As I.E. increases for the oversaturated rock amphiboles, V decreases from 145 to 40 ppm and A.177 is below sensitivity (5 ppm). Cr decreases from 95 to 15 ppm and A.177 is again below sensitivity (5 ppm). Co decreases from 50 to 15 ppm and Ni from 25 ppm to below 10 ppm in A.177. Cu increases initially but falls to 5 ppm in A.177. In the under-saturated rock amphiboles V decreases from 310 to 35 ppm and the most iron rich types have V below sensitivity. The most Mg rich

Table 26 : Distribution of V, Cr, Co, Ni and Cu in amphiboles

	V	Cr	Co	Ni	Cu	I.E.
A21	145	95	50	25	10	62.3
A439	120	45	40	40	25	65.2
A141	40	15	20	15	15	87.7
A177	x	x	15	x	5	88.2
A28	310	x	50	10	20	59.0
A26	160	30	40	25	7	65.0
A76	70	10	30	20	12	66.8
A31	25	x	25	15	10	67.9
A2	35	15	25	20	8	73.5
A20	x	x	20	x	10	77.2
A131	x	x	30	20	8	79.1
A15	x	x	x	25	13	88.0

amphibole (A.28) has 50 ppm Co but the others show little variation from 30 ppm except the most iron rich type A.15 which has Co below sensitivity (10 ppm). The distribution of Cr, Ni and Cu is haphazard.

C H A P T E R 6

PETROGENESIS OF THE MARANGUDZI COMPLEX

Simpson (1954) described the Okonjeje complex as consisting of two differentiation series. These are an early tholeiitic series consisting of gabbro, ferrogabbro and acid rocks and a later alkaline series consisting of gabbro, essexite and pulaskite with late stage foyaites and tingvaites. Simpson considered that the two rock series had differentiated from a common parent of basic composition. In the last section of Chapter 3 I described several complexes consisting almost entirely of syenite (e.g. Kûgnât, Ilimaussaq, Oslo, Sandyk) with only minor amounts of basic material present. In the S.W. Greenland province especially, there must have been large amounts of augite syenite parental magma present. The Nuanetsi igneous province, to the N.E. of Marangudzi, consists of ring complexes made up almost entirely of gabbro and granite with very few intermediate types present. The Leeds School of African Geology consider there to be two primary magmas, one basic and one acid, formed by differential fusion at depth. King and Sutherland (1960) showed that volcanic rocks of E. and S. Africa had very few intermediate types between nephelinite and trachyte-phonolite. They concluded that this lack was not easily explained if the more salic lavas had been derived from nephelinite magmas.

The Marangudzi complex has large amounts of gabbro and syenite present but intermediate types have not been found. I have only studied the gabbros briefly and, bearing in mind the lack of intermediate rocks, I cannot make any conclusions regarding the petrogenetical relationship between the gabbros and syenites. However, it is interesting to consider how the over- and undersaturated rock types could have been derived from a common parent.

a) Petrogenesis of over- and undersaturated rock types

The oversaturated rock amphiboles have a range of I.E. from 62.3 (A.21) to 88.2 (A.177) while the undersaturated rock amphiboles range from 59.0 (A.28) to 88.0 (A.15). Similarly overlapping ranges are seen for the $\text{Li/Fe}^{2+} + \text{Mg}$ ratios in the over-saturated (from 7.7 to 52) and undersaturated (from $7\frac{1}{2}$ to 42) rocks. If one of these rock types had been formed from the other by some differentiation process, parallel degrees of Fe and Li enrichment would be unlikely. It therefore seems likely that the over- and undersaturated rocks have crystallised from separate magmas which were formed from a common parent by some kind of branching mechanism.

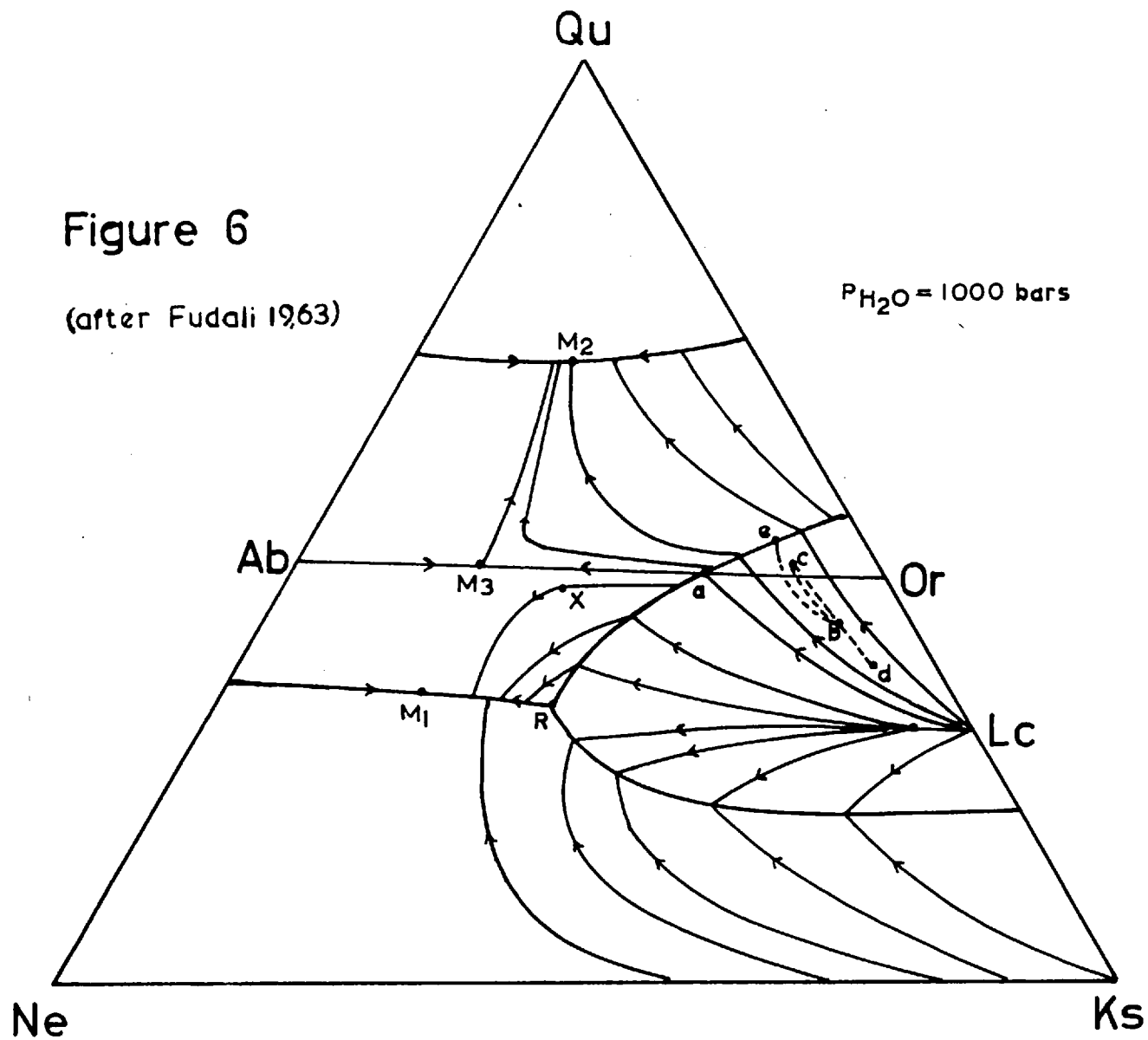
Crystallisation of leucite Bowen (1928) suggested that two magmas could be formed from a common parent by the fractionation of leucite. The liquid from which leucite was removed might eventually crystallise quartz and the liquid to which the leucite was added would crystallise nepheline. The fractionation of leucite might therefore be a possible mechanism for the development of over- and undersaturated magmas from a common parent. Fudali (1963) has

extended these arguments. He discussed the crystallisation of a magma composition b (Figure 6, this figure has been repeated on the next page.). By some mechanism leucite is removed from one part of the magma and enriched in another to give a magma composition d. As leucite crystallises the liquid moves along a curved path to c at which point leucite is no longer fractionated and equilibrium crystallisation becomes dominant. There are now two magmas present of compositions c and d. If these magmas continue to crystallise under approximately equilibrium conditions the final assemblage for c would be feldspar and quartz while that for d would be feldspar and nepheline. As pseudoleucites are rather common in Marangudzi rocks, it is interesting to consider whether the above mechanism played any part in the derivation of the quartz and nepheline syenites.

In Chapter 5 I have shown that rocks of the main oversaturated ring are very poor in Sr and Ba. The porphyritic quartz syenites are higher in Sr and Ba but the undersaturated rocks are much enriched in these elements. It is clear that any mechanism of petrogenesis must explain this phenomenon. The high Sr and Ba of the undersaturated rocks could be explained if leucite concentrated Sr and Ba and, by fractionation, became enriched in one part of the magma (composition d, Fig. 6). The oversaturated magma (composition c, Fig. 6) would then be impoverished in Sr and Ba. However, I have shown (Chapter 5) that leucite contains less Sr and Ba than the liquid from which it crystallised. The oversaturated magma c should therefore be enriched in these

Figure 6

(after Fudali 1963)



elements but this is opposite to that found in the main oversaturated ring rocks. The crystallisation and fractionation of leucite therefore cannot have played any part in their formation. However, the porphyritic quartz syenites have relatively high Sr and Ba and no such definite conclusion can be made regarding these rocks.

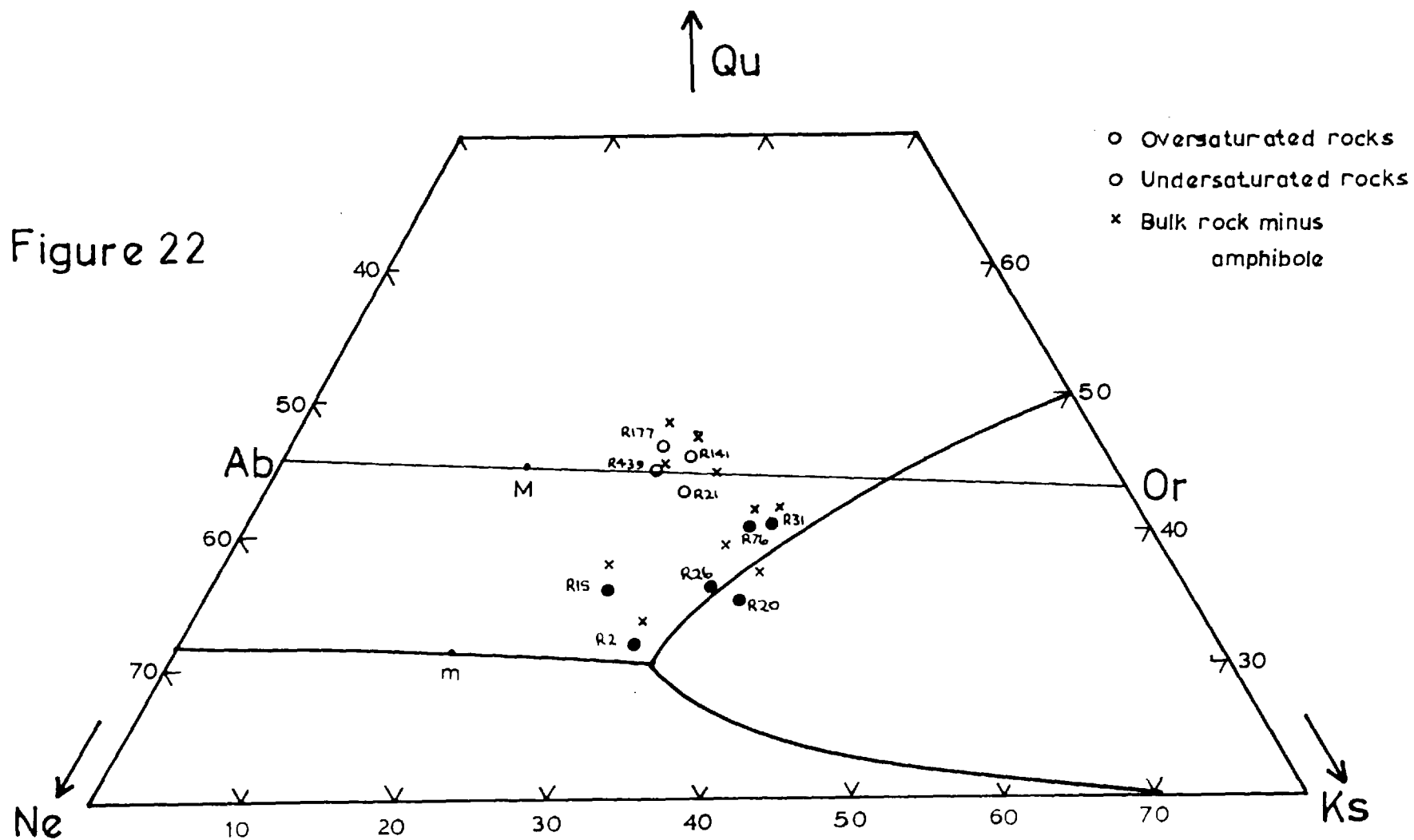
Crystallisation of a hastingsitic amphibole The Ab-Or join in the system Ne - Ks - Qu coincides with a hump on the liquidus surface. This 'thermal barrier' prevents the passage of liquids from one side of the alkali feldspar join to the other. Tilley (1957) has suggested that in natural magmas the precipitation of magnetite rather than aegirine would cause the liquid to become enriched in SiO_2 if the magnetite was not resorbed. A mechanism of this type could cause the formation of an oversaturated (quartz syenite) liquid from an undersaturated (nepheline syenite) liquid.

I have shown that the normative compositions of the hastingsite bearing Marangudzi rocks are less saturated than their modal compositions. It is convenient to consider the normative compositions of the amphiboles and these are shown in Table 15b. The oversaturated rock amphiboles have large amounts of normative Ol and all except A.439 have Ne. The undersaturated rock amphiboles have normative Ne and all except A.15 and A.31 have Lc. The modal contents (weight %) of amphibole in oversaturated rocks R.141, R.177 and R.439 are near 15% but R.21 is higher with 20%. The undersaturated rocks usually have more than 20% amphibole but R.15 is lower with 12%.

These amounts of hastingsite contain considerable proportions of felsic components. I have subtracted the contribution of the hastingsites to the chemical composition of the bulk rocks and have recalculated the norms. The resultant norms of bulk rock minus amphibole are more oversaturated or less undersaturated than the original bulk rock plus amphibole norms and this has been represented in Figure 22. Rocks R.141 and R.177 have modal and normative quartz, the norm of R.439 is only just saturated and the rock has quartz in the groundmass. R.21 has normative Ne and only a trace of groundmass quartz. When these rocks are corrected for modal hastingsite R.141, R.177 and R.439 become more oversaturated and R.21 becomes saturated, i.e. it plots on the alkali feldspar join (Fig. 22). R.89 has a little normative Ne and groundmass quartz. Although this rock has some hastingsite, the reason for its apparent undersaturation is attributed to the presence of a small amount of modal fayalite. The nepheline syenites also show the same effect of decreased undersaturation on subtraction of modal hastingsite from the bulk rock composition (Fig. 22).

It is interesting to consider whether the early crystallisation of hastingsitic amphibole could effectively oversaturate an initially undersaturated liquid of nepheline syenite composition. The amount of amphibole to do this would be prohibitively large except for compositions close to the feldspar join (e.g. R.21). However, the shape of the fractionation curves in the system Ne-Ks-Qu at 1000 bars (Fig. 6) are such that if a

Figure 22



magma was crystallising under conditions of fractionation, crystallisation of a hastingsite from a liquid composition X (Fig . 6) could easily cause the remaining liquid to become oversaturated. Under conditions of extreme fractionation this could give a small volume of a quartz rich residuum. Rocks of the main oversaturated ring cannot have been derived by this process because they are of much larger volume than the undersaturated rocks. They also have much lower Sr and Ba and oversaturated rocks formed by this process would have similar concentrations of these elements to the parent undersaturated magma. However, these objections do not apply to the porphyritic quartz syenites which are of comparatively small volume and have much higher Sr and Ba than the main oversaturated ring rocks. Their origin will be considered later in this Chapter.

If the hastingsite was of late crystallisation, it could not affect the course of crystallisation of the liquid but it would still affect the normative composition of the rock in which it was contained.

Crystallisation of biotite Bowen (1928) suggested that fractionation and subsequent resorption of hornblende or biotite might cause the formation of strongly femic alkaline rocks. Biotite concentrates Ba relative to K and Rankama and Sahama (1950) report up to 6% Ba, however, they also show that Sr is only present in small concentration. Malignite R.32 and biotite foyaite R.19 contain large amounts of modal biotite. Biotite from R.32 has 2.2% Ba and 260 ppm Sr, while that from R.19 has 2.4% Ba and 340 ppm Sr.

Fractional crystallisation and resorption of biotite would cause the resultant liquid to be enriched in K and Ba but separation from Sr would take place. In the Marangudzi rocks there is no separation of Sr from Ba and therefore the crystallisation of biotite can have played no part in the formation of the over- and undersaturated rocks.

Influence of volatiles Barth (1954) has suggested that a homogeneous magma of great vertical extent is not stable thermodynamically. There should be accumulation of H_2O , CO_2 , HF, HCl, chlorides of P, Ti and Zr etc. in the upper parts of such a magma chamber. He maintained that along with the volatiles there should be a corresponding increase of the strong bases Na_2O , K_2O and BaO . In recent years many authors have stressed the importance of volatiles in the formation of alkaline magmas. Amongst these are Saether (1948), Barth (1954), Simpson (1954), Kennedy (1955), Upton (1960) and Zlobin (1960).

The Marangudzi rocks crystallised in the presence of high volatile content as reflected by their relatively low FeO/Fe_2O_3 (Chapter 3) and presence of amphibole rather than pyroxene. The nepheline syenites often contain quite large amounts of sodalite. The oversaturated rocks have F from 0.05 to 0.35 % but are generally below 0.2% . The undersaturated rocks have the range 0.15 to 0.5 % F and are of generally higher tenure than the oversaturated rocks. Bearing in mind the conclusions of the authors listed above, it is

possible that the origin of the Marangudzi over- and undersaturated rocks is in some way connected with their high volatile content.

b) Petrogenesis of the porphyritic quartz syenites

The porphyritic quartz syenites have much higher concentrations of Sr and Ba than the main oversaturated ring quartz syenites. I have shown that the latter quartz syenites cannot have been derived from an undersaturated magma by early crystallisation of leucite or hastingsite because of their comparative lack of Sr and Ba. No such objections exist for the porphyritic quartz syenites and it seems likely that these rocks are more intimately related to the undersaturated rocks than to the main oversaturated ring quartz syenites. The evidence for this suggestion is:-

1. The centres of intrusion (Fig. 2) of the porphyritic quartz syenite ring and the undersaturated cone sheets are in close proximity.
2. The centre of intrusion of the main oversaturated ring lies to the S.E. of the others.
3. The porphyritic quartz syenites have Sr and Ba concentrations more similar to the undersaturated rocks than to the main oversaturated ring quartz syenites, and
4. Porphyritic quartz syenite R.21 is normatively undersaturated and R.439 is only just saturated.

It therefore seems possible that the porphyritic quartz syenites were formed from undersaturated magma and that the crystallisation of hastingsitic amphibole played a major part in their genesis.

c) Relative age of the juvites

Field evidence has shown (Chapter 1) that the juvites are the last of the major intrusions. However, certain aspects of the chemistry and petrography of the analysed juvites suggest that they crystallised from comparatively early formed liquids. The evidence for this suggestion is:-

1. They generally have low FeO/MgO and Li/Mg+Fe^{2+} ratios.
2. They have high Sr and Ba concentrations even though the previously intruded late stage foyaites and microfoyaites have very low Sr and Ba contents.
3. The plotted positions of the juvites in the system Ne-Ks-Qu suggest that they are comparatively high temperature liquids.
4. Amphibole from R.28 has a low value for I.E. and has high TiO_2 .
5. The rocks contain pyroxene and amphibole in approximately equal amount and the only other salic rocks to contain pyroxene are the early formed pulaskites, and
6. The amphiboles show brown pleochroism.

All the above properties are consistent with crystallisation from an early formed liquid. Juvites R.28 and R.276 have high values for D.I. and low K/Rb ratios and this is the only evidence that they may be of late formation. These rocks contain pseudoleucites and the very presence of these in a rock causes it to have high values for a differentiation index of the type D.I. ($= \frac{1}{3} \text{SiO}_2 + \text{K}_2\text{O} - \text{CaO} - \text{MgO} - \text{FeO}$). I have already shown (Chapter 5) that Rb is enriched in leucite relative to the liquid and these conflicting properties can therefore be safely discounted.

It is therefore reasonable to conclude that the juvites crystallised from liquids of comparatively early formation but are of late intrusion.

A P P E N D I X

Analytical methods

The major elements in the Marangudzi rocks were determined using a scheme of "rapid" analysis (Shapiro and Brannock, 1952) modified by Mercy (1956) and I.S.E. Carmichael. Amphiboles and nephelines were analysed by "classical" techniques and the methods of Vincent and Phillips (1954) and Carmichael (1962) were used in the analysis of magnetites.

Sr, Ba and F were determined spectrographically using almost identical methods to those set out in Ahrens and Taylor (1961). Li was determined spectrographically by a method similar to that of Bowden (1961). Amphiboles were analysed for V, Cr, Co, Ni, Cu, Y and Yb by a spectrographic method using negative excitation with Pd as internal standard. Sensitivities are Cu 3 ppm, V, Cr and Yb 5 ppm, Co and Ni 10 ppm and Y 15 ppm. The precision for all the spectrographic determinations except Li and F, is approximately $\pm 10\%$. The methods for Li and F are approximately $\pm 20\%$.

Rb, Sr, Y, Zr and Nb were determined by X-ray fluorescence analysis (Butler and Smith, 1962). The sensitivities of the method are; Rb and Sr 30 ppm, Y, Zr and Nb 40 ppm and the accuracy is $\pm 10\%$. Nb concentrations below 40 ppm were determined by a combined chemical and spectrographic method. Rh on feldspars, nephelines, leucites and pseudoleucites was determined using X-ray

fluorescence analysis. Sr, determined by emission spectrography, was used as internal standard and the accuracy of the method is $\pm 30\%$. Nb and Zr in the amphiboles were determined by X-ray fluorescence using Y as internal standard for Zr and then Zr as variable internal standard for Nb. The accuracy is not better than $\pm 30\%$. Cs and Ta were analysed for by radioactivation analysis (Butler and Thompson, 1962 a and b). Values found for G-1 are 1.6 ppm Cs and 0.83 ppm Ta.

Ge was determined by the method of Schneider and Sandell (1954) except that perchloric acid was used instead of sulphuric. Ge concentrations found for G-1, W-1 and the Canadian Syenite standard are 0.9 ppm, 1.5 ppm and 1.6 ppm respectively. The precision of the method is $\pm 10\%$.

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