

GEOCHEMICAL INVESTIGATION OF GRANODIORITES

AND GRANITES, WITH REFERENCE TO THE

SNOWY MOUNTAINS GRANITES, AUSTRALIA,

AND THE CAPE GRANITE, SOUTH AFRICA.

by

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STATEMENT

The mass spectrometric isotopic analyses reported in Chapter 7 were carried out at the Australian National University by Dr. H.L. Allsopp. Geological interpretation of these results is a joint effort by Dr. Allsopp and the candidate. All other parts of this thesis describe the candidate's own original work.

(Signed) *P. Kettle*

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INTRODUCTION

Ideally geochemical studies on rocks and their minerals are carried out only on rock units for which adequate information is available regarding their geological setting, structure and petrography. This condition is met fairly well by previous studies on the South African Cape Granite. Only very limited work has been done on the granitic rocks of the Snowy Mountains area, Australia. Since the inception of the Snowy Mountains Hydro-Electric Scheme large-scale underground operations have taken place in this geologically interesting region. In addition to many miles of excavated tunnel, underground power stations have been built, new roads constructed and a number of drill-cores have become available. Since the progressive flooding of the tunnels will prevent further access, this rare opportunity was taken of collecting fresh rock samples over a wide area, large parts of which are covered by a thick mantle of residual soil.

The work presented here is the first systematic trace element study of the granitic rocks from both areas. The granitic bathyliths of the Snowy Mountains area encompass the whole range of composition from tonalites to alkali granites. The more basic Snowy gneisses and granodiorites preserve distinct evidence of their origin. In contrast, the differentiated typically "high-level" Cape Granite plutons have passed beyond this stage largely obscuring their origin.

Part I of this study describes the geological setting of the Snowy Mountains granites and deals with their subdivision and origin

on the geochemical evidence. Part II describes the Cape Granites and their minerals and includes a chapter on the isotopic age determination of the Cape Granite and invaded Malmesbury sediments. A full discussion of the geochemical behaviour of individual elements in the rocks and minerals is given in Part III. A full description of the analytical methods used, bibliographies and all tables and diagrams referred to in the text are given in a separate volume.

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I. GRANITES OF THE SNOWY MOUNTAINS REGION, NEW SOUTH WALES,AUSTRALIA.CHAPTER 1. INTRODUCTION.1-1. General description.

The Snowy Mountains region is part of the Southern Highlands of New South Wales (DAVID, 1950, Vol. 2) which are continuous with the Eastern Highlands of Victoria. The regional setting of the area is shown in Fig. 1. Fig. 2 is a geological map of this area of nearly 10,000 square miles which lies between $147^{\circ}50'E.$ to $149^{\circ}15'E.$ Longitude and $35^{\circ}15'S.$ to $37^{\circ}00'S.$ Latitude.

The central complexly block-faulted region is made up of several partly dissected plateaus or tablelands, lying at different elevations, but dominated by the central Kosciusko Plateau, most of it above 4500 feet and including the highest country in Australia, culminating in Mt. Kosciusko, 7314 feet above sea-level. This plateau, about 15-20 miles wide, is elongated and gently tilted downwards in a north-north-easterly direction, merging there with the Kiandra Tableland, while passing into deeply and very irregularly dissected highlands in Victoria to the south. The western margin of the plateau is formed by a series of parallel south-west to north-east trending major fault-scarps, while the descent to the east is more gradual occurring in part along a broad warped zone, and in part along a series of step-like fault escarpments.

Immediately to the east lies the Adaminaby Tableland followed by the Berridale Tableland lying mostly at elevations between 2500 and 3500 feet.

The Snowy, Murrumbidgee and Murray Rivers rise in the Snowy Mountains; but the Great Divide of south-eastern Australia separates the drainage of the Murray-Murrumbidgee Rivers from that of the Snowy River system.

1-2. Previous work.

A great number of geological notes, papers and reports on the Snowy Mountains Region have been written. Some of these date back to the latter half of last century and are far too numerous to mention individually. An exhaustive bibliography, running to over 400 titles has been compiled by D.G. Moye (1964), Chief Geologist of the Snowy Mountains Hydro-Electric Authority. This includes references not only to previously published work on the area, but also to some unpublished reports by the New South Wales Department of Mines, the Bureau of Mineral Resources and the Snowy Mountains Authority itself. An excellent summary of the geology of the area has also been compiled by the geologists of the Snowy Mountains Authority (MOYE, SHARP and STAPLEDON, 1963), accompanied by a geological map on which Fig. 2 is largely based.

Reference is made in the text to a number of the more important papers dealing with the area, as well as with some of the adjoining regions of New South Wales and Victoria. These are all

listed in the bibliography dealing with the Snowy Mountains Area. Since the present contribution is essentially geochemical, the references cited are mainly those which include chemical data. These are not numerous.

Mention must be made of the detailed studies by JOPLIN (1942, 1943) on the Cooma Complex and on the Albury-Jingellic Area (1947), as well as a more general account of the Tasman Geosyncline (1962). Part 1 of the compilation of chemical analyses of Australian rocks (JOPLIN, 1963) contains a number of previously unpublished analyses of granitic rocks of the area. TATTAM (1929), EDWARDS and EASTON (1937) and CROHN (1950) described bordering areas in north-eastern Victoria and VALLANCE (1953, a, b, c and 1960) gave an excellent account of the geology of the Wantabadgery-Adelong-Tumbarumba District. SNELLING (1960) published chemical data on the Murrumbidgee Batholith. The paper by EVERNDEN and RICHARDS (1962) on K-Ar ages of rocks in the area provides a radiometric geochronological basis for regional correlation. The most recent contribution, due to PIDGEON and COMPSTON (1965), considers the age and origin of the Cooma Granite and its associated metamorphic zones on the basis of Rb-Sr age determinations and consideration of Sr isotope ratios.

1-3. Aims of present investigation.

The principal aims of this study are:

- (1) Establishment of the pattern of both major and trace elements for the granitic rocks of the area.

The only published analyses so far available, all confined to major elements, are from the Cooma and Adelong Areas, together with some analyses of rocks of the Murrumbidgee Batholith and a few analyses listed by JOPLIN (1963).

- (2) Subdivision of the granites on the basis of this data, using especially critical element ratios.
- (3) Testing of possible modes of origin of these rocks.
- (4) Comparison of the established composition with that of similar rocks from other parts of the earth's crust.

Due to the relatively large size and strategic, almost central position of the area in the Lachlan Geosyncline, such data and any conclusions arrived at may be of more regional significance and provide keys to the study of the granites over a large area.

1-4. Analytical methods.

Techniques of sampling, preparation and all methods of analysis are described in detail in the Appendix.

CHAPTER 2. GEOLOGICAL OUTLINE.2-1. The Lachlan Geosyncline.

Throughout the earth's crust granitic bodies of bathylithic dimensions appear to be intimately connected with past orogenic zones. The history of the Tasman Geosynclinal Zone, which extends along the eastern side of the Australian continent, will therefore have considerable bearing on the origin of the large granitic bodies occurring in south-eastern Australia.

PACKHAM (1960) divided the southern part of the Tasman Geosyncline into the western, and older, Lachlan Geosyncline taking in Tasmania, much of Victoria and south-eastern and central New South Wales, and the younger New England Geosyncline to the east, which occupies north-eastern New South Wales and extends into southern Queensland (Fig. 1). EVERNDEN and RICHARDS (1962), on the basis of K-Ar ages on granites, demonstrated a pattern of eastern migration of a submeridional axis of intrusions. JOPLIN (1962) described and compared the sequence of igneous events in the two geosynclines.

Precambrian and Cambrian: The only Precambrian rocks so far recognized within the Lachlan Geosyncline occur in Tasmania and consist of quartz and mica schists followed unconformably by quartzites, phyllites, graphitic slates and thick dolomites, which possibly extend into the Lower Cambrian. The unconformably overlying Middle and Upper Cambrian Dundas Group consists of 10,000 feet

of greywacke, conglomerate and sandstone, argillites, and some spilitic lavas and pyroclasts. In Victoria the oldest rocks known are Middle Cambrian, but the base of the succession is nowhere exposed.

Possible Cambrian rocks in New South Wales have been recorded from the Cobar district; and the Wagonga Series on the South Coast near Narooma (BROWN, 1933) is comprised of highly folded, black, banded radiolarian cherts, greywackes, phyllites and schists together with some volcanic igneous flows and tuffs, all unconformably overlain by Upper Ordovician graptolite shales. On lithological grounds the Wagonga Series has been correlated with the Cambrian of Victoria, although this must be very tentative in the absence of dated fossils from the Wagonga Beds. JOPLIN (1962), however, assumed that similar strata containing albitized basic lava underlie all southern New South Wales, although it still seems uncertain whether sedimentation over the whole of the Lachlan Geosyncline took place before the Ordovician.

Ordovician: The JUKESIAN MOVEMENT at the end of the Cambrian was probably restricted to Tasmania. It seems to have caused shallowing of the sea there, since the unconformably overlying 1000-3000 feet of Ordovician strata consist of conglomerates, quartz-rich sandstones and shales in the Lower Ordovician, and thick limestones in the Middle and Upper Ordovician. The lithology of the mainland Ordovician, on the other hand, is very uniform, consisting generally of quartz-rich greywackes, black graptolitic and siliceous slates and

occasional chert. Estimates of thickness show about 15,000-20,000 feet in Victoria and about 12,000 feet for the Upper Ordovician in the Goulburn district. In western Victoria apparently only Lower and Middle Ordovician rocks occur, conformable with the Cambrian, but in eastern Victoria and New South Wales strata are mainly confined to the Upper Ordovician.

Considering the extent and thickness of Ordovician sediments very little volcanism took place during this time, but andesitic volcanics were active in the Wellington district and some other andesitic rocks appear further south, while some rhyolite occurs in the Cooma district. JOPLIN (1946) suggested that the siliceous graptolite slates found at Cooma and other areas of eastern New South Wales formed largely from rhyolitic ash.

According to BROWNE in DAVID (1950) the Ordovician was closed by the BENAMBRAN OROGENY during which the beds were strongly folded and a broad median geanticline was formed which was at least 200 miles wide in New South Wales. Along this geanticline Ordovician and Silurian rocks are unconformable, with angular concordance on either side. He also suggested that the two parallel belts of regional metamorphism with accompanying "Ordovician" granites, one stretching from eastern Victoria far into New South Wales and the other at Cooma, were formed during this orogeny. K-Ar determinations by EVERNDEN and RICHARDS (1962) and some Rb-Sr dates (PIDGEON and COMPSTON, 1965) on some of these granites have

cast considerable doubt on their Ordovician age. These age results are further mentioned in the next chapter.

Silurian: The Silurian on the whole was a period of steady sinking and deposition with a total recorded thickness of over 20,000 feet in Victoria. Both there and in New South Wales the sediments consist mainly of shales, mudstones and often thick limestones, demonstrating the gradual increase in shallow water deposits from Ordovician to Middle Devonian time. Dacite tuffs and some rhyolites are found, mainly in New South Wales. The Silurian was closed by a strong folding movement, the BOWNING OROGENY, during which most strata were folded and uplifted. (JOPLIN (1962) placed this movement into the early Lower Devonian). The concordant, foliated and massive granite batholiths were formed and serpentinites and some ultrabasic rocks may also be of this age.

Lower - Middle Devonian: Sedimentation produced shales, conglomerates and important limestone formations. Widespread acid volcanics are found in eastern Victoria extending into New South Wales. During the following TABBERABBERAN OROGENY massive granites were introduced. However, JOPLIN (1962, p.64) stated: ".....it is possible that the Bowning and Tabberabberan Orogenies are movements of a single great orogeny, which partly stabilized the Lachlan Geosyncline".

Upper Devonian - Lower Carboniferous: After the Tabberabberan Orogeny sedimentation changed from the previously dominantly flysh phase into the molasse-like phase of the Upper Devonian to Lower

Carboniferous. The sediments are quartz-rich and composed mainly of sandstones.

No tectonic break occurred at the end of the Devonian and the KANIMBLAN OROGENY of Lower Carboniferous time was the final great folding movement in the Lachlan Geosyncline. High-level granites and granodiorites were produced on its northern flank.

Essentially only epeirogenic movements seem to have occurred in New South Wales after this stage.

2-2. The Snowy Mountains Region.

(a) Sedimentary and volcanic rocks: Most of the sediments occurring in the area (Fig. 2) are of Upper Ordovician age. They are of low regional metamorphic grade and tightly folded with strikes generally about meridional. Lithologically they are dominantly interbedded shales, siltstones and fine-grained sandstones (subgreywacke) with minor development of chert locally.

The ADAMINABY BEDS are part of a major belt of such Upper Ordovician sediments extending northwards from Victoria along the eastern side of the Snowy Mountains into the Australian Capital Territories. On the western side of the mountains similar sediments, dated by graptolites as Mid-Upper Ordovician (Eastonian), are represented by the BOGONG CREEK BEDS which also extend southwards into Victoria in the direction of Benambra and Omeo. A relatively small, wedge-shaped area in the vicinity of Tumut Pond tapers out to the south opening into two arms northwards. Upper Ordovician

KIANDRA BEDS with underlying probably Lower Ordovician BOLTONS BEDS form the eastern arm while the thin western belt is formed by O'HARES BEDS and the NINE MILE VOLCANICS which include some andesite, andesite tuffs and breccia.

During Silurian times deposition took place in much shallower water. The sediments, apart from shales, siltstones and sandstones, contain limestone, often thick and massive, and some conglomerate locally. In further marked contrast to the Ordovician, widespread volcanism occurred, producing dacite and more acid tuffs, crystal tuffs and lavas, often interbedded with the sediments. In the Blowering area probable Silurian quartz-feldspar porphyries are intruded by Bogong Granite and an extensive area of porphyry outcrops north-east of Yarrangobilly; while a belt of Silurian sediments, lavas and porphyry extends northwards from Cooma through the Australian Capital Territories. Sediments, probably an extension of the Victorian COWOMBAT GROUP, occur on the New South Wales - Victoria border and a narrow belt probably continues northwards to link up with the more extensive development in the Yarrangobilly - Tumut Pond area. Further Silurian sediments occur near Tumut and in the Cooleman Plains district.

Only few and relatively small occurrences of Lower-Middle Devonian rocks are found in the area. South-east of Talbingo thick rhyolite lavas and tuffs of Lower Devonian age are overlain by Middle Devonian shallow water marine sediments including shaley

siltstones, sandstones, conglomerates and thick limestones. This whole series forms an elongated structural basin of about 95 sq. miles outcrop area and overlies Upper Silurian rocks with a marked angular unconformity. North of Tantangara Reservoir occurs a belt of Lower to probable Middle Devonian age. This includes quartz-feldspar porphyry and rhyolite to andesite lava and tuff. Small outcrops of mainly acid lavas of Lower-Middle Devonian age also occur near Canberra and are exposed along the upper Murray River on the New South Wales - Victoria border.

(b) Metamorphic rocks: Geographically two roughly north-south trending metamorphic belts are recognized.

The western side of the Snowy Mountains Area is only a small part of a great belt of meta-sediments and associated gneisses which stretches some 300 miles in a north-north-westerly direction. It begins near Omeo in north-eastern Victoria (TATTAM, 1929; EDWARDS and EASTON, 1937; CROHN, 1950). It crosses the Murray River in the Albury-Jingellic Area (JOPLIN, 1947); includes knotted schists and quartzites of the Swampy Plain Metamorphics in the Khancoban Area as well as the Grey Mare Metamorphics, gradational into the Grey Mare granitic belt (MOYE, SHARP and STAPLEDON, 1963); the Tumbarumba-Wantabadgery Area described by VALLANCE (1953 a, b, c, 1960); and may be followed with some breaks at least as far as Condobolin in central New South Wales.

This great western metamorphic belt seems to stop abruptly along the Grey Mare Range, only to reappear on a very subdued scale at Cooma, about 40 miles to the east. The Cooma belt, with its concordant core of gneiss, has a maximum width of about 8 miles and has been traced for 30-40 miles in a meridional direction and may even extend further south under Tertiary basalt. It is cut off to the north by the younger granites of the Murrumbidgee Batholith. JOPLIN (1942, 1943) divided the metamorphosed Adaminaby Beds in the Cooma Area into the Coolringdon Beds, occurring to the west, consisting of psammites (quartzite) and siliceous slates with Upper Ordovician graptolites (JOPLIN, 1946) and the probably older Binjura Beds, which, however, were considered younger than the Coolringdon by BROWNE (1943). The Binjura Beds are made up of alternating pelites and psammites (originally banded aluminous shales, mudstones and sandstones), with sporadic lenses of calcareous (possibly tuffaceous) psammites and some thinly bedded basic igneous rocks.

According to JOPLIN (1942, 1943 and 1952) the area suffered regional metamorphism before the intrusion of the gneiss superimposed thermal metamorphism, which can now be traced in progressive zones with boundaries parallel to the gneissic core. This has been classified by MIYASHIRO (1961) as an example of his Andalusite-Sillimanite type regional metamorphism.

The graptolite slates of the Coolringdon Beds in the west are in the zone of clastic mica. The following 5 higher-grade zones are encountered as one passes eastwards across the strike of the Binjura Beds into the gneiss. In the chlorite-, biotite- and andalusite-zones the rocks are typically schists with knots of andalusite and cordierite occurring in the last-named zone. In the orthoclase-cordierite (formerly permeation) zone spotted granular pelites (formerly granulites), with spots composed of porphyroblasts of orthoclase around small fragments of schist, pass into mottled gneiss. In the migmatite (formerly injection) zone distinct lit-par-lit structure is developed.

Similar zones of progressive metamorphism have been described from the western metamorphic belt and the meta-sediments and gneisses show a remarkable uniformity in lithology and chemistry in both areas. The equivalent of the Cooma Coolringdon siliceous slates, however, seems to be lacking in the Albury and Tumbarumba-Wantabadgery Areas.

(c) Granitic rocks: Considerably more than half of the Snowy Mountains Area and surrounding regions is made up of large granitic batholiths, generally elongated and concordant with the north-south striking sediments. These batholiths are composite bodies made up of varying types of granitic rocks with regard to mineralogy, structure, texture and relation to country rocks, but biotite-granodiorite is the dominant type.

The subdivision of the granitic types is discussed in the next chapter, but geographically five main bodies can be recognized, although boundaries between them are not everywhere quite distinct with smaller outcrops occurring between them.

1. The Kosciusko Bathylith forms the central mass of the area stretching for more than 65 miles from south of the Victorian border to north of Kiandra. It forms most of the Kosciusko Plateau. To the west it is terminated by the long narrow strip of Silurian sediments and Geehi Metamorphics. On its eastern side it is separated from the Berridale Bathylith by Upper Ordovician sediments although the two granite bodies unite for a short distance near Lake Eucumbene. The main mass of Kosciusko Granite is intruded by the small Jindabyne, Island Bend and the more leucocratic Eucumbene Granites.

2. The Berridale Bathylith to the east varies between 10 and 20 miles in width and stretches for about 70 miles northwards from the Victorian Border. Southwest of Cooma it invades the Upper Ordovician Coolringdon Beds forming a contact aureole of quartzite, hornfels and chiastolite slate (JOPLIN, 1942). Like the other large granitic bodies the Berridale Bathylith is a highly composite mass. Thus LAMBERT (1963) mapped four separate components in the Berridale District alone.

3. The Murrumbidgee Bathylith has an outcrop area of about 550 square miles mainly in the Australian Capital Territory south

of Canberra, but its southern tip intrudes the Cooma Gneiss and its associated metamorphic aureole. It has been partly remapped for the 1964 Second Edition of the 1:250,000 Canberra Sheet S1 55-16. SNELLING (1960) described nine separate components. The earlier, more basic, xenolith-rich so-called "contaminated" types occur in the east and comprise the Clear Range (190 square miles), Callemondah ($8\frac{1}{2}$), Willoona ($4\frac{1}{2}$) and Bolairo (3) Granodiorites as well as the Murrumbucka Tonalite (20). The somewhat later, more massive and leucocratic, so-called 'uncontaminated' types in the west are made up of Shannons Flat Granodiorite (260) and Tharwa Adamellite (18), while the youngest components to the south-west are represented by the Yaouk Leucogranite (25) and Westerly Muscovite Granite ($5\frac{1}{2}$).

4. The Bogong Granite stretches 20 miles northwards from Yarrangobilly where it is intrusive into Silurian limestone. It is a massive pink granite low in ferro-magnesian minerals.

5. The Maragle Bathylith comprises the large mass of granitic rock to the west and north-west of the Kosciusko Bathylith. It extends from north of Adelong to south of the Victorian border where it was described as the Corryong Bathylith by EDWARDS and EASTON (1937). In the Tumbarumba-Wantabadgery Area to the north VALLANCE (1953c, 1960) distinguished two distinctly different groups of granite which seem to continue southwards into the Grey Mare Granitic Belt. The first group comprises the Wantabadgery and Green Hills Granites, associated with broad zones of metamorphism, resembling

therefore the Cooma and Albury Gneisses as well as the Boomerang Creek Granitic Gneiss in the area of the Tumut-1 and Tumut-2 power stations (MOYE, SHARP and STAPLEDON, 1963). The second group is represented in the Adelong Area by the younger Ellerslie-Wondalga Granites. They in turn are similar to the Happy Valley Granite further south which is intrusive into Boomerang Creek Granitic Gneiss, and thus resemble the bulk of the granitic rocks in the main bathyliths.

Younger intrusive, more leucocratic granite masses of the Maragle Bathylith are represented by the Welumba, Khancoban and Scamels Granites (MOYE, SHARP and STAPLEDON, 1963) due north, south and east of Khancoban respectively, as well as the red granites of Pine Mountain and Mt. Mittamatite (EDWARDS and EASTON, 1937) near Tintaldra on the Victorian side of the Murray River.

(d) Basic and ultrabasic rocks: A number of elongated, composite masses comprising pyroxenite, hornblendite, gabbro, diorite, monzonite, lamprophyre and gradational types occur roughly parallel and en echelon to one another in a zone stretching 35 miles north-north-eastwards from Geehi Dam to north of Kiandra. They are mostly intruded into Upper Ordovician Kiandra Beds and some are themselves contact-altered by Happy Jacks Granite. JOPLIN (1958, 1959), after a study in the northern area of this belt, tentatively concluded that they were all related and derived by mixing of basic and

granitic magmas just prior to the emplacement of the granite during the Bowring Orogeny (Lower Devonian).

VALLANCE (1953b) described a metamorphosed belt of intermediate to basic rocks of apparent igneous origin which are now mainly amphibolites and pyroxene granulites. This belt outcrops from Batlow to beyond Adelong and also predates the Ellerslie-Wondalga Granites. A sample of amphibolite from Batlow has been included in the present study (sample 36, Tables 1 et seq.); and the observed pattern of both major and trace elements agrees with the postulated origin from basic igneous rock.

JOPLIN (1939, 1942, 1943) also described small masses of amphibolite occurring both in and near the Cooma Gneiss as also as inclusions in the granitic rocks of the southern part of the Murrumbidgee Batholith. She considered these to have formed from basic and ultrabasic rocks respectively, originally intruded into the Ordovician sediments. PIDGEON and COMPSTON (1965) strengthened this conclusion by evidence from a large pyroxene-amphibolite xenolith in the Cooma Gneiss, which showed an initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio about 2% lower than that of the Cooma Gneiss and not distinguishable from that of recent basic igneous rocks. SNELLING (1958), on the other hand, found very low Ni (5 p.p.m.), Co (20 p.p.m.) and Cr (10 p.p.m.) in a similar amphibolite specimen, an inclusion in the southern extremity of the Murrumbidgee Batholith, and therefore suggested a possible origin for this specimen from an impure calcareous sediment.

It thus seems possible that amphibolites of both basic igneous and sedimentary origin occur in the area.

Further basic rocks in the Snowy Mountains Region are represented by two narrow belts of serpentine. One extends about 30 miles north-north-westwards from Tumut Pond and the other, roughly parallel and en echelon, occurs further north running towards Coolac. These belts consist of a series of disconnected lenses and sheets comprised of massive and foliated serpentine, often associated with amphibolites and diorite. Most contacts with other rocks seem to be faulted or sheared. The northern belt clearly intrudes Bogong Granite and therefore must be of Lower Devonian age or younger.

(e) Tertiary geology: At the end of the Cretaceous most of the area seems to have been reduced to a peneplain with monadnocks. Periodical disturbances from the late Mesozoic onwards raised this peneplain into a highland region. During Upper Eocene or possibly Oligocene time series of abundant olivine basalt flows became interbedded with lacustrine sediments. Uplift with consequent denudation and valley deepening continued and glaciation affected portions of the Kosciusko Plateau during the Pleistocene. Widespread seismicity in the area indicates continuing tectonic activity to the present.

CHAPTER 3. THE GRANITE TYPES.

The analytical data is utilized in this chapter to demonstrate the subdivision of the Snowy Mountains granites into various types; further points emerge from a fuller discussion on element abundances in granites generally, given in Part III.

3-1. Abundance and distribution of the elements.

New data for 31 major and trace elements is presented for 32 granitic rocks, 3 porphyry dykes and 1 amphibolite from the Snowy Mountains Region.

Sample locations are shown in the geological map (Fig. 2) and are described in Table 1. Table 2 lists the dominant structure and texture of the granites as well as their average modal composition determined from thin sections. This may be compared with Table 3 showing previously published modes of similar rocks in the area.

The analytical results are set out in Table 4 for: rocks of mainly granodioritic composition (samples 13-32), gneisses (samples 1-4), leucogranites (samples 5-12) and the 3 porphyry dykes and 1 amphibolite. Calculated averages are given for the granodiorites, gneisses and leucogranites. Elements are listed in order of increasing ionic radius, expressed as weight per cent for the major elements and as parts per million by weight (p.p.m.) for the minor and trace elements. Major elements, expressed as oxides, are included for comparative purposes.

3-2. Subdivision of the granites.

BROWNE (1929) and BROWNE in DAVID (1950) recognized three distinct types of granite in the Lachlan Geosyncline and correlated these granite intrusions with orogenic epochs.

Other workers have basically agreed with such a division. The features of these different types have been described as follows, using the nomenclature proposed by JOPLIN (1962):

1. Gneissic granites (Ordovician type). These are generally described as medium-grained, sporadically porphyritic, banded and contaminated rocks containing many xenoliths. They are two-mica granites, rich in biotite, and contain andalusite, sillimanite or cordierite. They are locally gneissic and are concordant to related, progressively zoned metamorphic belts of Ordovician meta-sediments. They appear to be the oldest granites in any one area, in places invaded by type 2; and BROWNE in DAVID (1950) considered them to be of Benambran age.

Included in this group are the following, all surprisingly similar to one another: Cooma Gneiss (JOPLIN, 1942, 1943; PIDGEON and COMPSTON, 1965); Albury Gneiss (JOPLIN, 1947); "Gneiss" of north-east Victoria (TATTAM, 1929); Wantabadgery and Green Hills masses (VALLANCE, 1953 c); Boomerang Creek Granitic Gneiss near Cabramurra (MOYE, SHARP and STAPLEDON, 1963).

Four new analyses of this type from the Snowy Mountains Area, including trace element data, are presented in Table 4 (samples 1 to 4). Modal compositions are given in Table 2.

Table 3 shows previously published modal compositions of this type and for further comparison Table 6 (column 5) lists the average of 11 previously published major element analyses from various areas. The distinctive chemical features of these gneisses are illustrated in a number of diagrams in the discussion given below, but the outstanding features may be listed as:

1. High concentrations of Mg, Fe and other "ferro-magnesian" elements. (Elements substituting mainly for Mg and Fe in 6-fold coordination in ferro-magnesian minerals; e.g. Cr, Ni, Co, Cu, V).
2. High K and concomitant Rb and Cs.
3. Very low Ca and Sr.
4. Relatively low Na.

2. Foliated granites (Silurian type). These are generally large, elongated and concordant (synchronous) bodies. Where they invade Ordovician or Silurian sediments, which generally only show regional metamorphism not exceeding the greenschist facies, they only produce very limited contact aureoles. They are medium to coarse-grained and often show pronounced foliation, but also grade into more massive varieties. They often contain abundant xenoliths and are mainly granodiorites, sometimes grading into tonalites, although some more acid members exist as well.

A Bowring age was attributed to these types by BROWNE in DAVID (1950), since they cut across the gneisses but are themselves invaded by type 3.

In the area considered here the following members fall into this group: the bulk of the Kosciusko Bathylith - Kosciusko and Happy Jacks Granite (MOYE, SHARP and STAPLEDON, 1963); the "contaminated" granites of the Murrumbidgee Bathylith (SNELLING, 1960); components of the Maragle Bathylith - Ellerslie - Wondalga Granites (VALLANCE, 1953 c) and Happy Valley Granite (MOYE, SHARP and STAPLEDON, 1963).

Samples 13, 14, 16 to 23, 26, 28 and 30 fall into this category.

3. Massive granites (post-Silurian types). These are described as massive, often more or less equidimensional bodies showing no meridional trend. They are transgressive (subsequent), and often surrounded by thermal aureoles of hornfels of the intruded sediments. They appear younger than the foliated granites and BROWNE in DAVID (1950) ascribed these massive types to the Tabberabberan and Kanimblan Orogenies.

MOYE, SHARP and STAPLEDON (1963) described such massive types in the Snowy Mountains Region. They contain few xenoliths and are generally adamellites grading into granodiorites or granites.

They include: components of the Kosciusko Bathylith -- Island Bend and Jindabyne Granites; most of the Berridale Bathylith; the "uncontaminated" granites of the Murrumbidgee Bathylith (SNELLING, 1960); and components of the Maragle Bathylith, such as the Khancoban Granite.

Into this group therefore would fall samples 15, 24, 25, 27, 29, 31, and 32.

However, all samples falling into groups 2. and 3. have been called granodiorites in this study, since the chemical evidence discussed below indicates such a degree of gradation and overlapping between these two types that no such stringent division seems warranted on chemical grounds. Possible exceptions are represented by the Khancoban Granite (sample 29) and the Island Bend Granite (samples 31 and 32).

4. Leucogranites. Although these are not generally placed into a special category, samples 5 to 12 are representatives of massive, cross-cutting, fine-grained to coarse porphyritic, acid granites. They occur as minor phases with the bathyliths of granodiorite and appear to be the youngest granites in the area.

As shown in the diagrams discussed below, they are clearly highly differentiated rocks, demonstrated by very low concentrations of Fe, Mg, ferro-magnesian elements, as well as Ca and Sr, while showing marked enrichment in Rb and Cs.

The correlation of different granite types with different orogenies was seriously questioned by EVERNDEN and RICHARDS (1962). K-Ar ages of the granites in the Lachlan and New England Geosynclines showed apparently continuous tectonic activity from Middle Silurian to Middle Devonian with a gradual eastward movement of the axis of intrusion. The K-Ar ages presented showed a complete overlap in

time between the foliated (Silurian type) and massive (post-Silurian) granites emplaced mainly during the Lower Devonian. The gneissic granites (Ordovician type) showed dominantly Upper Silurian ages although also overlapping the other two types to a considerable extent. These conclusions are basically confirmed by more recent, as yet unpublished, K-Ar determinations (RICHARDS, personal communication).

This is essentially corroborated by Rb-Sr age determinations (PIDGEON and COMPSTON, 1965) on the Cooma Gneiss and Shannons Flat Granodiorite (Murrumbidgee Batholith) indicating ages of 415 ± 12 m.y. and 417 m.y. respectively. Another unpublished K-Ar determination on biotite from the intrusive, leucocratic Scamels Granite (I. McDOUGALL, A.N.U., personal communication) gave an age of 370 m.y., which must be regarded as a minimum. Compared with the isotopic age results on other granitic rocks of the area the Scamels Leucogranite is therefore not much younger and the massive leucogranites generally are therefore regarded as part of the same general period of activity that produced the other granitic rocks.

JOPLIN (1962), while agreeing that the three types of granite could not be correlated with specific orogenies, cited major element chemical data from granites over a wide area to distinguish between the three types. All leucogranites were similarly chemically subdivided into three groups depending on their field occurrence with the three types of granite.

The chemical data presented in this study, however, only support a major division of the granites in the area into:

- (a) Gneisses, equivalent to the gneissic granites (Ordovician type).
- (b) Granodiorites, including both foliated (Silurian type) and massive (post-Silurian types) granites which show overlapping chemical compositions, so that they cannot be readily subdivided into these two types. Possible exceptions, however, are the Island Bend Granite (samples 31 and 32) and the Khancoban Granite (sample 29), both massive intrusive types, chemically dissimilar to the granodiorite group as a whole.
- (c) Leucogranites, similar to those described by JOPLIN (1962). They show different stages of differentiation although not divisible into groups depending on association with different types of granite.

The chemical divisions outlined above are illustrated in Figs. 3 to 13. An attempt is also made, using the major element chemical data available from previously published work, to demonstrate the chemical similarity between the granites here described and those from a wider area.

Fig. 3 shows the clear separation of the Snowy Mountains Granites into gneisses, leucogranites and granodiorites with respect to Na, K and Ca. These major elements are plotted here as oxides to allow easy comparison with similar plots of previously published analyses. These are presented in Fig. 4, which also shows plots of the calculated averages from the previous diagram.

The similarity of the data presented in these diagrams is even more remarkable when one considers that they were obtained by different analytical techniques, in different laboratories and over a considerable space of time.

The granodiorites numbered in Fig. 3 refer to samples from massive-type bodies. The spread of these plots throughout the granodiorite group is apparent.

The diagrams illustrate the low Ca content of both gneisses and leucogranites relative to the alkalis; but 3-component diagrams must obviously be used with caution since they may under some conditions subtly infer element relationships which are not real, and disguise others. Thus, without recourse to the actual values, it might be inferred from Fig. 3 that the gneisses contain more K than the leucogranites. It is clear from Figs. 5 and 6 that the leucogranites are richer in K than the gneisses, a fact obscured in Fig. 3 by the much higher Na content of the leucogranites. The low Na content of the gneisses relative to the granodiorites is also better shown on the 2-component diagrams, which give the actual concentrations. Furthermore, a possibly linear continuity for these elements between gneisses and granodiorites is suggested. This is further dealt with in the next chapter, which deals with the origin of the different granite types. Fig. 6 also suggests that the somewhat different, massive Khancoban Granite (sample 29) and Island Bend Granite (sample 31 and 32) have slightly higher Na concentration than the average granodiorite.

A further test of the similarity in major element composition between the granites of the Snowy Mountains Area and previously published analyses of similar granites from bordering areas is provided by the MgO-FeO plots of Figs. 7 and 8. A logarithmic plot is used to encompass the wider range in concentration shown by Mg and Fe (total Fe). Comparison between Figs. 7 and 8 reveals a far larger spread of results for the previously published analyses. This is probably at least partly due to analytical error of the wet-chemical methods used, especially at the low concentrations of Fe and Mg encountered in the leucogranites. The same relationship between results of the two analytical methods is demonstrated for the South African Cape Granites for which classical chemical Mg and Fe results are compared with the spectrochemical data on the same rocks. This serves as another illustration of the wellknown fact that at lower concentrations spectrographic methods are normally more precise than chemical methods. (See for instance STEVENS et al., 1960, Part 3).

Viewed in this light Fig. 8 shows good agreement between these two sets of FeO and MgO results. The similarity of average iron and magnesium concentrations for gneisses and granodiorites may be noted, as also the very low levels in the leucogranites.

Further logarithmic plots of some minor and trace elements in the Snowy Mountains Granites are shown in the next 5 diagrams.

The concentration range shown by some of the plotted trace elements is very great; this is an extremely useful feature in characterising rock types.

Fig. 9 shows the strong coherence between Mg and V. Both here and in the Fe-Ti plot of Fig. 10 the leucogranites are clearly demarcated from both gneisses and granodiorites by their very low content of ferro-magnesian elements, which show very similar concentration levels in the latter two rock types.

Figs. 11 and 12 illustrate the Ca-Sr-Ba relationship in the granites. Here is an evident chemical separation between the granodiorites and the gneisses, the latter being distinctly lower in both Ca and Sr, but not in Ba. The leucogranites further show the wellknown strong decrease in Sr and Ba with progressive differentiation, due to the capture of these two elements in early formed K-minerals. The apparently anomalously high Ba concentration in leucogranites 6, 11 and 12 (Fig. 12) is further mentioned in the following chapter, which also deals with a possible explanation for the observed overall pattern of these three elements in the granites.

Fig. 13 shows the K-Rb relationship for the different types of granite. The leucogranites are clearly enriched in Rb relative to K; and consequently show low K/Rb ratios (Table 5). The gneisses have somewhat higher K concentrations than the granodiorites, but neither of the latter two granite types show

Rb enrichment. This significant feature is also further discussed in the next chapter.

Figs. 7 to 13 also illustrate the varying degrees of differentiation among the leucogranites. Thus, compared with other leucogranites, the Welumba and Pine Mountain Granites (samples 5 and 7) appear the most highly differentiated showing the lowest Fe, Mg, V, Sr and Ba concentrations, as well as low Ca and Ti, coupled with high Rb. The Bogong, Scamels and Mt. Mittamatite Granites (samples 6, 11 and 12), by contrast, show higher concentrations of ferro-magnesian elements, Ca, Sr and especially high Ba, coupled with low Rb. The remaining three leucogranites show generally intermediate concentration levels for these elements.

3-3. Conclusions.

From the data presented thus far a number of preliminary conclusions may be drawn on the chemical subdivision of the Snowy Mountains Granites:

- (1) Using both major and trace element data the granitic rocks of the region can be broadly divided into "gneisses" (corresponding to Joplin's gneissic granites, Ordovician type), "granodiorites" (corresponding to both foliated, Silurian and massive post-Silurian types granites) and "leucogranites".
- (2) The granodiorites, which form the bulk of the bathyliths, show a strong, but apparently almost continuous, variation in major and trace elements when viewing the region as a whole. With the data

available they cannot therefore be readily further subdivided into "foliated" and "massive" types, although this may be possible for any particular smaller area, as shown, for instance, by the chemically somewhat distinctive intrusive and massive Island Bend and Khancoban Granites. This apparent overall chemical similarity between foliated and massive types finds a parallel in the K-Ar ages of these rocks, which also showed no real distinction between foliated and massive type granites on a broad regional basis, although the gneisses appeared somewhat older in any one area.

(3) The leucogranites sampled may be subdivided into three stages of differentiation which, however, are apparently not related to association with the different granite types in the area.

(4) The large bathyliths sampled are strongly composite bodies made up of several intergrading types of granitic rocks and may vary in relative proportions of these components; but variations in chemistry between the different components of any one bathylith appear to be larger than overall variations between different bathyliths. Therefore a very much larger number of samples would be needed to detect any significant difference in chemical composition between the great granodiorite bathyliths, if such a difference exists.

(5) Comparisons of the major element data presented here from the Snowy Mountains Region with previously published analyses from a wider area indicates that the new trace element data, and other

conclusions reached in this study, may be applicable to the granitic rocks of a similarly wider area of the Lachlan Geosyncline.

CHAPTER 4. ORIGIN OF THE SNOWY MOUNTAINS GRANITES.4-1. The Gneiss.

An outline of the field occurrence, age, mineralogy and main distinctive chemical features of these rocks has been given in the previous two chapters. It is apparent, that, compared with granites of similar SiO_2 content, the gneisses have an unusual chemical composition (Table 6). A high concentration of K, Fe, Mg and other ferro-magnesian elements is coupled with very low Ca, Sr and relatively low Na. Clearly these rocks have not formed by any normal magmatic process of differentiation.

The field evidence (JOPLIN 1942, 1943, 1947; VALLANCE, 1953 c), the similar composition of biotites from the granitic rocks and surrounding high grade meta-sediments of the area described by VALLANCE (1960) and the Sr isotope data from the Cooma Area (PIDGEON and COMPSTON, 1965) suggest that these rocks have at least partially formed from sediments. Possible sedimentary parent material must therefore be considered.

The Ordovician sediments associated in all areas with these gneisses have been described in chapter 2. Table 7 (Columns 1 and 2) lists the averages of 17 published major element analyses of pelites and 10 psammo-pelites from the Cooma Area (JOPLIN 1942, 1943), the Albury-Jingellic Area (JOPLIN, 1947), the Tumbarumba-Wantabadgery Area (VALLANCE, 1953 a) and from north-east Victoria (TATTAM, 1929).

This data has been used in Fig. 14, a triangular diagram of $\text{CaO-Na}_2\text{O-K}_2\text{O}$, which compares sediments well since it dispenses with the need for recalculation on a water-free basis. The calculated average gneiss (Table 6, Column 2) is included for comparison as well as averages of a number of other commonly occurring sediments, all listed in Table 7.

It is evident from Fig. 14 that the Ordovician sediments in the areas considered are exceptionally poor in Ca, but rich in K, when compared with world averages of normal geosynclinal deposits such as shales, greywackes and subgreywackes. This suggests an original sediment poor in limestone and carbonate cement but rich in clay minerals. The chemical composition of the gneiss, with regard to the ratios of the three oxides plotted, is similarly characteristic and close to that of the psammo-pelites which form the dominant sediments in all areas where these gneisses occur (VALLANCE, 1953 c).

The same author, after a comparison of major element composition of the gneisses and the psammo-pelitic Ordovician sediments, showed their composition to be similar for all elements except Na, which seemed to be too low in the sediments. From such a comparison and the abundance of meta-sediment inclusions in the gneiss he concluded "...it seems clear that a good deal of sedimentary material has been added to them even if the granites were not largely derived from the meta-sediments at a lower level".

JOPLIN (1962), discussing the origin of these gneisses, stated ".....at this stage, however, the writer is not prepared to say that the gneissic granites are entirely the products of mobilized sediments in situ, and still believes that some granitic material, possibly sediments differentially melted at a still lower level, have been added to a partially melted and mobilized psammo-pelitic sequence". Dr. Joplin then showed that the major element composition of the gneiss could be derived by mixing these psammo-pelitic sediments with a leucocratic oligoclase-rich granite in proportions of from 2:1 to 1:1 respectively. This would also account for the apparently slightly higher Na concentration observed in the gneisses when compared with the psammo-pelitic parent material.

Trace element considerations presented below make it appear unlikely that any such large-scale addition of leucocratic granite to the sediments played a role in the genesis of the gneiss, and the following considerations may at least partially explain the apparent discrepancy in Na content.

The following major element compositions of the "average igneous rock" (Clarke) and the "average sediment" (Correns) are taken from BARTH (1962, p.375), both here recalculated on a volatile-free basis:

	<u>Av. igneous rock</u>	<u>Av. sediment</u>
SiO ₂	60.1	62.1
Al ₂ O ₃	15.6	16.1
Fe ₂ O ₃	3.1)	7.6
FeO	3.9)	...
MnO	0.12	0.13
MgO	3.6	3.3
CaO	5.2	5.2
Na ₂ O	3.9	1.3
K ₂ O	3.2	3.2
TiO ₂	1.1	0.8
P ₂ O ₅	<u>0.3</u>	<u>0.19</u>
Sum	100.0	99.9

Although such compilations can be criticised in some details, it is clear that the composition of the average sediment, ultimately derived by weathering of igneous rocks, is reasonably similar to the latter, with the marked exception of Na which is seemingly enriched in the average igneous rock by a factor of about 3.

On the basis of this Na missing from the sediments, accumulated presumably in the ocean, both Clarke and Goldschmidt attempted to calculate the total amount of rock weathered during geological time. BARTH (1961, 1962) criticised such calculations because the Na would not stay in the ocean indefinitely but would be

recycled as sediment after what he called its "period of passage", calculated at about 120 m.y. for the Na ion. These newer calculations gave far larger estimates of the total amount of sedimentation, viz. 30 km over the total surface of the globe in 3000 m.y. Using the same concept of recycled Na, LIVINGSTONE (1963) attempted a new estimate of the "Na-age" of the oceans.

The simple calculation presented below represents the Na budget of the crust at the present geological time and is based only on direct estimates. The only underlying assumption made in the argument is that ultimately all sediments are derived by weathering of igneous rocks, and "crust" in this context refers to that (upper) part of the earth's crust, which, at some time during the geological past, has been subjected to cycles of erosion and sedimentation. In general, too, such a restricted concept of "crust" may be more practically useful in geochemical computations than the one used at present, since it, after all, represents the only portion of the crust which has been directly and widely sampled.

Na ₂ O in ocean (LIVINGSTONE, 1963):	19.0 x 10 ¹⁵ tons.
Na ₂ O in all sediments: (POLDERVAART, 1955, based on 1.1%):	18.3 x 10 ¹⁵ tons.
Rock salt deposits (KUENEN, 1941):	<u>0.4 x 10¹⁵ tons.</u>
Total Na ₂ O in sediments and ocean:	37.7 x 10 ¹⁵ tons.

According to POLDERVAART (1955) the total mass of all sediments is 1702 x 10¹⁵ tons, made up as follows: deep oceanic 217;

sub-oceanic 1005; young folded belts 340; and continental shields 140×10^{15} tons. Thus "putting back" all Na from the ocean and rock salt deposits into the crust's sediments, the total possible percentage of Na_2O in all sediments is :

$$\frac{37.7 \times 10^{15} \times 100}{1721 \times 10^{15}} = 2.2$$

If sediments are all derived by weathering of igneous rocks, comparison of this figure with the 3.9% Na_2O of the average igneous rock shows that, unless the direct estimate of the total amount of sediment is far too high, or Na has been lost to outer space or the lower crust or mantle, all rather improbable, the Na content of sediments sampled has been consistently underestimated.

For instance, GOLDBERG and ARRHENIUS (1958) found Pacific pelagic clay to contain 4% Na, which included some salt in pore solutions, but it seems very likely that some of this Na will be retained even after loss of some of the water during compaction. Especially the fine-grained sediments such as the abundant shales may be expected, in addition, to hold after compaction a considerable amount of Na loosely adsorbed on particle surfaces.

Normal geosynclinal sediments similarly laid down in sea-water are only sampled after uplift and prolonged passage through the zone of ground-water during which much of this loosely held and extremely soluble Na would be leached out and returned to the ocean

by rivers. Thus normal sampling at the earth's surface would seriously underestimate the Na content of very fine-grained sediments such as clay and shale, but probably is more reasonably accurate for most arkoses, greywackes etc.

It is also apprent that sediments metamorphosed and "granitised" at depth have not passed previously through the zone of percolating groundwater and therefore retain sufficient Na to form normal metamorphic and igneous rocks without the otherwise necessary addition of large amounts of "magmatic" Na emanations.

It therefore seems quite possible that the apparent slight Na deficiency of the Ordovician psammo-pelites in the region here considered vis-a-vis the Snowy Mountains gneiss may be due to the underestimation of Na in the original sediments at depth. This serious objection to the proposed origin of the gneiss entirely from these sediments is therefore not necessarily valid.

In considering the origin of the gneiss it would be of great interest to compare its trace element composition with that of the proposed sedimentary source material. Unfortunately no such data is available for these psammo-pelitic sediments, and their rather unusual modal composition precludes the use, by analogy, of any normal sedimentary type averages in the literature.

Such trace element data has, however, been obtained, although not yet published, for apparently rather similar sediments from the Malmesbury Formation, south-western Cape Province, South

Africa (ERLANK, 1965). Table 7, Column 3 lists the average composition of Malmesbury Shales which are found interbedded with argillaceous siltstones (Column 4). The average of these two Malmesbury sedimentary types (Column 5), although containing slightly more Fe, Mg and Na, is rather similar to the major element composition of the psammo-pelites here considered (Column 2). The trace element content of the South African sediments should therefore be also broadly comparable to the psammo-pelites of the Snowy Mountain Area, and hence also similar to the gneisses, if these are derived wholly, or in part, from such material. It may be mentioned also, that the trace element data shown for the South African sediments are of especial value to the present study, since the same analytical methods were used and a number of standards were exchanged as interlaboratory checks.

Such a comparison of the trace elements of the average gneiss with the average of the Malmesbury Sediments in fact shows a remarkable similarity. In the absence, at present, of any such trace element data from the Ordovician psammo-pelitic sediments in the area, it is therefore argued, by analogy, that the gneisses could have formed entirely by transformation of such sediments.

Another argument against the suggested origin of the gneiss by addition of differentiated leucocratic granite to the sediments is demonstrated by Fig. 15, which shows the K-Rb plots of the average gneiss, granodiorite and leucogranite, as well as the sediments listed. (All granite data points are shown in Fig. 13). The

K-Rb relationship is particularly interesting because abundance data for these two elements is good and the K/Rb ratio for most types of geological materials is well established with an average of about 220 (AHRENS, PINSON and KEARNS, 1952; HEIER and ADAMS, 1963). Any strong deviation from this ratio, shown by plots approaching or crossing the limits of normal scatter (dashed lines), has geological significance. Any marked enrichment of Rb relative to K, as shown for instance by the leucogranites (K/Rb about 100), is due to strong magmatic or metamorphic differentiation (for a discussion see, e.g., TAYLOR, 1965).

The normal K/Rb ratio shown by the gneiss (about 205) conversely precludes any such strong differentiation process from its origin since the sediments from which it could have formed would be expected to show similarly normal K/Rb ratios. It is also apparent from Fig. 15 that the gneiss could not have formed by the addition of any significant amount of differentiated leucocratic granite showing such abnormally low K/Rb ratio to any of the sediments considered.

Cs and Tl usually show even more marked enrichment than Rb in a differentiation sequence. For a more detailed discussion of all trace element data, see Part III of this study. Unfortunately the analytical data for these two elements is not as good as for Rb since the concentrations encountered are near spectrographic sensitivity limits. Cs may also show erratic fluctuations in

granites (e.g. BUTLER and THOMPSON, 1963). The conclusions drawn above from the K/Rb ratios are, however, strengthened by the K-Cs and K-Tl ratios of the different granites and sediments. Again the leucogranite is strongly enriched in both Cs and Tl relative to K whereas the gneiss (and granodiorite) shows "normal" K/Cs and K/Tl ratios, similar to those of the sediments.

While this data thus precludes significant addition of strongly differentiated leucogranite material as found elsewhere in the Snowy Mountains Area, it does not, by itself, rule out the possibility that very small amounts of material, formed by partial melting or metamorphic segregation from the pre-existing sediments, were added. Such material, for instance, could account for the small pegmatitic dykes observed. One such dyke, transgressing the orthoclase-cordierite zone at Cooma, was found by PLIDGEON and COMPSTON (1965) to have a Rb-Sr age (402 ± 7 m.y.) and initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio ($.724 \pm .004$) very similar to the gneiss itself.

Such small segregated pegmatitic bodies usually have normal K/Rb ratios (e.g. HEIER and TAYLOR, 1959 a) and addition of such material to the sediments to form the gneiss would therefore not significantly alter an originally normal K/Rb ratio. If the gneiss as a whole was formed by any truly large-scale process of partial melting and differentiation of the psammo-pelitic sediments, it would be expected to show a far lower concentration of Fe, Mg and other ferro-magnesian elements than actually observed. The close chemical similarity of the gneiss and its sedimentary parent material

thus rules out the possibility of any large-scale differential melting of the sediments, or addition of such material.

It may therefore be concluded that the gneiss formed entirely from the psammo-pelitic sediments in the area, without any significant addition of material. Whether granitization took place in situ or whether the transformed mobilized sediments were intruded at a slightly higher level, as suggested by Vallance, cannot be decided from the chemical evidence. However, considering the similarly unusual chemical composition of both the gneiss and its source rock, it seems reasonable to argue that any such source material at a deeper level must have been very similar to the Ordovician psammo-pelitic sediments now found at the surface.

The conclusions reached here on chemical grounds are corroborated by the Sr isotopic data of PIDGEON and COMPSTON (1965). They found an unusually high uniform $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of $.7179 \pm .005$ for the Cooma Gneiss (Rb-Sr age 415 ± 12 m.y.) with a very similar ratio and age for the surrounding high-grade meta-sediments, while the more distant greenschist facies meta-sediments showed a significant greater age of 460 ± 11 m.y. and a lower initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of $.710 \pm .002$. From the data presented the authors inferred that the gneiss could have formed from the local meta-sediments more or less in situ.

4-2. The Granodiorites.

The mode of occurrence and structure of these rocks forming the bulk of the bathyliths in the Snowy Mountain Area have been

described in Chapters 2 and 3. Modal compositions are given in Table 2 and 20 analyses are listed in Table 4.

Although these analyses show some range in composition, the observed variation is continuous and the wide geographical spread of sample locations over different types seem to justify the calculation, for purposes of comparison, of the average granodiorite given in Table 6, Column 1.

In considering the origin of these rocks a number of possibilities must be considered in the light of both major and trace element data. Such possibilities include:

1. Differentiation from a basic magma.
2. Mixture of basic magma with some sedimentary material (DEN TEX, 1956, a,b).
3. Mixture of basic magma with a primary differentiated granitic magma.
4. Mixture of a differentiated granite magma with sedimentary material.
5. Melting of sedimentary material.

Purely from volume considerations it seems very unlikely that granodiorite bodies of batholithic dimensions could form directly by differentiation of a basic parent magma. Furthermore, the granodiorites have quite normal K/Rb, K/Cs and K/Tl ratios, which rule out any envisaged large-scale differentiation process. In fact, the overall major and trace element pattern of these granodiorites, when compared with typical high-level granites such as the South African Cape Granites described in Part III, shows clearly that no strong

fractionation process was involved in their formation. This consideration therefore also precludes the addition to any material of differentiated granite magma in any significant amount. On the other hand, the direct admixture of basic magma in amounts necessary to yield the required proportions of major elements is equally untenable. Table 6, Columns 9 and 10, lists the composition of the average basalt and ultrabasic rock taken from TUREKIAN and WEDEPOHL (1961). The concentration of some ferro-magnesian elements, for instance, in basaltic (gabbroic) magma e.g. Cr (170 p.p.m.), Ni (130 p.p.m.), Co (48 p.p.m.) and Ti (1.38%) is clearly far too high in comparison with the average granodiorite with Cr (34 p.p.m.), Ni (15 p.p.m.), Co (13 p.p.m.) and Ti (.25%) to explain the granodiorites as products of such a mixing process, involving more than 10-20% basic magma.

Just such a mixing of basic and acid magmas is usually invoked as origin for intermediate rocks if major element oxides produce reasonably straight-line plots on variation diagrams, such as the silica variation diagram. Such plots of Al_2O_3 , FeO (sum Fe) and MgO are shown in Fig. 16. (The Cape Granite data also shown is discussed in Part III). These three oxides in the granodiorites show possible straight-line relations with SiO_2 , but this cannot be claimed for similar plots of CaO, Na_2O and K_2O versus SiO_2 shown in Fig. 17. However, these 2 diagrams should be compared with Figs. 18 and 19, showing the same six major oxide versus silica variation diagrams for the 15 average sedimentary types of world-wide occurrence listed in Table 7. These show a greater than four-fold range in SiO_2 compared with the Snowy Mountains Granodiorites.

It is apparent that even over this great range of silica variation these very diverse sediments show an almost straightline relationship for Al_2O_3 , FeO (sum Fe), and MgO , but again a not well developed relationship for CaO , Na_2O and K_2O , when all different types are considered together. Observed straightline plots for any element for the limited SiO_2 range shown by quartz diorites, granodiorites to adamellites can clearly not be used as argument for an origin by admixture of basic and acid magmas, but may simply be due to a variable mixture of two or more dominant sedimentary parents or the progressive dilution of one or more sedimentary types with increasing amounts of silica (quartzite).

In summary, none of the four magmatic processes considered above seems probable and a sedimentary origin must therefore be considered for the granodiorites, as was done for the gneisses in the previous section.

Comparison of the composition of the granodiorites and gneisses shows similar concentrations of SiO_2 , Al_2O_3 and ferromagnesian elements, but higher Na and especially Ca, coupled with lower K content in the granodiorites. This is shown in Fig. 26 which includes plots of the unusually clay-rich Upper Ordovician psammo-pelitic parent material of the gneisses, together with more normal geosynclinal sediments such as average greywacke, subgreywacke and normal shale, all listed with references in Table 7.

If both gneisses and granodiorites, now occurring in the same area, originated from sediments, the difference in their

chemical composition must be sought in different sedimentary source materials. The peculiar clay-rich Upper Ordovician shales that served as parent material for the gneisses are so constant in mineralogy and chemistry that it may be assumed that they covered most of the area at the time. The granodiorites may therefore be expected to be partly composed of such material as well.

Unfortunately no reliable estimates of its thickness exist for the area and it is not certain what sediments underlie them. As outlined in Chapter 2, however, earlier sediments from other parts of the Lachlan Geosyncline seem to contain more normal geosynclinal deposits, viz. greywackes and shales. Thus JOPLIN (1962) assumed that the basement rocks of the geosyncline were of greywacke composition.

Following PETTIJOHN (1957) and KRUMBEIN and SLOSS (1951) normal sediments can be mineralogically described in terms of four dominant end-members: quartz, clay, feldspars and limestone. Figs. 21 and 22 outline such a division showing approximate plots of the average granodiorite and gneiss, based on their chemical composition. On this basis the granodiorite may be presumed to have originated from material containing greater proportions of feldspar and limestone but less clay-minerals. Fig. 23 adapted from PETTIJOHN (1963) illustrates especially well the high Na/K ratio of normal greywackes compared with shales and argillites generally, although the argument was advanced in the previous section that Na is normally somewhat underestimated in the fine-grained sediments.

Summarizing the evidence thus far: the major element composition of the granodiorites, especially their higher Ca and Na but lower K content as compared with the gneisses, can be accounted for by an origin from a variable mixture of the Ordovician clay-rich psammo-pelites in the area, and assumed underlying normal greywackes and shales — on an average all three components in about equal proportions.

The calculated composition of such a sedimentary mixture is given in Table 7, Column 8. Compared with the average granodiorite (Table 6, Column 1) the trace element data also shows reasonable agreement except for apparently anomalously high values of Cr and Ni in the sediment parent material. The following considerations, however, indicate that both elements have probably been overestimated in the sedimentary mixture:

1. The Cr (140 p.p.m.) and Ni (43 p.p.m.) values cited for the greywacke by WEBER and MIDDLETON (1961) are probably far higher than normal because that sediment was derived from a somewhat unusual basic source area. Furthermore their samples were crushed in a steel mortar and contamination by these two elements is likely.
2. FROEHLICH (1960) cites three greywackes with an average Cr content of 35 p.p.m., while his average sandstone contained 58 p.p.m.
3. PETTIJOHN (1963) estimated the average sandstone to contain only 10-20 p.p.m. Cr and only about 2 p.p.m. Ni. Furthermore, much of the Cr in sandstones is probably present as the mineral chromite apart from its presence in the clay components.

Thus, summarizing, the trace element concentrations of the granodiorites and the proposed sedimentary mixture agree reasonably well considering the uncertainties of present trace element data for sediments; and the apparently low Ni and Cr values of the granodiorites in fact show that little, if any, basic rock and certainly no ultrabasics served as their source material. Further treatment of the trace element data of the Snowy Mountains Granites is given in Part III in which the geochemistry of individual elements is discussed as observed for the Australian and South African Granites.

At first sight a more direct approach to the origin of the granodiorites would have been furnished by the analyses of all the sedimentary types actually encountered in the area, as was done for the parent material of the gneiss. Practical considerations, however, would rule out such an attempt. Present exposures of such sediments in the area are restricted and not good, and the sediments thus sampled would in any case not represent the original parent material of the granodiorites which, as the field evidence shows, have obviously been faulted or otherwise moved out of their original position to higher levels.

The proposed origin of the granodiorites from the typical sedimentary mixture considered above would explain a number of other observed chemical features:

1. The considerable but continuous variation among the granodiorites of the area and between granodiorites and gneisses is explained simply by the continuously varying proportions of the three types of

sedimentary source rock. Thus the gneisses are part of the whole process — they represent only one of the components, the Ordovician clay-rich sediments. The inverse relation between Na and K for the different granodiorites and for the gneisses and granodiorites as a group (Fig. 6), as well as the direct relationship between Na and Ca clearly do not point to a process of magmatic differentiation, but can be explained by the sedimentary mixing process. The observed variation of these three major elements also shows that the leucogranites from the area, on the other hand, could have formed by normal magmatic differentiation processes (Chapter 4-3).

2. Considering the whole region the granodiorites show a fairly continuous variation in composition but some of the massive transgressive (post-Silurian) types described in Chapter 3-2 do contain less Fe, Mg and other ferro-magnesian elements while Na is higher and Ca is variable, but remains at relatively high concentrations. Examples of this type are the Khancoban Granite (Sample 29), the Island Bend Granite (31 and 32) and also probably the "uncontaminated" granites of the Murrumbidgee Batholith (e.g. Shannons Flat Granodiorite) which were described by SNELLING (1960) as representing a parental granite magma. Here these massive types are simply regarded as representing the original sedimentary mixture relatively richer in the greywacke component. This would account simultaneously for lower Fe, Mg and other ferro-magnesian elements (less clay), higher Na and high Sr and Ba (more feldspar). By contrast, such lowered ferro-magnesian values coupled with undiminished Ca and high Sr and Ba would be difficult to reconcile with an origin from a normal magmatic sequence.

3. Figs. 11 and 12 presented in the previous chapter show up distinctions in Ca/Sr and Ba/Sr ratios between gneisses and different granodiorites. This may also be explained, at least qualitatively, by their origin from a variable mixture of sediments, which show the following average concentrations of these three elements:

		<u>Clay-rich shale</u>	<u>Shale</u>	<u>Greywacke</u>	<u>Sed. Carbonate</u>
Table 7,	no.	5	6	7	TUREKIAN and WEDEPOHL (1961).
Ca%		.76	2.44	1.95	30.2
Sr p.p.m.		107	300	260	610
Ca/Sr		71	81	75	495
Ba p.p.m.		630	580	380	-
Ba/Sr		5.9	1.9	1.56	-

From this data one would expect fairly constant Ca/Sr ratios for the gneisses (formed mainly from clay-rich shale) and the massive-type granodiorites (formed from a sedimentary mixture enriched in greywacke), their ratios being somewhat lower than for the granodiorites generally (which may in addition to all three sedimentary types include a small proportion of sedimentary limestone). Such a relation is in fact evident from Fig. 11, with gneisses and massive Island Bend Granite (Samples 31 and 32) showing a Ca/Sr ratio of about 55 while the bulk of the granodiorites have a Ca/Sr ratio of about 120.

The Ba/Sr ratio, on the other hand, should decrease in the order: gneiss, granodiorites generally, massive-type granodiorites. From Fig. 12 it can be seen that the Ba/Sr ratio is about 5.2 for the

gneisses, about 3.7 for the average granodiorite but dropping to about 2.5 for some of the more massive-type granodiorites represented by samples 31 and 32.

In the light of the conclusions reached here on the different sedimentary source materials for the Snowy Mountains Gneiss and Granodiorite it may be mentioned that PIDGEON and COMPSTON (1965) reported data on a sample of Shannons Flat Granodiorite. This gave an indicated Rb-Sr age of 417 m.y., thus virtually identical with that of the Cooma Gneiss, but its initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio was found to be some 1.4% lower than that of the gneiss. This was interpreted by the authors as suggesting that the Sr in the two masses had different source material.

4-3. The Leucogranites.

In marked contrast to the gneisses and most granodiorites considered above the leucocratic granites, described in Chapter 3-2, are massive, high-level, crosscutting granites, and therefore apparently the last granites to form in the Snowy Mountains Region. Absolute age determination, however, suggests an age comparable to that of the other granitic rocks in the area. They may therefore be regarded as representing an endstage of the same general period of activity.

Their modal compositions (Tables 2 and 3) show somewhat lower plagioclase and very low ferro-magnesian minerals. This is reflected in their very low content of Ca, Fe, Mg and ferro-magnesian trace elements (Table 4). Their highly differentiated nature, shown also

by high alkali and silica content (SiO_2 averages over 75%), is further demonstrated by abnormally low K/Rb, K/Cs and K/Tl ratios (Table 5). Their strong depletion in Ca, Sr and Ba is shown in Figs. 11 and 12.

As outlined in Chapter 3-2 the leucogranites may be subdivided into three groups showing differing degrees of differentiation. Among the major elements only Fe, Mg and to some extent Ca show this distinction but a number of trace elements considered together are again more useful in this connection. The three groups are:

(1) The Welumba and Pine Mountain Granites (Samples 5 and 7) appear to be the most strongly differentiated. They are distinguished from the other leucogranites by their extremely low content of Fe, Mg, V, Ti, Ca, Sr and Ba, as well as low Zr and La, coupled with high Li, Rb, Cs and Tl.

(2) The Bogong, Scamels and Mt. Mittamatite Granites (Samples 6, 11 and 12), on the other hand, represent the least differentiated granites of the group. They show higher concentrations of the ferromagnesian elements mentioned in (1), higher Ca, Sr and Ba as also the highest Zr and La content among the leucogranites while their trace alkalis are relatively low.

(3) The Eucumbene and Yaouk Leucogranites (Samples 8, 9 and 10) are generally intermediate between (1) and (2).

Considering the limited number of leucogranite samples used the above subdivision cannot be more than a preliminary outline since conceivably local, somewhat untypical phases may have been sampled in

one or two cases. Further more detailed work on the leucogranites may reveal correlations between the degree of fractionation and factors such as: the size of the leucogranite intrusions, differences between their cores and border facies, geographical distribution and association with different granites in the area. From the limited data considered here no such correlations are apparent.

Since the leucogranites must have formed by differentiation at a deeper level, not open to inspection at present, one may speculate on possible parent material. Is it possible, for instance, that they originated from a normal basic magma or even more basic "mantle material" by fractionation before being intruded to their present high crustal level? Such a process was, after all, until recently invoked to explain the origin of granites generally. Moreover, recent isotopic studies involving $\text{Sr}^{87}/\text{Sr}^{86}$ ratios have led to the setting up of petrogenic models seemingly demanding the addition of "mantle strontium" to explain the observed Sr isotope ratios in many granites. The well-known fact that fractionation of a basic magma cannot yield much more granitic material than about 5% of its volume by fractionation makes such an origin for the huge granitic batholiths of the earth's crust very doubtful. But such volume considerations do not apply to some granite bodies of small dimensions and cannot be invoked, for instance, for the leucogranites of the Snowy Mountain Region, since they represent a relatively minor phase (Fig. 2).

Major and trace element data is available from two well-documented examples of such strong differentiation of basic magma producing significant amounts of acid material. Table 6, Column 7 lists the composition of the average acid granophyre of the Skaergaard Intrusion (WAGER and MITCHELL, 1951, Table F). Column 8 similarly shows the average of six granites and granophyres from the Bushveld Igneous Complex (LIEBENBERG, 1960, Table 21). Comparison with the average leucogranite from the Snowy Mountains Region (Column 3) reveals such similarity in SiO_2 , K and other major elements that on such major element data alone plainly no evidence against an origin of the leucogranites from a similar basic magma could be gleaned. This similarity, however, shows that we are dealing with acid rocks that have reached roughly equivalent degrees of fractionation. Therefore conclusions may presumably be drawn from a comparison of some of the trace element data shown by these three granites.

Fig. 24 shows a logarithmic plot of Mg versus Ni. At similar average Mg concentrations of about .12% the average Ni values of Skaergaard and B.I.C. Granites are 8 and 22 p.p.m. respectively; the Snowy Mountains leucogranites, in strong contrast, all showed less than 1 p.p.m. The Mg/Ni ratio therefore increases strongly, from about 100 to over 1200. The high Ni values found in the acid differentiates of the basic magmas are in fact comparable to those obtained in the undifferentiated Snowy Mountains gneisses and granodiorites, which show, however, a 10-fold higher Mg concentration.

Compared to the Snowy leucogranites the acid fractions derived from basic magma are also rich in other ferro-magnesian elements such as Cr, Ti, Co, Cu, V and Mn.

All these elements considered have very high concentrations in the original basic parent magmas and though their acid "offspring" are extremely differentiated with respect to all major elements, their origin is revealed by some of their trace element "birthmarks". On this evidence the Snowy Mountains leucogranites did apparently not originate from a basic magma, but may have originated by a large-scale process of partial melting and differentiation either of pre-existing sediments or of some of the granitic or gneissic rocks deeper in the geosynclinal pile before intrusion into higher levels.

The origin and magmatic history of the leucogranites may also be considered by reference to the system Ab-Or-Q-H₂O studied experimentally by TUTTLE and BOWEN (1958) to 4000 kg/cm² (P_{H₂O}) and extended to 10,000 bars by LUTH, JAHNS and TUTTLE (1964). This "granite system" was used for instance by BROWN (1963) to demonstrate that the Tertiary granitic rocks in Skye and Rhum were derived mainly by partial melting of Lewisian basement gneiss with subsidiary amounts of granitic magma similarly formed from Torridonian arkose.

Table 8 lists the calculated molecular norms (wt %) of the leucogranites, the average granodiorite, average gneiss and also five of the average sediments listed in Table 7. In the absence of separate FeO and Fe₂O₃ analyses for the granites the FeO/Fe₂O₃ ratios

used in the calculations were based on the averages of the previously published analyses of leucogranites, granodiorites and gneisses from the area. The normative Ab-Or-Q ratios are plotted in Fig. 25 taken from TUTTLE and BOWEN (1958, Fig. 38). The quartz-feldspar boundaries at water-vapour pressures of 500, 1000, 2000 and 3000 kg/cm² are also shown projected to the anhydrous base of the tetrahedron. The isobaric temperature minima for these pressures are indicated by crossbars. The crosses indicate the further shift of the isobaric eutectic with increasing P_{H₂O} from 3600 to 10,000 bars (LUTH, JAHNS and TUTTLE, 1964). The enclosed oval represents the region of maximum distribution of all 571 analysed plutonic rocks in Washington's Tables that carry 80% or more normative Ab+Or+Q.

It can be seen that the Snowy Mountains leucogranites plot close to the region of minimum melting temperatures in this system suggesting that they originated by crystallization of the liquid residuum of fractional crystallization. Reference to Table 8 shows that for all leucogranites the sum of normative Ab+Or+Q lies between 90% and 95% of the rock's normative constituents. Therefore recalculation in terms of the coordinates of the Ab-Or-Q ternary diagram involves neglect of only very minor amounts of other constituents. This, however, is clearly not the case for the average granodiorite, gneiss and sediments which all have less than 80% Ab+Or+Q. Their plots can therefore only serve as rough comparison since the addition especially of An produces a marked change in the position of the

critical silica-alkali feldspar boundary. The leucogranites plot close to the 1000 kg/cm^2 isobaric section and Fig. 26 therefore shows all specimens from the previous diagram plotted in relation to the isobaric section for $1000 \text{ kg/cm}^2 P_{\text{H}_2\text{O}}$ projected onto the anhydrous base of the tetrahedron. (TUTTLE and BOWEN, 1958, FIG. 30). The important isobaric fractionation curves are reproduced together with the quartz-feldspar boundary (E-E') and the so-called feldspar "thermal valley" (Pm) which separates the Ab and Or fields.

Reference to these two diagrams shows that, although the leucogranite plots lie close to each other clustering about the ternary minimum, their subdivision outlined previously mainly on the basis of trace element data is reflected here as well to some extent. Thus samples 5 and 7 representing the Welumba and Pine Mountain Granites respectively virtually coincide with the ternary temperature minimum for the 1000 kg/cm^2 isobar shown. These two granites were shown above to be the most highly differentiated members of the leucogranites. The Eucumbene and Yaouk Leucogranites (Samples 8, 9 and 10) were previously called group (3) showing intermediate degrees of fractionation. These three samples seem to form a cluster slightly apart from the rest, but the remaining leucogranite samples 6, 11 and 12 seem to show some spread.

The small but perhaps real scatter of plots observed for the leucogranites could possibly be ascribed to the changing positions of the ternary minimum at different water-vapour pressures — i.e.

related to varying depths of formation and water contents of the granite magmas. Thus, for instance, samples 8, 9 and 10 could be considered as clustering rather around the ternary temperature minimum for the 500 kg/cm^2 isobar. The similar crustal level to which the leucogranite masses were intruded and their similar structure and mineralogy, however, seem to indicate that the physical conditions prevailing during their formation were also at least broadly similar. But small differences in the original source material, water content and depth may explain the observed varying degrees of fractionation of the different leucogranite magmas.

A few additional comments can be made on the origin of the leucogranites:

1. Whatever isobaric section is selected, the leucogranites do plot on the Or side of the feldspar "thermal valley" or on the SiO_2 side of the quartz-feldspar boundary. Therefore they cannot have formed by fractional crystallization of a basic magma since such a process would produce liquids either in the Ab-Q region of the low temperature trough E'P or on the Ab side of the feldspar "thermal valley" mP (cf. WYLLIE and TUTTLE, 1961, Fig. 3B). This conclusion also is in accord with the trace element evidence considered earlier.
2. The leucogranites do not fall on a single isobaric fractionation curve and therefore did not form by differentiation of one single type of homogenous magma.
3. Experimental melting studies (e.g. WINKLER and VON PLATEN, 1961) have shown that various sedimentary rocks such as shales and greywackes

can, by a process of partial melting, produce granitic melts close in composition to the ternary minimum. The various sediments plotted in Fig. 25, as well as the average gneiss and granodiorite, all fall well into the quartz field showing considerable scatter, and it may be quite reasonably assumed that the leucogranites formed by partial melting and fractional differentiation of a mixture of such typical sediments. Such an origin would also explain their oversaturation with respect to alumina shown by the presence of normative corundum (Table 8).

Considering all the granitic rocks of the geosyncline the leucogranites thus are the only differentiated granites, form only a minor phase estimated at roughly 5% and are in all cases the youngest granites crosscutting all other types. The connecting link between these facts might be sought in the geometry of the partially stabilized geosynclinal block. The earlier formed gneisses and enormous granodiorite batholiths may impede the upward advance of any subsequently heated and mobilized sediments which would normally have risen as granodiorite without significant differentiation. This material would now, however, be only able to advance upwards after strong differentiation has produced the necessary build-up of volatile pressure to force a way through the gneissic and granodioritic cover.

4-4. Porphyry dykes and basic rocks.

Table 4 lists the analyses of three samples of feldspar and quartz-feldspar porphyry dykes intrusive into the granitic rocks. Their compositions and calculated element ratios (Table 5) are very

variable and no firm conclusions can therefore be based on such few samples. Their K/Rb ratios, however, plotted in Fig. 13 are normal as are their levels of Tl and Cs. These dykes therefore do not appear to represent material that has undergone strong differentiation.

Sample 35, a small dyke in the Boomerang Creek Granitic Gneiss, was found to be somewhat altered and threaded by a few thin later calcite veins. This would partially account for the low sum (94.3%) of major element oxides since H_2O and CO_2 were not determined. Except for slightly higher Ca, also explained by the calcite, this dyke is otherwise close enough in composition to the gneisses, so that it may be regarded as having formed from remobilized gneissic material or from its original mica-rich meta-sediment. It has somewhat lower SiO_2 and Al_2O_3 concentrations but the combination of very high ferro-magnesian content, appropriately high K, Rb and Ba together with very low Na and Sr concentrations is characteristic of the gneiss.

The quartz-feldspar porphyry dyke, Sample 33, on the other hand, shows much higher concentrations of Na, Ca and Sr but less K (and Rb). Its composition is therefore rather more similar to the granodiorites, particularly the more massive types; and may represent such material remobilized and intruded at a later stage.

By contrast, feldspar porphyry dyke, Sample 34, approaches the composition of the Snowy Mountains leucogranites in its high levels of SiO_2 (73%), Na and K and relatively low concentrations of Sr and ferro-magnesian elements. However, a normal K/Rb ratio (249),

low Cs and Tl and very high Ba (920 p.p.m.) and Ni (18 p.p.m.) among others indicate that this dyke did not form from material similar to the differentiated leucogranites. It is also distinguished by unusually high Zr (380 p.p.m.), Y (63 p.p.m.) and La (62 p.p.m.). This combination of observed element concentrations shows this dyke cutting the Boomerang Creek Granitic Gneiss at the Tumut-2 power station to be quite distinct from any of the granitic rocks examined. Conceivably it may thus be related to the Lower Devonian rhyolite lavas and tuffs found in abundance only little further north (Fig. 2). But this must remain a speculation until something is known about the chemistry and origin of these lavas, which may be quite unrelated to the granites in the area.

Table 4, no. 36 represents a sample from the belt of intermediate to basic rocks stretching northwards from Batlow, described in Chapter 2-2. The rock has been strongly metamorphosed and must now be described as a foliated amphibolite. SNELLING (1958) suggested a possible sedimentary origin from an impure calcareous sediment for a small amphibolite specimen found as inclusion in the granodiorite of the southern extremity of the Murrumbidgee Batholith since it combined low concentrations of Ni, Co and Cr with low Na. But the amphibolite analysed here although also showing relatively low Ni (17.5 p.p.m.), Ti (0.36%), Cu (22 p.p.m.) and also lower Sr (162 p.p.m.) and Ba (145 p.p.m.) when compared for instance with TUREKIAN and WEDEPOHL's (1961) average basalt (given here in Table 6, Column 9) does show an

overall pattern of major and trace elements that suggests an originally basic parent.

4-5. Conclusions.

Although further reference to the Snowy Mountains granites is made in Part III the principal conclusions on the origin of these granitic rocks may be conveniently summarized here as follows:

- (1) On both major and trace element data the gneisses (gneissic granites, Ordovician type) could have formed entirely from the Upper Ordovician psammo-pelitic, clay-rich sediments with which they are associated, without differentiation or addition of any significant amount of magmatic material.
- (2) The granodiorites forming the bulk of the bathyliths in the area show a limited but continuous variation in both major and trace elements. This is attributed to their origin by mobilization and melting at depth, without significant magmatic differentiation, of varying proportions of geosynclinal sediments that can be represented on an average by equal parts of normal shale, greywacke and Upper Ordovician clay-rich psammo-pelite.
- (3) Some massive (post-Silurian types) granodiorites exemplified for instance by the cross-cutting Island Bend Granite may have originated from a similar sedimentary mixture containing, however, a greater proportion of greywacke and less clay-rich shale.
- (4) The leucogranites are strongly differentiated granites and may be subdivided into three groups showing varying degrees of magmatic

fractionation. They did not originate by fractionation of basic magma but probably formed by partial melting and magmatic differentiation from pre-existing geosynclinal sediments.

(5) Samples of three quartz-feldspar porphyry dykes examined indicate that they are chemically very dissimilar to one another but do not represent strongly differentiated material. One is chemically similar to the gneisses, another resembles the massive type granodiorites, while the third may possibly be related to Lower Devonian rhyolite lavas in the area.

II. CAPE GRANITE, SOUTH-WESTERN CAPE PROVINCE, SOUTH AFRICACHAPTER 5. INTRODUCTION.5-1. General description.

Physiographically the Cape Area at the southern tip of the African continent (Fig. 27) forms a strongly varied region. Its topography is almost entirely dependent on the geological structure, dominated by the sediments of the Cape System, which form the Cape Folded Ranges. These represent a formidable barrier between the Coastal Forelands and the arid interior regions of the Little and Great Karroo, the latter extending northwards to the Great Escarpment, which generally forms the watershed of coastward drainage and interior river systems in the subcontinent.

The almost unbroken line of high ground formed by the Cape System Sediments, especially the dominant Table Mountain Series (TMS), exhibits two main structural lines. The Cedarberg Foldings extend from near Van Rhynsdorp south-south-eastwards roughly parallel to the Atlantic coastline terminating finally at Cape Hangklip. At right angles to this belt the east-west zone of the Cape Foldings stretches in a gently curved belt, at least 100 miles wide, from the region of syntaxis of these two axes in the Worcester-Ceres Area to beyond Port Elizabeth in the east, where it is terminated by the Indian Ocean. The average height above sea level of these N-S and E-W ranges in the

south-western Cape is between 4000-5000 feet with individual peaks exceeding 7000 feet.

Especially in the extreme western portion of the Western Province, however, the protective covering of the TMS has been almost entirely removed by erosion leaving only such conspicuous outliers as the mountains of the Cape Peninsula and Riebeeck Kasteel, thus exposing the underlying older Malmesbury Beds and the granite bodies intruded into the latter. The Malmesbury Sediments seldom give rise to any pronounced relief but characteristically form flat undulating country unless either somewhat metamorphosed by the granite or protected by a covering of more resistant TMS.

Thus the present configuration of the West Coast is largely determined by the general NW-SE trend of the granite plutons which follow the foldings of the Malmesbury Series (Fig. 27). Many of the coarse porphyritic granites occur in large naked dome-shaped outcrops but areas in which the finer even-grained variety of granite predominates are usually rocky, rugged and more densely vegetated.

The Saldanha and Darling granite plutons, their bases hidden by sand, rise above the Mio-Pliocene surface as a chain of separate hills about 70 miles long from St. Helena Bay to Katzenberg with peaks rising to over 1800 feet. The separate Malmesbury Granite striking in a similar NW-SE direction reaches a height of nearly 2500 feet in the rugged Paardeberg. The Paarl Boss to the south-east rises into dramatic bare domes with a maximum height of 2392 feet. Another

elongated mass of granite near Wellington, however, passes beneath the younger TMS and other granite bodies further south similarly do not form conspicuous topographic features, but generally occur as dissected slopes skirting the Cape Mountains. The Stellenbosch-Kuils River Pluton includes the granite of Somerset West, Schaapenberg, Kuils River, Banhoek and French Hoek although some outcrops are separated from each other by strips of Malmesbury Sediments. The Cape Pluton due west extends the full length of the Cape Peninsula but is largely concealed by a thick cover of TMS.

Of the relatively minor plutons further east, including granite outcrops at Robertson, Swellendam, Greyton and near Hermanus, only the Robertson Pluton has been sampled. It forms the fairly prominent Tierberg (3112 feet) intruding low-lying Malmesbury but is partially concealed by the younger TMS of the Langeberg Range to the north and has been exposed indirectly through the action of the Great Worcester Fault.

In contrast to the majority of the "south-western" granite plutons described above the "eastern" plutons represented by the gneissic granite of George and Woodville do not produce any prominent topographic features but have been levelled to the 700-800 feet Mio-Pliocene marine erosion surface probably due to their highly crushed and sheared condition and the subtropical climate of the Eastern Coast. Both plutons, also intrusive into Malmesbury Sediments, are greatly elongated in a WSW-ENE direction.

5-2. Previous work.

The granites of the Cape of Good Hope have left a mark on the development of classical geology and publications date back to the first decade of last century. In 1813 Captain Basil Hall discovered the granite-hornstone contact in the Platteklip Gorge near Cape Town. PLAYFAIR and HALL (1915) used this evidence in support of Hutton's pioneering theory on the igneous origin of granite. In his classic major work PLAYFAIR (1802, 398-400 and 410-411) also referred to the granite at Paarl. Now protected by the Historical Monuments Commission the even more famous contact with its spectacular migmatite zone (Fig. 28) along the foreshore at Sea Point, Cape Town, was first described by C. ABEL (1818) and seems to have been examined subsequently by every geologist stepping ashore at Table Bay. DARWIN (1844) visited the locality briefly in 1836 on the return voyage of HMS "Beagle" and drew attention to and explained the structural continuity of the granite xenoliths and the metamorphosed wall rocks.

The systematic geological survey of the Western Province by the then Geological Commission of the Cape of Good Hope commenced in 1897 and much basic geological data on the region was published by this organization and subsequently by the Geological Survey.

Independent workers generally have dealt with more specific problems.

MATHIAS (1940), on the basis of mineralogical and some chemical data, suggested a correlation of the Cape Granite, as exemplified by the Paarl and Cape Peninsula Granites, with the

granite-gneiss which forms the major portion of southern Namaqualand; but this conclusion was criticised by GEEVERS (1940), JOUBERT (1941) and BRINK (1945) and is also unlikely on the basis of recent work including isotopic age studies which are discussed in Chapters 6 and 7.

Most other important earlier papers dealing with the Cape Granite were referred to by SCHOLTZ (1946) in the first comprehensive study of these post-Malmesbury granites, including generalized out-crop and structural maps and a compiled list of 43 major element chemical analyses covering various granite types, xenoliths and some Malmesbury Sediments. For descriptive purposes Scholtz subdivided the granites geographically into: the Northern Plutons lying east of the Orange River Mouth in Northern Namaqualand, the South-Western Plutons situated to the south-west of an arbitrary line joining St. Helena and St. Sebastian Bay and the Eastern Plutons near George and further east (Fig. 27). Scholtz concluded that the south-western plutons are very similar petrologically and related genetically to the granites of the northern and eastern areas and were emplaced both by forceful injection and passive replacement of the Malmesbury Sediments in the late Precambrian at the close of the Malmesbury Orogeny.

The work of Scholtz has subsequently been extended by other workers, also from the University of Stellenbosch, who have generally dealt in greater detail with more local aspects of the granites. Thus POTGIETER (1950) made a structural, petrological and chemical study of the eastern, George Granite and country rocks, and also

concluded that the granite was probably related to the south-western plutons, which it resembles chemically. OTTO (1956) described the geology and petrology of a small subparallel swarm of acid dykes traversing the marginal facies of the Saldanha Pluton at Cape St. Martin. McIVER (1957) investigated the contact between the Saldanha Granite and Malmesbury Sediments exposed on the coast at Slippers Bay and concluded that the contact was intrusive. More recently SCHOCH (1962) described the deformation phenomena of the Saldanha Granites at Northwest Bay.

Other more recent papers include a detailed study by WALKER and MATHIAS (1946) on the granite-slate contacts at Sea Point and Kloof Quarry, Cape Town. They concluded that alkaline emanations from a contaminated and differentiated biotite-granite magma softened the Malmesbury Sediments at the contact and then formed the migmatite zone by addition of granitic material, while late potash-rich solutions were responsible for the growth of the large microcline porphyroblasts and phenocrysts, not only in the meta-sediments of the migmatite zone (Fig. 28), xenoliths in the granite and some pegmatites, but also in the Cape Peninsula Granite itself. This proposed late origin of the microcline phenocrysts especially in the granites was criticised by MENNEL and SPENCER (1947), SHAND (1949) and BOOCCOCK (1950). After a visit to the Cape READ (1951) agreed that the Sea Point contact was "magmatic" and described the Cape Granite as a "pluton" in terms of his Granite Series.

In a short note McLACHLAN (1950) described two varieties of Cape Granite on Dassen Island lying off the south-west Cape. Finally, a concise account of the Cape Granite appeared in A.L. DU TOIT's "Geology of South Africa" (1954, 171-175).

Published trace element data on Cape Granite include some radium determinations by IMMELMAN (1934), spectrographic boron determinations by WASSERSTEIN (1951), and a few determinations by a combined spectrochemical-anion exchange technique of a number of rare elements by L.H. Ahrens and coworkers at the University of Cape Town. These results, with references, are listed in Table 9.

5-3. Aims of present investigation.

- (1) Establishment of a comprehensive pattern of minor and trace elements for the granites, to be used in conjunction with the major element data obtained for the same samples.
- (2) Determination of the trace element concentrations of some of the coexisting minerals of the granites to illustrate the distribution of trace elements between them.
- (3) Study of the variation in composition of the granites at some contacts with the intruded Malmesbury Sediments and analyses of inclusions in the granite.
- (4) Establishment of possible differences in major and trace element composition between different granite plutons and between those in the south-western and eastern areas.

- (5) Establishment of the differences in composition between the coarse porphyritic granite of the plutons and their finer-grained facies, using such a comparison to throw light on their genetic relationship.
- (6) Use of the data to test possible modes of origin of the granite plutons as a whole.
- (7) Comparison of the established Cape Granite composition with that of the Snowy Mountains Granites and other reported granite data.
- (8) Radioactive age and isotope study on the Cape Peninsula Granite and invaded Malmesbury Sediments.

CHAPTER 6. GEOLOGICAL OUTLINE.

The basic geological structure of the southern and south-western Cape is rather simple: the oldest sediments in the area, represented mainly by the Malmesbury Formation, were invaded during the Middle Cambrian by the stocks and plutons of the Cape Granite. After prolonged erosion had produced a well peneplaned surface of these rocks, deposition of thick sediments of the Cape System on this platform commenced towards the close of the Silurian or earliest Devonian, followed without break by the further deposition of the conformably overlying rocks of the Karroo System. Due to later erosion of much of this sedimentary cover, especially in the present coastal areas, parts of the old Malmesbury-Cape Granite surface have again become exposed.

6-1. Pre-Cape System Sediments.

The greatest development of the Malmesbury Sediments occurs south of Piketberg mainly in the coastal districts of Malmesbury and Stellenbosch including outcrops on the Atlantic coast from Table Bay to St. Helena Bay, some 80 miles to the north. Other smaller outcrops in the south-western Cape occur as inliers brought up from below the Cape System, as for example, the long narrow strip between Tulbagh and Swellendam bounded on the south by the Great Worcester Fault, and patches in the Caledon and Bredasdorp Areas. In none of these occurrences can the base of this succession be seen and all normal contacts with the various granite bodies are intrusive.

The strata are dominantly blue arenaceous clay-slates or fine-grained argillaceous quartzites that alternate with groups of phyllite, quartzite, ferruginous quartzite, dark feldspathic grit and occasionally conglomerate, limestone, dolomite and chert. Veins of white quartz are frequent. Basic lavas and tuffs are reported from the Berg Valley near Honigberg and HAUGHTON (1933) described highly altered and sheared originally probably trachytic lavas at Blaauwberg Strand opposite Cape Town and a hornblende-lamprophyre sheet-like intrusion at Bellville. Dolerite dykes, apparently of various ages, are also known to occur. Thick accumulations of fresh but highly sheared arkoses, difficult to distinguish from sheared acid igneous rocks, are found near Robertson. Coarse conglomerates occur at Honigberg on the Berg River and in the Robertson Area. Although calcareous rocks are comparatively rare in the Malmesbury of the south-western Cape some interbedded bands of crystalline limestone occur in the northerly parts of this area, e.g. at Piketberg and Moorreesburg, and towards the east near Robertson and Swellendam. The limestones are generally low in Mg although some dolomitic ones occur.

Detailed work on the Malmesbury Sediments has been hampered considerably by the weathered condition of the rocks, the paucity of outcrops and the difficulty of distinguishing between pre- and post-Cape deformation. L.P. Rabie's work (SCHOLTZ, 1946) on the sediments in the Malmesbury District, however, has shown the Malmesbury Series

to be probably more than 20,000 feet thick. The sedimentary strata have been subjected to extensive deformation and always appear strongly folded, usually dipping at high angles with a fairly regular strike between NW and NNW. According to L.P. Rabie strike faulting has interfered with the full sedimentary succession of the Malmesbury south of Piketberg but the strata are apparently arranged in two anticlinoria, one coinciding with the upper part of the Berg Valley, the other, in which the lowest horizons are seemingly represented, passing through Moorreesburg.

The possible northward extension of the folded Malmesbury Sediments is hidden by overlying T.M.S. but the folded pre-Cape and pre-Nama rocks in the Van Rhynsdorp-Bitterfontein Area have been correlated with the Malmesbury on lithological and structural grounds. Thus JANSEN (1960) subdivided the "Malmesbury Formation" in the Bitterfontein Area into calcareous, phyllite and quartzite suites and considered the pink (Namaqualand) paragneiss in the area to have formed by large-scale granitization of these "Malmesbury Sediments". However, if this field interpretation is accepted, the Rb-Sr age of the Malmesbury in the Cape Area obtained here and discussed in Chapter 7 indicates that these pre-Nama sediments in the Bitterfontein Area are not of Malmesbury age but represent an older formation, possibly Kheis System.

Further north still, in the vicinity of the Orange River Mouth, the sediments intruded by the northern granite plutons, the

largest of which is the Kuboos Mass, were regarded by SCHOLTZ (1946) as possible local equivalents of the Malmesbury System.

Regarded as the eastward extension of the Malmesbury Series of the Worcester-Swellendam Belt, the Cango Beds occupy a lenticular area in the Oudtshoorn District some 75 miles long. The beds are highly folded and sheared and generally inclined southwards at high angles with the T.M.S. of the Swartberg Range apparently dipping in below them from the north due to inversion. On the south the belt is bounded by a thin strip of sandstone or else by downfaulted and crushed Cretaceous Beds. Detailed work by McINTYRE (1933) showed the presence in the south of a basement of gneiss, granite and schists overlain unconformably by the base of the series of grits, arkoses with very fresh feldspars, and conglomerates followed by slates and phyllites with bands of grey or black limestone low in Mg. In the thickest of these limestones are situated the famous stalactitic Cango Caves discovered in 1780. Occasionally obolitic types are seen, but no determinable shells have been found in the limestones and the Cango Beds are tentatively correlated with the northern facies of the Malmesbury Formation.

A strip of similar strata in an inverted position beneath the T.M.S. reappears further east in the Gamtoos River Area, west of Port Elizabeth (HAUGHTON and VISSER, 1937). Again the lower beds consist of phyllites with two thick horizons of limestone, followed by quartzites, feldspathic grits and small pebble conglomerates.

Pre-Cape sediments in the George Area (VISSER, FROMMURZE and HAUGHTON, 1937), correlated with the Malmesbury in the south-west Cape, were investigated in more detail by POTGIETER (1950). These sediments, intruded by the eastern plutons of George and Woodville, form an anticline overfolded towards the north and are comprised of seven different horizons with a total thickness of at least 13,500 feet, with no lower contact encountered. The sediments mapped are comprised mainly of shales, slaty shales, phyllites, quartz schists and feldspathic quartzites.

Considering the origin of the Malmesbury System as a whole, SCHOLTZ (1946) proposed the existence of a late Precambrian Malmesbury Geosyncline (Fig. 27) paralleling portions of the present southern and south-western coast of the Cape Province and extending north-west at least as far as the Richtersveld. He considered that the elongated Cape Granite Plutons played an integral role in this geosyncline and were emplaced concordantly along the cores of unsymmetrical anticlines under waning stress during the close of the Malmesbury Orogeny. The Cape Granites were thus placed into the late Precambrian, since an extensive period would be required for peneplanation of the pre-Cape platform and deposition of post-Malmesbury and pre-Cape successions (including perhaps the Nama) until the beginning of the Cape System sedimentation towards the close of the Silurian. (Although the Cape Granite now appears to be rather of Middle Cambrian age, Scholtz's concept is basically

corroborated by the Rb-Sr ages obtained here, which indicate an age of 595 ± 46 m.y. for the Malmesbury and 553 ± 8 m.y. for the Cape Granite in the Cape Peninsula Area). The fresh angular alkali feldspars and acid plagioclase found as relatively prominent constituents in many of the especially upper Malmesbury horizons and the occurrence of conglomerates in the Robertson and Cango Areas suggest limited transport and rapid deposition from a relatively nearby area, in which rocks of granitic composition were prominent. Furthermore, since the great thicknesses of relatively fine-grained sediments begin to appear towards the south and south-west the pre-Malmesbury distributive province probably was an elevated Precambrian continental area lying adjacent to the northern flank of the Malmesbury Geosyncline. The invading granite plutons also attain their largest dimensions and are more numerous in this region of apparently greatest accumulation of sediments. Lastly, considering the dominant regional strike of the sediments, their overfolding to the north-east, the sympathetic internal structure of the granite plutons and their apparent asymmetrical areal distribution relative to that of the invaded sediments, Scholtz suggested that the regional stress of the Malmesbury Orogenetic Cycle operated from the S.W. or W.S.W.

Thus prior to the intrusion of the granite, the Malmesbury Sediments seem to have been subjected to low-grade dynamic regional metamorphism up to, but not exceeding, the biotite stage. In the

more feldspathic and arenaceous upper horizons the granular minerals are often sheared and recrystallized and the principal foliated minerals are sericite and chlorite. Some thin sandstone horizons have been disrupted, contorted and partially recrystallized, while limestones yielded by flowage and recrystallization. In arkoses some clinozoisite and epidote formed from plagioclase grains. Argillaceous rocks were locally transformed into quartz-chlorite-sericite phyllites or, where less deformed, flakes of biotite developed in flow-cleavage planes.

After this regional metamorphism the Malmesbury Sediments were contact metamorphosed to varying extent by the intrusive granite plutons. The width of the resulting contact aureole depends on factors such as the composition of the wall rock, inclination of the contact and its depth relative to the roof of the original pluton. Thus highly susceptible argillaceous rocks may show "spotting" at distances of more than a mile from the contact. But generally, as for the clay-slates around the Paarl, Stellenbosch and Somerset West Granites, the contact aureole does not exceed about 300 yards. In some instances, especially in highly quartzitic beds, the effects are barely visible to the naked eye. These "spotted" contact rocks, typical of the south-western area, are due to the presence of oval patches of poikiloblastic cordierite, often partly replaced by sericite or chlorite. In the George Area andalusite is a common contact metamorphic mineral, and in places slates become highly micaceous near the contact and pass into typical quartz-mica schists.

Although they are generally rare in the Malmesbury Sediments, calcareous rocks in contact with the Robertson and George Granites have produced minerals such as diopside, grossularite, wollastonite, clinozoisite, epidote, vesuvianite and occasionally sphene. In the Darling and Robertson Areas garnet and acicular sillimanite have also been observed, but quite generally a medium grade of metamorphism is rarely attained, and the normal products are biotite-plagioclase and cordierite-biotite-quartz hornfels. Extensively eroded plutons may also exhibit comparatively broad belts of migmatite at the contacts. This is shown especially well at Sea Point (Fig. 28).

Superimposed on the early regional metamorphism and subsequent, far more local contact metamorphism associated with the granites, are further low grade regional metamorphic effects associated with the later Cape Orogeny. This is observed as contortion and shearing of the Malmesbury Beds near the unconformable contact with overlying T.M.S.; it occurs mainly in areas of strong folding or overfolding of the Cape System Beds.

Apart from the Malmesbury Formation two other, apparently different successions of pre-Cape Sediments have been mapped in the Western Province:

The French Hoek Beds, outcropping mainly in the French Hoek-Stellenbosch Area, are comprised of highly sheared slates, arkoses, grits and conglomerates, in places associated with presumed contemporaneous cherty felsites and felsitic tuffs (HAUGHTON, 1933). The French Hoek Beds are regarded as younger than the Cape Granites

and associated quartz porphyries in DU TOIT (1954) although HAUGHTON (1932) cast doubt on their post-granite age.

In the area around Wellington a number of elongate strips of arenaceous rocks are exposed. In places they rest unconformably on Malmesbury Slates and Cape Granites and are themselves overlain unconformably by the Cape System. These Klipheuvel Beds consist of probably more than 5000 feet of red, brown and purple sandstones, grits, quartzites and conglomerates with interbedded coloured shales. They have been tentatively correlated with the Nama rocks north of Van Rhynsdorp.

6-2. The granites.

The areal distribution of the Cape Granite Plutons has been described in Chapter 5-1 and is illustrated in Fig. 27. The following general description of the rocks is based mainly on the comprehensive geological study by SCHOLTZ (1946).

(a) Textural types: Table 10 lists the approximate dimensions, outcrop areas and estimated proportions of different textural types of the plutons. The textural classification used here is outlined in Table 11, based on Scholtz.

Although a considerable variation in texture is encountered, coarsely porphyritic biotite granites (C-2) predominate, especially in the more deeply eroded plutons. Thus phenocrysts may almost constitute the bulk of the rock, as for example, in parts of the Cape Peninsula Granite. In other regions the C-2 type may grade

locally into the M-2 variety, as in the Paternoster and Somerset West Areas. The C-2 variety has also been observed to pass into C-3 and C-4 types in the Stellenbosch and Wellington Areas. Such reduction in the matrix grain-size suggests possible marginal chilling. The G-2 variety granite also is common and limited to the more central and deeper portions of the plutons. It similarly shows gradations into M-2, G-3, and G-4 types. Both C-2 and G-2 types may develop secondary gneissic texture, as in the Saldanha Area, but rarely to the extent as in the case of the eastern George Pluton.

On a general broad two-fold field grouping one can distinguish a coarse-grained C-1, C-2, G-2, M-1 suite and a finer-grained M-2, M-3, G-3, G-4 suite, with an approximate areal distribution ratio of 71:29 for the south-western plutons. The finer-grained suite is generally confined to the crests and somewhat thinner margins of the plutons. Where younger intrusive phases of granite occur, as at Saldanha and Onrus, they also belong to the finer-grained suite. The vast majority of younger quartz-porphyry dykes are of the G-4 type. Minor transgressive type M-4 dykes are comparatively rare, although found, for instance, on the northern side of the Hoedjies Bay Peninsula, Saldanha, where the younger quartz porphyry has intruded "normal" C-2 granite.

In summary, the fine-grained suite may either constitute the probably almost contemporaneous hood facies of a pluton, or may represent slightly younger, usually marginal or dyke-like intrusions.

(b) Structure: The outstanding structural characteristic of the

south-western granite bodies is their elongation parallel to the dominant NW-SE regional tectonic axes of the intruded Malmesbury Formation. Therefore most visible contacts are broadly concordant and only discordant in minor detail. Although generally neither foliation nor lineation are well developed in the south-western plutons, a similar dominant NW-SE direction is apparent. The majority of xenoliths are also elongated in this direction.

Fairly extensive cataclastic deformation of the granites in some areas is shown by the presence of crush breccia and mylonite. Scholtz considers this deformation not to have been restricted to a definite epoch, but to have occurred from time to time. The most prominent directions of shear strike in a general NW-SE and a NE-SW direction. The latter is considered younger, since it offsets effects of the former. Thus the older coarsely porphyritic granites as well as the invaded Malmesbury Sediments were sheared in the NW-SE direction prior to the intrusion of the younger granites. Mineralization also took place in this direction. But most aplites, quartz veins, and acid dykes in the northern Saldanha Area, as well as swarms of pre-Cape dolerites, e.g. in the Somerset West Region, mainly follow the NE-SW direction.

The George Pluton to the east (POTGIETER, 1950), which also mainly consists of coarsely porphyritic biotite granite, is also elongated (parallel to W.S.W.) and generally concordant with the invaded sediments. But in contrast to the generally massive granites

in the south-western area, where deformation has produced gneissic types only locally, the George Granite is highly gneissose with well developed lineation and foliation. Biotite flakes are usually orientated parallel to the foliation planes and show definite elongation in the direction of the lineation. SCHOLTZ (1946) suggested that the deformation was associated with the most intense phase of the Cape Orogenetic Cycle during the Permo-Triassic. Such deformation, affecting the overlying Cape Strata as well, would be more marked in the eastern area, where the more predominant highly incompetent Malmesbury Beds and smaller granite bodies formed a less rigid pre-Cape platform. But POTGIETER (1950) concluded that the gneissic texture of the George Granite was mainly primary; the granite magma crystallised under directed pressure from the south-west.

(c) Petrography: The bulk of the granites (C-2 variety) are coarsely porphyritic biotite granites.

The conspicuous euhedral to subhedral phenocrysts of microcline microperthite or microcline perthite reach up to almost 20 cm in length but average 4-5 cm. They are usually simply twinned according to the Carlsbad Law and colourless except for some pink ones in the C-type granites of the northern Saldanha Area and some G-textural varieties. Apart from the sometimes patchy plagioclase (Ab-01) segregations the phenocrysts often enclose numerous small crystals of quartz, biotite and plagioclase, often arranged zonally.

Microcline microperthite also occurs in the matrix of the porphyritic granites and increases in relative abundance in the more equigranular leucocratic types.

Colourless plagioclase ranges from albite to oligoclase. It is usually slightly zoned and often shows somewhat saussuritised cores.

Quartz normally occurs in scattered anhedral crystals, often strained. While normally colourless they are reddish-brown in some of the younger Saldanha Granites.

Pleochroic reddish-brown biotite is by far the commonest ferro-magnesian mineral present. It is usually scattered throughout the matrix, but sometimes aggregated into small clusters or schlieric bands (Fig. 29). The biotite normally constitutes about 10% or more by weight of the porphyritic granites, but less than 5% in the finer-grained more leucocratic varieties (Fig. 40). It is sometimes altered to a green variety or chlorite, and then often accompanied by segregated iron ore.

Small irregular flakes of muscovite are found scattered throughout most granites and may become a more important constituent in some finer-grained leucocratic varieties as at Kloof Quarry, Cape Town (Fig. 30). Probably only part of the muscovite is primary. Some (sericite) seems to be altered from perthite, plagioclase or chloritised biotite, and is sometimes concentrated along joints.

Isolated pleocroic brownish-green hornblende crystals are present in some granites, which then sometimes also show euhedral crystals or irregular grains of sphene.

Another relatively common accessory mineral is tourmaline, usually pale yellow or brown, sometimes associated with a marginal younger blue variety. The tourmaline shows a rather patchy distribution in the granites.

Colourless, often rectangular, crystals of cordierite in various stages of alteration to pinitite are often found, especially nearer sediment contacts and where biotite is particularly abundant. In such granite varieties small grains of pink almandine garnet are sometimes observed, probably also of xenolithic derivation.

Apart from common but small amounts of apatite, zircon, magnetite and pyrite the granites much more rarely show small crystals of topaz, purple fluorite in some finer-grained granites, pleocroic andalusite, zonal allanite and sometimes xenotime (VAN DER LINGEN and WALKER, 1925).

Many granite specimens show some, and occasionally strong, signs of strain. This is revealed by the undulose extinction of quartz grains, some fractured feldspars and contorted biotites.

The important, relatively large mass of Younger Saldanha Granite (Fig. 27) grades from a quartz-feldspar porphyry near its chilled contacts against the older granite to a generally medium-grained granite further away from the contacts. The dark grey-blue

porphyry occasionally contains rounded inclusions of the Older, coarsely porphyritic, Saldanha Granite, as at the Hoedjies Bay Contact, Saldanha (Fig. 31). The porphyry consists of euhedral or rounded, white or pink phenocrysts of microcline perthite and some usually rounded and embayed quartz phenocrysts set in a microcrystalline or cryptocrystalline matrix. The matrix was originally probably glassy and sometimes displays flow structures. Occasionally severe cataclastic deformation is revealed in the Younger Granite by shattered phenocrysts dispersed through the gneissose matrix and biotite occurring in small irregular highly contorted fragments or even pulverised and scattered in sub-parallel streaks in a mylonised groundmass.

(d) Inclusions: Xenoliths of various sedimentary materials in different stages of incorporation and assimilation are widely distributed throughout the plutons. They range in size from microscopic dimensions to some massive blocks of hornfelsed country rock several hundred feet long, found near sedimentary contacts; but dark, rounded or sub-rounded xenoliths, a few inches in diameter, are most common. (Fig. 32).

The xenoliths have a granitoid texture, generally finer in grain size than the host rock. They consist of biotite, some cordierite, feldspar and quartz in various proportions. Sometimes biotite and pinitised cordierite constitute up to 90% in volume, then often associated with a little green spinel, sillimanite or pink almandite. Hornblende-bearing xenoliths are common in the Paarl and Swellendam Granites.

Some occurrences of xenoliths in isolated clusters is suggestive of the local disruption of a larger inclusion. But some, like the remarkable large xenolith at Clifton, Cape Town (Fig. 33), which consists of alternating dark biotite-rich and more leucocratic layers, show strong reaction with the granite, but only slight deformation.

(e) Ore deposits: Small ore deposits in the south-western area, probably genitidally related to the older Cape Granite, are found mainly in a zone of mineralization trending NW (parallel to the prominent older shear zones) from Helderberg probably right up to Yzerfontein on the Atlantic Coast (SCHOLTZ, 1946).

Only small amounts of cassiterite (KRIGE, 1922; RABIE and CONRADIE, 1944) have been mined in the past from lodes, eluvial and alluvial deposits, as at Langverwacht near Kuils River. Even smaller amounts of wolframite have been recovered. Minor concentrations of molybdenite, pyrite, chalcopyrite, arsenopyrite and traces of gold, bismuth and silver have been recorded.

(f) Origin of the granite: According to SCHOLTZ (1946) granites of two distinct but very similar ages were intruded under waning compressive stress at the close of the Malmesbury Orogeny. He regarded the exposed south-western plutons as parts of the very irregular roof of one parent subjacent intrusion.

The finer-grained hood facies of the plutons, enriched in silica, alumina and alkalis, and grading into the main, coarser

granite, represent a chilled and contaminated differentiation product of the parent magma. This magmatic differentiation could be explained by the process of diffusion-convection along a thermal gradient advanced by WAHL (1946).

The main granite of the central and deeper parts of the plutons become more basic in depth, mainly due to gravitational differentiation, modified in part by mechanical incorporation of down-stoped sedimentary material and its partial or complete assimilation. Local variations in the composition of the granites were also regarded as due to varying degrees of contamination of the original granite magma by predominantly argillaceous Malmesbury Sediments, such as shale.

POTGIETER (1950) concluded that the George Granite was chemically similar to the granites in the south-western area, but further differentiated and slightly more acid.

6-3. Dioritic intrusions.

Three relatively small occurrences of basic rocks are known in the south-western Cape Province.

VAN ZIJL (1950) described four small composite dioritic stocks lying on a line striking NNW-SSE on the western side of the Malmesbury Pluton. They are also intrusive into the Malmesbury Greywacke, but are believed to be older than the Cape Granites. Petrologically the rocks vary from normal gabbros to quartz diorites and are considered to have formed from successive intrusions of a

pre-granite basaltic magma which had undergone different degrees of differentiation at depth.

Another gabbroic-dioritic suite occurring at Yzerfontein on the Atlantic Coastline west of the Darling Granite Pluton, was investigated by MASKE (1951). He concluded that a pre-granite basaltic magma, comagmatic with the Malmesbury Basalt, differentiated at depth to form a gabbroic body. A hybrid dioritic liquid was then produced at depth by mixing of the gabbro with the marginal facies of the Darling Granite, which had itself assimilated argillaceous country rock.

The Brewelskloof Diorites, occurring about 6 miles north-east of Worcester, also invade pre-Cape sediments. This composite stock-like body, investigated by P.J. Joubert, consists of a central, more basic portion surrounded by a more acid margin.

6-4. Cape System and post-Cape geology.

After the end of activity of the Malmesbury and Nama Geosynclines, erosion was active over a long period of crustal stability producing a very nearly perfect peneplain, especially in the west and south-west. This surface probably sloped gently southwards and gradual depression of this southern part of South Africa in late Silurian time marked the beginning of the roughly E-W trending geosyncline in which there was the maximum deposition of the thick Cape and conformably overlying Karroo System Sediments.

The lowest member of the Cape System, 5000 feet of dominantly massive unfossiliferous sandstones and quartzites of the Table Mountain Series (TMS), were derived mainly from the north. These sediments were laid down in a shallow fluviatile basin under cool or cold conditions, revealed by a tillite horizon. In the succeeding shallow sea 2500 feet of the Bokkeveld Shales alternating with subordinate sandstone groups were deposited. Lower Devonian marine fossils occur mainly in the lower horizons of this series. The following 2500 feet of dominantly white quartzites with very subordinate shales of the Witteberg Series indicate a return to shallower, lacustrine conditions up to the Lower Carboniferous.

By the beginning of Karroo times the E-W Cape Geosyncline was well established. Rising land to the north and south contributed the extensive Karoo Sediments, reaching a maximum of about 25,000 feet in the south, but thinning out northwards. During the early very cold climate of the Upper Carboniferous up to 2000 feet of Dwyka Tillite accumulated, followed by 6000 feet of dominantly shales of the Permian Ecca Series. From Upper Permian to Lower Triassic up to 10,000 feet of Beaufort sandstones and shales were deposited in the now rapidly shallowing trough. But neither the overlying Molteno Beds, Red Beds and Cave Sandstone of the Stormberg Series, nor the following enormous outpourings of the basic Drakensberg Volcanics and their connected Karroo Dolerites of Jurassic age are represented in the south-western and southern Cape.

The deformation of these geosynclinal sediments took place in a number of stages (DE VILLIERS, 1944):

1. A weak Middle Carboniferous pulse, prior to the deposition of the Dwyka Tillite, affected only the western belt.
2. A stronger, Upper Permian (Lower Beaufort) pulse is noticeable near the eastern extremity of the southern belt.
3. The third and important period of compression during the Early-Middle Triassic (pre-Molteno) ended the geosynclinal phase in the south.

These pulses not only produced the two main structural fold-lines, viz., Cedarberg and Cape Foldings, but also affected the pre-Cape platform and strata up to and including the Lower Beaufort to varying extent, probably depending partly on the size and disposition of the Cape Granite Plutons.

During the Cretaceous relatively small, marine and continental, deposits of the Uitenhage Series, derived from the earlier uplifted sediments, were laid down in a few coastal areas of the southern Cape Folded Belt. Intense normal faulting with downthrow to the south and west occurred during the Mid-Cretaceous. In many cases this coincided with the major pre-Cape NW-SE and NE-SW trending shear zones of the basement rocks in the south-western Cape, and the E-W zones in the south.

Although largely obscured by more recent windblown sand, shelly limestones and calcareous sandstones were deposited during the Tertiary in various localities along the coast. Conspicuous

raised beaches demonstrate strong uplift of the southern continent during the Late Tertiary and Pleistocene, but a more recent depression may be indicated by drowned estuaries, such as Saldanha Bay and the Knysna Lagoons.

CHAPTER 7. ISOTOPIC AGE DETERMINATIONS.7-1. Introduction.

The principal purpose of this work was to determine the age of emplacement of the Cape Granite by a study of total rock samples using the Rb-Sr method. In addition it was hoped that the isotopic Sr data would throw light on the genesis of the granite.

ALDRICH et al. (1958) reported isotopic age measurements by the Rb-Sr and K-Ar methods on a biotite, and by the U-Pb and Th-Pb methods on a zircon; both minerals came from a single sample of the normal granite of the Cape Peninsula Pluton at the Lower Cable Station Quarry, Cape Town. The results obtained are listed below:

Biotite	K-Ar	505 \pm 25 m.y.
	Rb-Sr	600 \pm 30 m.y.
Zircon	U ²³⁸ - Pb ²⁰⁶	330 m.y.
	U ²³⁵ - Pb ²⁰⁷	355 m.y.
	Pb ²⁰⁷ - Pb ²⁰⁶	530 \pm 40 m.y.
	Th ²³² - Pb ²⁰⁸	238 \pm 30 m.y.

The spread of these results is sufficient to suggest that the mineral-ages have been influenced by the loss through diffusion of radiogenic daughter-products. This is consistent with the reported partially chloritised nature of the biotite used.

The abundance and wide distribution of sedimentary xenoliths in the granite showing all stages of assimilation suggests that at least a substantial part of the granite was derived from the invaded

Malmesbury Sediments. A detailed geochemical study on these sediments by ERLANK (1965) is at present nearing completion, and the geochemical data on the granites (Chapters 8 and 9), showing various stages of differentiation, do not preclude the possibility that the granite was ultimately derived by mobilization of the Malmesbury Sediments at depth.

For example, if the age of the Malmesbury were at least 2000 m.y., as indicated by its possible correlation with the Transvaal System (DU TOIT, 1954), and if the average Rb/Sr ratio of the Malmesbury Sediments were about $2\frac{1}{2}$, it follows that remobilization of the sediments about 1500 m.y. later would have resulted in the formation of a granite having the unusually high primary $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of .85. Initial results on the granite showed, however, that its primary $\text{Sr}^{87}/\text{Sr}^{86}$ ratio was much lower at .71. Measurements of present-day $\text{Sr}^{87}/\text{Sr}^{86}$ ratios were thus made on the Malmesbury Sediments as well.

The mass spectrometric isotopic analyses and calculations reported in this chapter were done at the Australian National University by Dr. H.L. Allsopp and this, and some additional data is to be published shortly in a mutual paper.

The following physical constants were used:

Rb-Sr method: $\beta = 1.39 \times 10^{-11} \text{ yr}^{-1}$, $\text{Rb}^{85}/\text{Rb}^{87} = 2.600$, $\text{Sr}^{88}/\text{Sr}^{86} = 8.340$.

K-Ar method: $\beta = 4.72 \times 10^{-10} \text{ yr}^{-1}$, $K = 0.584 \times 10^{-10} \text{ yr}^{-1}$,

$\text{K}^{40} = 1.19 \times 10^{-4} \text{ mole/mole K}$.

Duplicate Rb and Sr measurements normally agree to better than 1%,

and K and Ar measurements to better than 2%. Taking into account all factors except the uncertainty in the value used for the decay constant of Rb^{87} , apparent Rb-Sr ages are thought to be accurate to within 2%, and K-Ar ages to within 3%.

7-2. The Cape Granite.

Sample locations of all granite specimens used for the isotopic work are shown on the simplified geological map of the Cape Peninsula and neighbouring areas in Fig. 36. These same granite samples and some of their minerals are also included in the general geochemical work discussed in the next chapters (see Tables 18 to 24); but for convenience the detailed sample localities, short petrographic notes and descriptions of the mineral fractions used here are also given in the appendix.

Samples 104, 108 and 110 represent the normal coarsely porphyritic granite of the Cape Peninsula, while Samples 136, 145 and 147 are from a finer-grained granite facies exposed near the Granite-Malmesbury contact at Kloof Quarry, Wyllies Siding (WALKER and MATHIAS, 1946). There the normal coarsely porphyritic Cape Granite passes gradationally into a finer-grained porphyritic granite (Sample 136), which grades into a microgranite (Samples 145, 147; Fig. 30), finally pinching out into a thin pegmatitic vein intruded into the Malmesbury country rock. The three samples 136, 145 and 147 are thus clearly of the same age, but could be significantly younger as a group than the normal coarsely porphyritic granite, since their highly differentiated nature relative to the normal coarse granite is

well demonstrated, for instance, by lower K/Rb, K/Cs and K/Tl ratios and very low Ba and Sr content (Table 18).

Table 12 summarises the Rb-Sr total-rock measurements on the Cape Granite. The usual isochron approach may be applied to a group of data only if all the samples are known to be of the same age. It was shown earlier that the three samples of the fine-grained, differentiated facies satisfy this condition, although they may be slightly younger than the normal granite samples. However, if a regression line is fitted to all the points, as shown in Fig. 37, it is noted that there is no systematic divergence from the line, and it is concluded that there is unlikely to be a significant difference in age between the two facies. Further support for the procedure of grouping all points is derived from the mineral-fraction results discussed below.

Duplicate analyses were made on four of the total-rock samples and in the least squares analysis of the data the duplicates were regarded as separate data-points. From the slope and intercept of the regression line obtained it is calculated that the age of the granite is 553 ± 8 m.y., and the primary $\text{Sr}^{87}/\text{Sr}^{86}$ ratio (R_i) is $.710 \pm .003$, where the errors quoted are at the 95% confidence limit.

Although the Rb/Sr ratios of the three samples of normal granite do not differ sufficiently from one another for the age and R_i to be determined from these points alone, this information can be deduced from the mineral-fraction results if it is assumed that since

crystallization each mineral has remained a closed system with respect to Rb and Sr. The relatively coarse-grained minerals of the normal granite are the most likely to have fulfilled this condition and measurements were thus made on K-feldspar and biotite fractions from each of Samples 104, 108, and 110, as well as on 104 plagioclase. These data, summarised in Table 13, are also shown in Fig. 37.

Taking R_i as .710, the total-rock value, the apparent ages of the K-feldspars and biotites (except 104 A) are found not to differ significantly from the total-rock age. Biotite 104 A, which contains slightly more chlorite than Sample B (see Appendix), gives a significantly lower age and this indicates that the chloritized sample has leaked radiogenic Sr. Further evidence of Sr migration is afforded by the trend of all other mineral points. Although none of these deviate significantly it is noteworthy that the ages of the Rb-rich minerals, biotite and K-feldspar, are lower whereas the single plagioclase "age" (Sample 104, Fig. 37) is higher than the total-rock age. It is concluded that a mild metamorphism has influenced the mineral ages causing the apparent ages of the K-feldspars and biotites to be somewhat lower than the true ages. The observation, therefore, that minerals from the normal coarse granite give ages apparently concordant with the total-rock age supports, but cannot be considered conclusive evidence for, that all the granites, both coarse and fine-grained, are of the same age.

K-Ar measurements were made on the two biotites 104 B and 108 and the results are shown in Table 14. The results on the two samples are in agreement and also agree reasonably with the value given by ALDRICH et al. (1958), but are considerably lower than the Rb-Sr ages on the identical samples. The fact that the K-Ar ages on the two biotites are identical indicates that metamorphism was widespread and not confined to proximity with intrusions of aplogranite or pegmatite.

The $\text{Pb}^{207} - \text{Pb}^{206}$ age of 530 ± 40 m.y. for the zircon given by Aldrich et al. is consistent with the Rb-Sr total rock age reported here, and the discordant pattern of the uranium-lead and thorium-lead ages is also consistent with the supposition of a later metamorphic event. On the other hand, the value of 600 m.y. given by Aldrich et al. for the Rb-Sr age of the biotite disagrees with the ages given here, and the reason for this difference is not understood.

7-3. The Aplogranite, Sea Point.

Another granitic rock of particular interest for geological age determination is the aplogranite found near the Sea Point Contact (WALKER and MATHIAS, 1946). A sketch map of the area is shown in Fig. 38. Evidence of post-granitic or late-stage granite activity is afforded by veins and nests of pegmatite (e.g. Sample 170, Table 17 et seq., Fig. 34) found in the normal coarsely porphyritic granite, and thin veins of aplite are found cutting the granite and Malmesbury meta-sediments near the contact. These veins are petrologically very

similar to a large cross-cutting mass of aplogranite intruded into the Malmesbury Hornfels, and this mass is represented by Sample 156, for which full geochemical data is also given in Tables 18 et seq.

Total-rock sample 156 was also analysed by the Rb-Sr Method and measurements were also made on the K-feldspar and plagioclase which together with quartz virtually constitute the whole rock, as shown in Table 21. The Rb-Sr data are shown in Table 15 and also in Fig. 37. The total-rock point differs significantly from the other granite points and this result could be interpreted in several ways, the most probably being:

- (1) The aplogranite may have been derived from a different source than the other granites, in which case its R_i ratio may also have differed. In particular, if $R_i = .700$ for the aplogranite its age would be 550 m.y., the same as that of the main granite body.
- or
- (2) The aplogranite may have been derived from the same source and had the same R_i ratio. In this case the aplogranite is significantly younger - 500 ± 15 m.y.

The second possibility seems the more likely if the aplogranite mass is considered to be a counterpart of the thinner, petrologically very similar, aplite veins which cut the main granite. Furthermore, a value of R_i as low as .700 has not been reported previously for a granitic rock and further evidence is afforded by the aplogranite minerals.

These data points together with that of the total-rock lie close to an "isochron" passing through .710, the Ri ratio of the main granite. Against this it might be argued that in this fine-grained rock sufficient migration of radiogenic Sr from the microcline to the plagioclase could have occurred during metamorphism to produce this pattern. However, assuming interpretation (1), and using the following data:

(a) the K-feldspar and plagioclase each comprise 30% of the rock,

(b) the plagioclase fraction analysed is 50% pure and the K-feldspar fraction is 100% pure,

(c) the deviations of the K-feldspar and plagioclase points from the appropriate isochron,

an order-of-magnitude calculation shows that the amounts of radiogenic Sr apparently gained by the plagioclase exceeds by a factor of 4 that apparently lost by the K-feldspar. Since apart from the K-feldspar there is no other significant source of radiogenic Sr the hypothesis that the aplogranite has the same age as the main granites is unlikely. The alternative age of 500 ± 15 m.y. would be consistent with an association between the metamorphism of the older granites and the intrusion of the aplogranite.

Furthermore, although the samples of granite and aplogranite are from the Cape Peninsula Pluton only, it is tempting to speculate that such a metamorphic event about 500 m.y. ago was more widespread and possibly marked the intrusion of "younger" granites in the southwestern Cape generally, e.g. the Younger Saldanha Granite.

However, although the Sea Point Aplogranite appears to be relatively fresh and unaltered, the possibility exists that its K-feldspar has suffered some chemical alteration, perhaps due to weathering. Since this is a virtually biotite-free granite, the K-feldspar essentially determines the total-rock age and concordance between total-rock and K-feldspar is not of such critical value. In the absence of more than only one total-rock sample of aplogranite, the conclusion reached here on its age must therefore still be regarded with some caution.

7-4. Malmesbury Sediments.

A generalized description of the Malmesbury Sediments has been given in Chapter 6-1. The sediments in the Cape Peninsula and surrounding areas here considered in connection with the age-work (Fig. 36) consist of fine-grained arenaceous strata with interbedded slaty layers, both strata being hornfelsed in the vicinity of the granite.

Mr. A.E. Erlank, Department of Geochemistry, University of Cape Town, has kindly supplied the Malmesbury samples considered here together with petrographic notes on the specimens. His original sample numbers are retained here since detailed geochemical data on these and other samples of Malmesbury will become available shortly (ERLANK, 1965).

The more abundant arenaceous bands of the formation (represented by samples M9-B, M-15 and M-41) consist mainly of fresh clastic grains of quartz, sodic plagioclase and subordinate microcline

in a groundmass composed mainly of somewhat chloritized biotite and sericite. Gradations are common to the interbedded argillaceous bands (represented by Samples M-14A, and M-40). These are too fine-grained for detailed optical mineral determination, but show fewer and much smaller clastic grains and also contain clay-minerals in the matrix.

Rb-Sr measurements were made on the five total-rock samples mentioned above. The data is summarised in Table 16. It is apparent from the isochron presentation of Fig. 39 that the data points are closely colinear. This is a rather unexpected and important finding for sediments which include reasonably coarse-grained clastics in view of previous investigations on sediments (COMPSTON and PIDGEON, 1962; HURLEY et al., 1962).

That the "isochrons" pertaining to partially clastic sediments are not usually closely colinear is attributed to the incorporation of varying amounts of excess radiogenic Sr carried by detrital minerals, mainly micas. The linearity of the Malmesbury data could be accounted for in three ways, but present evidence does not permit a definite choice among them:

1. The Rb and Sr of the rocks may be predominantly authigenic. This is somewhat improbable because of the existence of detrital minerals and because the observed Ri ratio of $.712 \pm .003$ exceeds significantly the "sea-water" $\text{Sr}^{87}/\text{Sr}^{86}$ ratio for 600 m.y. ago obtained by measurements made on limestones (HEDGE and WALTHALL,

1963). The latter objection would not apply if the Malmesbury Sediments, at least in the Peninsula Area, were deposited in water isolated from the ocean, since in such conditions a higher than oceanic $\text{Sr}^{87}/\text{Sr}^{86}$ ratio could occur. This possibility is still to be checked at a later time by measurements on limestones or other Rb-free rocks. It would also be of great interest to find where the bulk of the Rb and Sr in the coarser clastics lies, i.e. whether most of it is in the mica-clay fraction.

2. The $\text{Sr}^{87}/\text{Sr}^{86}$ ratio throughout the Malmesbury may have been homogenized to .711 by a metamorphic event. Homogenization over distances of the order of 20,000 feet, an estimated thickness of the sediments, would seem somewhat unlikely except perhaps after prolonged high-grade metamorphism, whereas there is evidence only of low-grade metamorphism. However, it may be possible that during processes of diagenesis, accompanying expulsion of connate water through compaction, considerable changes take place in the clay-mineral structures, thus homogenizing the isotopic composition of the Sr in the layer-lattice mineral components. Again it would be very interesting to know where the bulk of the Rb and Sr lies. Perhaps the homogenization may even have affected the K-feldspar and plagioclase, but this would be quite unexpected.

3. Whether by chance or by some mechanism imperfectly understood the detrital components of the sediment may have been distributed such that their Rb/Sr ratios were related to their $\text{Sr}^{87}/\text{Sr}^{86}$ ratios. But, even if it is assumed that all detritus came from a common

source, such a relation is considered unlikely since each rock contains mineral species with widely varying Rb/Sr ratios. However, if possibility 3. is true, the isochron age obtained is too high and should be reduced.

But on the empirical approach, accepting the prima facie interpretation that the data-points define a real isochron, a least squares analysis on all points gives an age of 595 ± 46 m.y. and Ri ratio of $.712 \pm .003$ where the errors given are 95% confidence limits. The calculated age is acceptable on geological grounds and accords with the views of SCHOLTZ (1946) that the Cape Granite was intruded only shortly after the deposition of the Malmesbury.

The latest Precambrian to early Cambrian age obtained here for the Malmesbury also throws light on its possible correlation with the pre-Cape and pre-Nama rocks in the Bitterfontein - Van Rhynsdorp Area. Thus JANSEN (1960) considered the paragneiss in the Bitterfontein Area to have formed by granitization of the "Malmesbury System" Sediments. However, NICOLAYSEN (1962) reported age measurements in Namaqualand and concluded (Page 594 and 595) that the paragneisses must have formed prior to 1050 m.y. ago. Therefore, if Jansen's field interpretation is accepted, these pre-Nama Sediments in the area must represent a formation considerably older than the Malmesbury. For instance, BRINK (1950) correlated the pre-Nama paragneisses about 13 miles north-east of Bitterfontein with the Kheis System.

The observed ages and Sr isotope ratios also allow some speculation on the origin of the Cape Granite. If, approximately 40 m.y. after it was deposited, a portion of the Malmesbury were mobilized to form the Cape Granite, the radiogenic Sr accumulated in the Malmesbury during this relatively short space of time would be sufficient only to increase the primary $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the granite by .003. The observed Ri ratio of $.710 \pm .003$ of the granite does not differ at the 95% confidence limit from the value of $.714 \pm .003$ obtained by adding .003 to the Ri ratio of the Malmesbury. It is therefore feasible that this granite pluton was formed entirely by mobilization of the sediments. On the other hand, the observed Ri ratio is not exceptional for a young granite (HEDGE and WALTHALL, 1963) and an altogether different mechanism may well have operated in forming the granite.

7-5. Conclusions.

The principal conclusions reached in this chapter may be summarised as follows:

- (1) The Rb-Sr age of the normal coarse Cape Peninsula Granite is 553 ± 8 m.y. with a primary $\text{Sr}^{87}/\text{Sr}^{86}$ ratio (Ri) of $.710 \pm .003$. Following SCHOLTZ (1946), and in the absence of any data to the contrary, this age may be assumed to be the age of emplacement of all "older" south-western Cape Granite Plutons.
- (2) No significant difference in age appears to exist between the normal coarse Cape Peninsula Granite and its finer-grained differentiated border facies.

(3) A mild metamorphism causing very slight migration of radiogenic strontium from K-feldspars and biotites into plagioclase may have affected the granite after its intrusion.

(4) K-Ar ages on two biotite samples from the normal coarse granite suggest that this metamorphism was widespread and not confined to local intrusions of aplite or pegmatite.

(5) Preliminary data on a relatively large crosscutting mass of aplogranite at Sea Point suggests that it was derived from the same source as the granites, but intruded 500 ± 15 m.y. ago. This event may be associated with the metamorphism of the main granite body. It is conceivable that this event was more widespread and therefore also marked the intrusion of "younger" granites in the south-western Cape generally, e.g. the Younger Saldanha Granite.

(6) An apparent "isochron" observed for the Malmesbury Sediments, which shows an unexpected and remarkably strong colinearity, indicates an age of 595 ± 46 m.y. with an R_i ratio of $.712 \pm .003$. This age accords with the views of SCHOLTZ (1946) that the Cape Granite was intruded only shortly after the deposition of the Malmesbury.

(7) On observed Sr isotope data it appears possible, but unproven, that the granites were formed entirely by mobilization of the Malmesbury Sediments.

CHAPTER 8. PETROLOGICAL AND MINERALOGICAL DATA.8-1. Total rocks.

Sample localities of specimens used for total-rock or mineral analyses are shown in Fig. 27 and listed in Table 17. Analytical results of 32 major and trace elements are set out in Table 18 for 34 total-rock samples of normal coarse, medium and fine-grained granite, 6 younger intrusive granites, 1 contaminated granite, 2 xenoliths and 2 samples of the gabbro-diorite intrusives near Malmesbury.

Elements are listed in order of increasing ionic radius, and are expressed as weight per cent for the major elements and as parts per million (p.p.m.) for the minor and trace elements. Major elements expressed as oxides are given in the same table. Some critical element ratios are shown in Table 19. The analytical data are discussed in the next chapter.

8-2. Modal and textural variations.

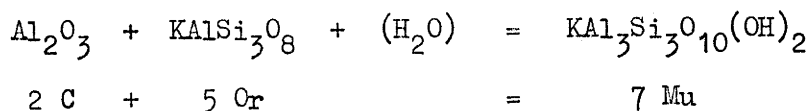
A general petrographic description of the granites is given in Chapter 6-2. More detailed descriptions including mineral optical data from a number of specific areas are referred to in Chapter 5-2. Since the majority of the granites are very coarse-grained and contain large K-feldspar phenocrysts, normal thin section analyses, even of a number of slides cut from each specimen, gave rather variable results besides being excessively time-consuming. Therefore

the best alternative seemed to be a calculated mode based on the chemical analyses of the very large and thus more representative samples used. In a number of cases such calculated modal compositions could be checked by the actual yields of minerals obtained during mineral separation. In addition, upper limits on the biotite content could be computed from the Mg concentration in total rocks and their analysed biotites, since in most granites the bulk of the Mg is contained in this mineral.

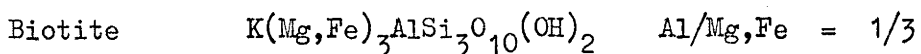
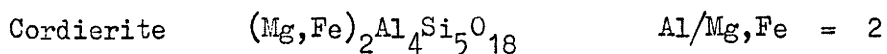
One of the primary purposes of a calculated norm is for the chosen standard normative minerals and mineral associations to correspond as closely as possible to natural conditions. The usually calculated CIPW norm is therefore entirely unsuitable for granitic rocks since the ferro-magnesian elements are calculated as normative hypersthene instead of biotite, muscovite or hornblende which are actually present. Furthermore, normative Or, which should represent K-feldspar in the rock, will be overestimated, because no K is allotted to hypersthene. For instance, in a normal granite (K±3.5%) containing 10% mica (K±7%), the normative Or will be overestimated by 25%. The fact that Or in many published granite norms corresponds rather closely to "K-feldspar" determined by thin section analysis is quite coincidental. The K-feldspar of most granitic rocks is perthitic or microperthitic containing on an average about 15-25% plagioclase, so that these two opposite effects will often cancel each other.

The best way of dealing with granitic rocks containing micas and hornblende, minerals of the mesozone, is the mesonorm devised originally for metamorphic rocks (BARTH, 1959). The calculation adopted here is basically the reverse process of the estimation of chemical composition from the mineralogical mode described by HEIER (1961). The major element oxide chemical composition of the granites (Table 18) is used to calculate cation percentages on a water-free basis (BARTH, 1955). This data is shown in Table 20. Barth's method for rocks with excess silica is then followed with three modifications:

1. Ti, present in only small amounts, is not formed into ilmenite, $\text{FeO} \cdot \text{TiO}_2$, but goes into biotite (and hornblende, where present). This can be justified by inspection of the Ti concentrations of the total rocks (Table 18) and analysed biotites (Table 24).
2. Since analyses of the K-feldspars are available (Table 22), the calculated pure K-feldspar component is increased in each case by the requisite amount of plagioclase to show the actual modal perthite content of the rock; the calculated plagioclase content is decreased accordingly to show actual modal plagioclase.
3. In the mesonorm excess Al is stated as corundum. But this is not actually present as mineral in the rocks. Thus HEIER (1960) calculated it, together with the corresponding amount of Or, as muscovite according to the scheme:



However, only part of this "excess" Al will appear as actual muscovite in the rock since some will enter into both biotite and hornblende lattices. Furthermore, cordierite is present as minor constituent in some of the Cape Granites. Since this is not separately calculated in the mesonorm, Mg' appearing as biotite, too little Al is used, as can be seen from their respective normalized formulae:



Small amounts of tourmaline ($\text{Al/Mg,Fe} = 2$) will have the same effect.

Lastly, the chemical determination of Al_2O_3 in rocks is probably the least satisfactory of all major elements and small amounts of apparently excess Al_2O_3 may simply be due to the usual small overestimation of this oxide, as shown for instance for G-1 (STEVENS et al., 1960). For these reasons, where excess Al appears in the mesonorms of the granites, which actually do contain small amounts of muscovite, half of the excess Al is used to make muscovite according to the formula given, and the remaining half stated as corundum. Although this may appear to be a somewhat arbitrary assumption, the amounts involved are relatively small and the thus calculated composition is found to be very close to the observed mode in terms of muscovite and K-feldspar.

The "modes" thus calculated are shown in Table 21. Composition of perthites refers to their actual analyses (Table 22), but composition of plagioclases is calculated from the mesonorm,

"Calculated maximum" biotite is calculated directly as a comparison in all cases where both analysed total-rock and biotite was available assuming that all Mg in the rock formed biotite. As expected, this figure is in all cases slightly higher than modal biotite since some Mg actually forms small amounts of cordierite, tourmaline, hornblende and ore. A further check on the calculated modal biotite is given by the average total ferro-magnesian mineral content of 13.1% w/w determined by weighing during mineral separation for the normal coarsely porphyritic granites. This is in good agreement with an average of nearly 13% shown in Table 21 as mean for these granites. Lastly, the optical determination of one sample of normal Cape Peninsula Granite cited by WALKER and MATHIAS (1946, Table I) may be compared with the average of 8 Cape Peninsula Granite calculated modes given in Table 21 (Samples 101-106, 117-118):

	<u>Optical data</u>	<u>Calc. mode</u>
Quartz	31.4%	28.4%
K-feldspar	28.4	28.1
Plagioclase	26.3 (Ab ₇₅)	28.0 (Ab ₇₆)
Biotite	9.4	9.7
Muscovite or sericite	2.5	4.1
Cordierite	variable, about 2	-
Ore	-	.6

The calculated modes shown are thus accepted with confidence, especially in fulfilling their primary purpose of indicating systematic modal variations among the different types of granite.

Although considerable distances separate some of the exposed granite plutons preliminary results confirmed SCHOLTZ's (1946) view that no strong systematic chemical or mineralogical differences exist between their normal granites. But, as outlined in Chapter 6-2, individual plutons show varying proportions of different textural facies (Tables 10 and 11), distinguished also by different modal compositions. This probably has genetic implications and all data were therefore grouped on this basis rather than on the geographical distribution of samples — a procedure also followed by Scholtz.

Although some gradations occur normal granite samples in all tables have thus been subdivided into:

(1) Coarsely porphyritic granites. These include the greatest number of samples as they form the bulk of the exposed granite plutons, generally their core. They are predominantly textural type C-2, occasionally grading into C-1 or G-2.

The finer-grained granites generally form the exposed hood or border-facies of the plutons.

(2) Medium-grained granites are mainly porphyritic granites (G-2), often grading into M-2 and occasionally into G-3.

(3) Fine-grained granites are generally microgranites (M-3) or granite porphyries (G-3).

The differences in modal composition of these three main textural types as listed in Table 21 are illustrated in Fig. 40. The fine-grained varieties always contain a considerably smaller proportion of femic minerals (mainly biotite). The other major

minerals show less systematic variation, but on an average the finer-grained granites also have somewhat less plagioclase (containing less An), but relatively more quartz and K-feldspar. The modal variation is reflected strongly in the major and trace element chemistry of the different granites and their minerals indicating progressive differentiation; this further justifies the grouping adopted. The remaining samples represent relatively less important granite modifications:

(4) Younger intrusive granites. Samples 155 and 156 from Sea Point (Fig. 38) represent fine-grained (M-3) intrusive granites showing high modal quartz and very little biotite. Aplogranite 156 was shown in Chapter 7-3 to be probably significantly younger than the Cape Granite.

The larger mass of Younger Saldanha Granite is represented by samples from the Hoedjies Bay Contact (Fig. 27). There the granites grade from chilled quartz porphyries (G-4) with partially devitrified groundmass near the contact to coarser granite porphyries (G-3) further away. Their modes show high quartz and K-feldspar but low plagioclase and biotite. Their major and trace element composition, however, distinguishes them from the normal highly differentiated fine-grained granites. Dyke rock 168 with high quartz and plagioclase cuts the Older Saldanha Granite at the contact.

(5) Pegmatites. Table 17 lists four samples of coarse pegmatitic granites for which no modes could be calculated since total-rock analyses were considered unrealistic. But K-feldspar and mica analyses are shown in Tables 22 and 24.

(6) Contaminated granite, Sample 174, is distinguished by exceptionally high modal mica.

(7) Xenoliths 175 and 176 from the Cape Peninsula Granite show even higher modal mica content at the expense of quartz and feldspars.

The diorite-gabbro intrusions near Malmesbury (VAN ZIJL, 1950) are represented by Samples 177 and 178. They are composed mainly of hornblende, plagioclase and biotite with very little quartz and almost no K-feldspar.

8-3. Minerals.

(a) Analyses of 70 K-feldspars separated from the granitic rocks are given in Table 22. All samples are arranged in the same categories as the total rocks. Besides some calculated critical element ratios this table also shows the K-feldspar data recalculated as ideal feldspar formulae in terms of Or, Ab, An, $\text{SrAl}_2\text{Si}_2\text{O}_8$, $\text{BaAl}_2\text{Si}_2\text{O}_8$ and $\text{RbAlSi}_3\text{O}_8$. The calculated summations are considered satisfactory since 75% of the samples show summations falling within $\pm 1\%$ of 100%, 13% fall within $\pm 2\%$, and the remaining 12% range between totals of 96% to 98%, probably indicating slight quartz contamination.

For completeness, the Rb and Sr isotope dilution data from the isotopic age work on a few additional feldspar and biotite samples are included in the respective mineral-tables.

(b) Table 23 shows the analyses of coexisting plagioclases from two typical granite samples and two plagioclases from the diorite-gabbro intrusion. Because of overlapping densities the

granite-plagioclases could not be effectively separated from quartz. The analyses were therefore done on the purified plagioclase/quartz mixture and the theoretical plagioclase composition was calculated assuming the quartz to be pure SiO_2 .

(c) Analyses of 23 coexisting biotites from the various rock types are shown in Table 24. Also included are four selected samples of muscovite and a specimen (Sample 106) of chlorite derived by alteration from biotite 106.

8-4. Feldspar variations.

(a) Major elements: The major feldspar components Or, Ab and An (wt.%) are plotted in Fig. 41 on the projection of the quaternary system Or-Ab-An- H_2O at 5000 bars H_2O pressure (YODER et al., 1957). The cotectic curve separating the fields from which OrAb-rich feldspars and AbAn-rich feldspars crystallize is indicated.

The bulk of the microclines can be seen to contain between 10% and 30% plagioclase, all showing less than 3% An. Although the average composition of coexisting plagioclases changes from Ab_{73} for the coarse granites to about Ab_{90} for the fine-grained, most differentiated varieties (Tables 21, 25; Fig. 40), no clear trend emerges for the equivalent microcline compositions from the major granite types.

However, as a group, the K-feldspars from the Younger Saldanha Granite contain slightly more plagioclase. The relatively high Ab but very low An content of alkali feldspar 151 from the Darling microgranite reflects the high Na concentration (3.19%) but

extremely low Ca (.05%) of the highly differentiated host rock. Alkali feldspars from pegmatites show the greatest variation in plagioclase content, ranging from 8.5% to 46%. A number of trace elements, discussed in the following chapter, also reflect these differences; e.g. the K/Rb ratios of these small pegmatites show a concomittant increase from 196 to 317 respectively.

Also plotted in Fig. 41, plagioclases 177 and 178 from the diorite-gabbro intrusion are readily distinguished by their much higher An content from the granite-plagioclases 106 and 137.

BARTH (1956) used the distribution coefficient:

$$k = \frac{\text{mol fraction of albite in alkali feldspar}}{\text{mol fraction of albite in plagioclase}}$$

as a two-feldspar geothermometer for granites and gneisses. The established curve relating K to temperature was regarded by Barth as an "average" since k does not depend entirely on temperature, but to some extent on pressure, bulk composition of the rocks and possibly other factors as well (BARTH, 1961; WINKLER, 1961; DIETRICH, 1961).

The calculated temperatures of formation of the Cape Granite feldspars, based on Barth's "1956 values for the feldspar crystallization temperatures" are listed in Table 25. The K-feldspar determinations are all chemical (Table 22); the plagioclase compositions shown are from optical (universal stage), chemical (Table 24) and modal (Table 21) data.

It is apparent that the temperatures obtained are rather variable and lower than would be expected for "magmatic" granites.

A number of factors may be pertinent:

1. If the K-feldspar phenocrysts are of late origin, as suggested by WALKER and MATHIAS (1946) for the Cape Peninsula Granite, the calculated distribution ratios would obviously be quite meaningless. However, this suggestion was criticised by a number of workers and the trace element data discussed below also indicates that the K-feldspars were at least in approximate chemical equilibrium with other phases. This makes their late origin unlikely. The analysed perthitic microclines are considered to have formed by exsolution from originally homogeneous alkali feldspars, but it is quite feasible that hydrothermal activity at the close of the "magmatic" stage caused varying degrees of element migration and rearrangement, especially of the alkalis.
2. Apart from the difficulties of accurately estimating their composition, the usually slightly zonal nature of the plagioclases also attests to gradually changing chemical equilibria with time; and it is not known at what precise stage the K-feldspars crystallized.
3. As mentioned in the description of sample preparation (Appendix), it is possible that during separation of some K-feldspar perthites slight fractionation may have occurred with consequent underestimation of their Ab contents. This would result in anomalously low calculated temperatures.

4. As stressed by DIETRICH (1961) the temperature recorded only reflects the most recent lowest temperature at which equilibrium existed between the feldspar phases. The observed deformation of some of the granites as well as the isotopic age data presented suggest post-granite metamorphic activity. This could well have caused further departure from an original equilibrium, especially in the areas most strongly affected. It is probably significant that the lowest temperatures obtained are for the obviously most strongly deformed granites. Thus Sample 123 (370°) represents a highly sheared Darling Granite in which K-feldspars probably re-crystallized. Sample 132 (490°) is from a "gneissic" part of the Saldanha Pluton, and all three calculated temperatures from the overall strongly deformed George Granite are also apparently anomalously low, i.e. Samples 135 (450°), 142 (400°), 143 (490°). The observed obliquities of the K-feldspars, discussed in the next section, also show a concomitant sudden increase for these deformed samples.

Keeping the stated uncertainties in mind, the average calculated temperatures of 580° for all normal coarse Cape Granites (excluding the five samples mentioned) and the somewhat lower 520° for the fine-grained facies may be compared with 550° obtained by BARTH (1956) for the diapire granites of the Southern Norwegian Precambrian and 650° and 580° used by him for the coarse and fine granites of the S. California Batholith. It may be noted that the

average of the four samples of finer-grained "chilled" Younger Saldanha Granites (158, 159, 163 and 166) is rather higher at about 660° , very close to a likely magmatic temperature. In this connection DIETRICH (1961, p.16) stated, that "...probably the thermometer is best for rocks formed as the result of relatively rapid cooling of a magma — the temperature recorded would be essentially that of consolidation". The apparently also low temperature of 490° for the contaminated Darling Granite (Sample 174) and 540° for the Clifton Xenolith (Sample 175) may be affected at least partly by the strongly differing bulk composition of these rocks. But the pegmatitic segregation in the normal coarse granite (Sample 171, 500°) and especially the pegmatitic vein (Sample 169, 390°) probably reflect late-stage hydrothermal activity.

It is concluded that the recorded temperature obtained for the more quickly cooled Younger Saldanha Granites may approximate their actual temperature of crystallization. But the lower and variable temperatures shown by most of the normal Cape Granites probably indicate varying degrees of late-stage hydrothermal activity and/or post-granitic metamorphism, even if these granites were not really completely "magmatic" but partly diapiric in the sense used by Barth.

(b) K-feldspar obliquity: The structural state of K-feldspars may also throw light on the petrogenesis of their containing rocks. Recent work has shown that monoclinic sanidine, formed at high

temperature, has Si and Al atoms completely randomly distributed over their lattice positions, while the low temperature, triclinic microcline structure exhibits the highest degree of Al/Si order. "Orthoclase" shows intermediate degrees of Al/Si order forming a continuous sequence of intermediate states (GOLDSMITH and LAVES, 1954b; LAVES and GOLDSMITH, 1961). Rather than truly monoclinic it is only "pseudomonoclinic" also because of the smaller size of its crystal domains, which themselves vary in size and triclinicity (order) even within a "single" crystal. As these units become very small, even although each may be highly ordered, the triclinicity is affected by their mutual stress-strain relations; so that such material may be monoclinic optically, and even appear monoclinic on X-ray patterns.

Microcline has been transformed into sanidine by dry-heat treatment slightly above 1000°C, and by hydrothermal treatment as low as 525° (GOLDSMITH and LAVES, 1954a). The reverse process has not been achieved in the laboratory, but HEIER (1957) concluded that the "orthoclase"- microcline transition takes place in nature at about 500°, very close to the conventional granulite-amphibolite facies transition.

GOLDSMITH and LAVES (1954a) used the difference in spacing of the (131) and ($\bar{1}\bar{3}\bar{1}$) lines as a measure of triclinicity (obliquity) according to the equation

$$\text{Obliquity, } \Delta = 12.5 (d_{(131)} - d_{(\bar{1}\bar{3}\bar{1})}).$$

The obliquities of a number of K-feldspars, determined as described in the Appendix, are listed in Table 25 and plotted against their "temperature of formation" in Fig. 42. The majority of K-feldspars investigated show low to intermediate Δ -values (.2 - .55), but a few approach the highly ordered triclinic state. In spite of fair scatter the latter also show the lowest temperatures and an inverse relation is apparent between Δ and temperature.

Since the microclines show "grid" twinning they may be assumed to have crystallized originally in the monoclinic form (LAVES, 1950). However, as for the temperature of formation, the observed Δ -values will not necessarily reflect the conditions under which the granites formed, if altered by later processes. Thus HEIER (1957) explained the varying increasing triclinicities of originally monoclinic feldspars from postorogenic granites and pegmatites on Langfj, Norway, by the action of post-magmatic hydrothermal solutions. And DIETRICH (1962) believed that the observed increase in K-feldspar Δ -values (.05 to .50) with increasing differentiation of the Boulder Bathylith Granites is due not only to lowering of temperature of consolidation but possibly also to increase of volatile content.

It is noteworthy that, with the exception of the pegmatite vein (Sample 169, presumably crystallized at lower temperature and with high volatile pressure), all other observed high Δ -values (Samples 123, 132, 134 and 135) are from K-feldspars of visibly deformed granites, which also indicated abnormally low temperatures.

The triclinicity under equilibrium conditions is not only influenced by the degree of Al/Si disorder as a function of temperature, but also by the Na content in solid solution. GOLDSMITH and LAVES (1961) observed that highly triclinic microclines have exsolved virtually all their Ab and retain 5% or less Ab in solid solution. Although the amount of Ab in actual solid solution is not known for the microcline perthites here studied, Fig. 43 demonstrates the inverse relation between Δ and total Ab of the feldspars. The high- Δ , low temperature feldspars contain distinctly less Ab.

It therefore seems likely that postmagmatic hydrothermal solutions and/or deformation during a later metamorphic event caused some Na redistribution between the K-feldspar and plagioclase of the granites from some areas (e.g. George) resulting both in anomalously low "temperatures of formation" and in high obliquity values of their K-feldspars. Whether small amounts of Na were lost completely from these rocks cannot be decided, but their total Na content, compared with the other granites, is not significantly lower. The bulk of the south-western Cape Granites probably were affected much less. The general low-intermediate obliquities of their K-feldspars fall rather neatly into the intermediate Δ -value "gap" (.3 to .65) discussed by DIETRICH (1961, 1962). A rather mild metamorphism was also indicated for the Peninsula Granite by the Rb-Sr and K-Ar data.

III. GEOCHEMISTRY OF THE ELEMENTS.CHAPTER 9.

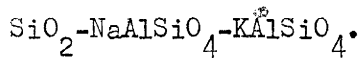
This chapter deals with the observed geochemical behaviour of the individual elements in both the Snowy Mountains granites and Cape Granites, as well as the analysed minerals from the latter. Elements are discussed in the general order of decreasing ionic radii, except that the major elements in each size range are treated first, followed by the trace elements which substitute for them.

9-1. Potassium.

Among major elements, K, together with Si and perhaps Mg, is a most useful guide in a comparison of granite types, and in special cases may even suggest modes of origin. Thus, the relatively high K concentration of the Snowy gneisses (3.5%) coupled with unusually low Na ($K/Na = 3.0$) and high ferro-magnesian concentration is indicative of a direct origin from a shale-rich sediment (Chapter 4-1).

Plots of K_2O versus SiO_2 are shown in Fig. 17. The Snowy granodiorites, which form the bulk of the Snowy Mountains granites, are rather variable but average only 2.63% K. They are regarded as representing a variable but essentially undifferentiated mixture of typical geosynclinal sediments and thus contrast strongly with the differentiated Snowy leucogranites ($K = 3.9\%$) and the "high-level" Cape Granite ($K = 4.2\%$). Among the latter a clear trend of increasing

differentiation with decreasing grain-size is noted for some other major and trace elements; but K shows no clear systematic increase. No marked increase in K, however, would be expected for granites which already approach the ternary minimum in the system



The Younger Saldanha Granites (Samples 163, 166, 167, Table 18) show the highest K concentration of about 4.5%. Xenoliths 175 and 176 with very high modal mica and low quartz have 6% and 4.9% K respectively, but the biotite-rich "contaminated" Darling Granite (Sample 174) has only 2.8% since K-feldspar is very low. This illustrates the difficulty of relating small inclusions of diverse sedimentary origin, undoubtedly substantially altered by hydrothermal diffusion especially of the alkalis, to any sedimentary source rock which may have contaminated portions of the granite magma to varying degrees.

The K content of granites is of special interest for the establishment of a crustal average in connection with heat flow calculations. TAYLOR (1964) used VINOGRADOV's (1962) average of 3.34% to calculate a crustal average of 2.09% K (granite:basalt, 1:1). But this figure may be somewhat high if the bulk of the granitic rocks of the crust are "granodiorites" rather than "true granites". TUREKIAN and WEDEPOHL's (1961) estimate of 2.52% K for high-Ca granitic rocks (granodiorites) and 4.2% for low-Ca granites is almost identical with the average Snowy granodiorite and Cape Granite respectively. Undoubtedly the less abundant but

petrologically "more interesting" low-Ca granites have been consistently oversampled.

9-2. Rubidium.

Rb^{1+} forms the now well known close geochemical association with K due to closely similar chemical character. (Table 26 lists ionic radii, ionization potentials and electronegativities). The tendency for Rb to become enriched relative to K under processes of extreme differentiation is usually ascribed to the 10% larger ionic radius. The K/Rb ratio is therefore a good indicator of such differentiation processes and has been used as such in a number of previous studies. (For the latest reviews, see AHRENS, 1963; HEIER and ADAMS, 1963; TAYLOR, 1965).

A plot of K versus Rb for the Snowy rocks, shown in Fig. 13, has been discussed in Chapter 4. The conclusion was reached that the composition of the bulk of the granitic rocks, granodiorites (K/Rb av. 217) and gneisses (K/Rb av. 205) reflects that of their sedimentary source rocks; while the leucogranites showing K/Rb ratios varying from 55 to 150, av. 100, had formed from a magma that had undergone varying strong degrees of differentiation.

A number of points emerge from a similar K/Rb plot for the Cape Granites, shown in Fig. 44. (Table 19 lists calculated element ratios from total rock data of Table 18).

(1) The bulk of the Cape Granites, formed by the coarsely porphyritic cores of the plutons, show a slight but definite enrichment of Rb relative to K, with an average K/Rb ratio of 160; this suggests that

the Cape Granite Plutons formed after some distinct process of differentiation.

(2) The gradational medium-grained granites of the hood facies show rather variable K/Rb ratios averaging 163, but the finest-grained border facies granites have a lower K/Rb ratio (av. 137) and are regarded as even more strongly fractionated. The lowest K/Rb ratio obtained was from the Darling Microgranite (Sample 151, K/Rb = 98).

(3) Too few samples are available to firmly delineate degrees of differentiation between the different plutons, but the George Granite in the east (Samples 135, 142, 143) shows slightly higher K/Rb ratios averaging 190.

(4) The younger intrusive granites (Samples 163, 166, 167) from the Hoedjies Bay Contact, Saldanha, in spite of extremely high K and Si, also show unexpectedly "normal" K/Rb ratios of about 200.

(5) The "contaminated" Darling Granite (Sample 174) shows a slightly higher K/Rb ratio of 196, in spite of the fact that it contains over 20% modal mica (Table 21). This is consistent with an origin by contamination of normal Cape Granite magma with intruded Malmesbury Sediments. Although no data on the sediments in that area are as yet available, preliminary results by ERLANK (1965) on the Malmesbury in the Cape Peninsula region indicate a "normal" K/Rb ratio of about 210 (Table 7, no. 5).

(6) The biotite-rich xenoliths 175 and 176 from the Peninsula Granite, on the other hand, although presumably also of sedimentary

origin, are slightly enriched in alkalis with K/Rb ratios of 137 and 117 respectively. This is interpreted as due to some diffusion of Rb into these relatively small bodies. A similar but even more marked enrichment of trace alkali metals was noted by BOWLER (1959) for the contact aureoles and especially the small xenoliths in granites from south-western England.

Similar K/Rb ratios for K-feldspars separated from the different granites are shown in Fig. 45, while the following two figures show plots of all coexisting minerals analysed. In the normal, coarsely porphyritic granite the K/Rb ratio can be seen to increase in the order: biotite < chlorite < total rock < muscovite (sericite) < K-feldspar \approx plagioclase. Rb obviously enters the larger, 12 coordinated K site of the mica structure in preference to the 8-10 coordinated K site of feldspars.

Fig. 45 shows that the three main granite types are more readily distinguished by the K/Rb ratios of their K-feldspars than by similar total rock data. Thus, the average K/Rb ratio of the K-feldspars decreases from about 265 for the coarse granites to 214 for the medium-grained to 172 for the fine-grained, most differentiated granites. But it is shown below that this decrease is due not only to the real decrease in the K/Rb ratio of the more differentiated magma, but also to the approximately 6-fold decrease in mica content.

A different situation is shown, however, by the small K-feldspar phenocrysts from the Younger Saldanha Granites nearest the Hoedjies Bay Contact (Fig. 48, Samples 163, 164, 165, 166). These chilled granites contain very little biotite but have a cryptocrystalline or glassy matrix. The average K/Rb ratio of these four K-feldspars is as high as 360 compared with about 200 for their total rocks. This may be due to the preferential exclusion of Rb from the relatively few and small, early formed K-feldspars; subsequent rapid chilling at the contact prevented attainment of equilibrium and Rb was preferentially concentrated in the glassy matrix. On the other hand, the large K-feldspar phenocryst 173 from the migmatite zone, Sea Point (e.g. Fig. 35), and especially K-feldspar 174 from the contaminated Darling Granite show high K/Rb ratios due mainly to the large amount of coexisting biotite, which incorporates Rb preferentially. The K-feldspars from the relatively small pegmatitic bodies in the Peninsula Granite (Samples 169, 170, 171) show K/Rb ratios similar to the feldspars from the finer-grained granite; this indicates that they were not formed from a later, even more highly fractionated rest-liquid.

Within the limits of analytical uncertainty the K/Rb ratios of granite plagioclases 106 and 137 (Fig. 46) are the same as their coexisting K-feldspars.

Analysed biotites from the normal coarse granites show an average of about 1000 p.p.m. Rb and a K/Rb ratio of about 70

(Fig. 46). A slight decrease in K/Rb ratio is again indicated for biotites from the more differentiated finer-grained granites. Thus, biotite 149 shows a K/Rb ratio of only 52. But the biotites from the "contaminated" granites 173 and 174 and the Clifton Xenolith 175 contain less than normal Rb and higher K/Rb ratios of about 100; no doubt due to the unusually high biotite content of these rocks. Biotites from the Clifton Xenolith (Fig. 33) are also in other respects dissimilar enough from the biotites of the enclosing normal Peninsula Granite (e.g. Samples 117 and 118) to rule out an origin of this body from simple accumulation of granite biotites.

Biotites from the diorite-gabbros contain less Rb (520 p.p.m.) and higher K/Rb ratios than any granite biotites examined. Although the trace alkalis are probably less reliable as indicators of origin than some other trace elements, due to their high mobility, such strongly varying levels of trace elements can be of use in deciding on the origin of clastic micas derived from such different rock types.

The biotites used in this study were cleaned where necessary from any traces of chloritic alteration product. A chlorite concentrate from one normal, coarse granite (Sample 106, Fig. 47) was analysed as well. It was estimated still to contain 15-20% brown "biotite" as composite flakes. The K concentration of 1.48% shows that the material has lost most of this element, but a higher K/Rb ratio of 118 compared with 77 of the coexisting biotite shows clearly that Rb was lost preferentially during the alteration process.

Fig. 47 also shows the relatively high K/Rb ratio of 200 for the muscovite (sericite) in the normal coarse granite. This supports the idea that these small flakes are not of primary origin but are replacement products mainly of the feldspars. In the fine-grained granite, however, (Sample 147) which contains only traces of biotite, the muscovite contains 1400 p.p.m. Rb with a K/Rb ratio of 61, and is considered mainly primary. But in the small pegmatite, Sample 171, Rb entered the biotite (970 p.p.m., K/Rb=69) slightly more readily than the coexisting primary muscovite (900 p.p.m., K/Rb=96).

The Rb data for K-feldspars and micas suggested a mutual dependence on the modal composition of the granites. Therefore, in Fig. 49 the K/Rb ratios of K-feldspars from all normal granites, for which modal data was available, were plotted as a function of the biotite content of the rocks. Clearly, the K/Rb ratios of K-feldspars decreases significantly with decreasing biotite content of their host rocks. That only part of this decrease in K/Rb ratio is due to a concomittant decrease in the original magma from which the feldspars crystallized is shown by the smaller slope of AB, the average differentiation curve of the total rocks, plotted on the same scale. Neglecting the relatively much less important modal variations of other minerals and of K-feldspar itself, the difference in slope of the two trendlines in Fig. 49 therefore is a measure of the changing K/Rb ratio of the K-feldspars due to varying biotite content alone. This effect can only be explained

if Rb distributed itself between the two phases, K-feldspar and biotite, at least approximately according to the distribution law.

This is further suggested by the fact that the ratio

$\frac{\text{K/Rb in K-feldspar}}{\text{K/Rb in biotite}}$ varies about an average of about 3.8 for all rocks, for which the appropriate data were available.

A few points arise:

(1) The relative constancy of the Rb distribution between K-feldspar and biotite may indicate insensitivity of the equilibrium to changes in temperature and pressure. On the other hand, the granites studied probably crystallized under rather similar physical conditions.

BARTH (1961a) found that the ratio of the distribution of Rb (as also Li, Cu and Pb) between K-feldspar and plagioclase was not related to temperature. But plagioclase in granitic rocks contains only a very small proportion of the Rb present and K-feldspar and mica, although structurally different, have more comparable Rb levels and may be a more suitable pair for future investigation.

(2) It is obvious that quite generally trace element studies on only one mineral species in a rock mass must be interpreted with great caution since the distribution may be strongly affected by systematic modal variations.

(3) WALKER and MATHIAS (1946) suggested that the K-feldspars of the migmatite zone, Sea Point, in xenoliths, and in the Peninsula Granite itself were formed by a general late-stage potash enrichment.

However, this cannot be true unless this event resulted in conditions

enabling Rb to come to approximate chemical equilibrium between K-feldspars and biotites. Neither mineral could have been simply added subsequent to crystallization of the granite.

A small-scale example is demonstrated in Fig. 50 which shows plots of the K/Rb ratios of two samples (117 and 118) of normal Peninsula Granite, coexisting biotites and K-feldspars at indicated distances from Sample 175 of the dark, biotite-rich band of the Clifton Xenolith (Fig. 33). These samples contain 9.3%, 12.8% and 37.1% biotite respectively, and the sympathetic increase of the K/Rb ratios of K-feldspars and biotites indicates approximation to chemical equilibrium.

A similar pattern is shown at the Sea Point Contact (Figs. 28 and 38). Both the microcline porphyroblast, Sample 173, in the biotite-rich migmatite zone (e.g. Fig. 35) and the surrounding biotite flakes have distinctly higher K/Rb ratios than observed for these minerals in the other granite samples containing much less biotite. It again appears that this large K-feldspar did not form by a later, simply mechanical addition of alkalis, but crystallized in approximate chemical equilibrium with the biotite, presumably as part of the main granite intrusion, which resulted in free ionic mobility between the feldspar and the recrystallizing biotite derived from the meta-sediments.

The dependence of the K/Rb ratio of K-feldspars on the biotite content is also well illustrated by the Saldanha Granite

total rock analyses from the Slippers Bay Contact (McIVER, 1957) which show only small variations in K/Rb ratio. Towards the contact, the K/Rb ratio of the K-feldspars shows a sharp decrease in close sympathy with the sharply decreasing biotite content of the granites.

9-3. Cesium.

Cs^{1+} has an even lower ionization potential and electro-negativity than Rb (Table 26), but the more ionic character of the Cs-O bond is overshadowed by the much larger ionic radius of 1.67 Å. It is accordingly excluded from early formed K-minerals and is even more strongly concentrated than Rb at later stages of fractionation.

The most recent estimate by HEIER and ADAMS (1963) gives an average Cs content of 3 p.p.m. ($\text{K/Cs} = 7500$) for granodiorites and about 7 p.p.m. for granites ($\text{K/Cs} = 5000$). The Cs concentration of the granitic rocks here investigated ranges from 2.6 p.p.m. to 27 p.p.m.

A plot of the Rb-Cs relationship for the Snowy granites is shown in Fig. 51. The granodiorites and gneisses average 4.8 p.p.m. Cs ($\text{K/Cs}=5500$) and show a fairly constant Rb/Cs ratio of about 28. This is consistent with their proposed origin from essentially undifferentiated sedimentary material. By contrast, the strongly differentiated leucogranites (Cs averages 12 p.p.m., and $\text{K/Cs}=3200$) show a higher but far more variable Cs concentration, and the steeper line of Fig. 51 indicates a range of Rb/Cs ratios

from about 70 to 25. This could be interpreted as solely due to strong magmatic crystal fractionation, but the surprisingly low Cs concentration relative to Rb of some leucogranites is ascribed to variable loss of this highly mobile alkali element.

A somewhat similar pattern emerges from the Rb-Cs plot for the Cape Granites (Fig. 52). The high Cs average of 12 p.p.m. ($K/Cs=3300$) for the normal, coarse granites suggests that the Cape Granites generally formed as a result of a fractionation process. Preliminary results by ERLANK (1965) indicate an average of about 3.8 p.p.m. Cs for the Malmesbury Sediments in the Cape Peninsula Area (Table 7, no. 5). The general Cs average reported here for the Cape Granite is closely comparable to the K/Cs ratio of 3000 found by EDGE and AHRENS (1963) for one sample of Peninsula Granite (Table 9). As in the case of the Snowy granites, however, the most strongly differentiated finer-grained Cape Granites, although showing decreasing K/Rb ratios, seem to have lost variable amounts of Cs causing a shift in their Rb-Cs plot shown in Fig. 52. They therefore only average 10 p.p.m. Cs with a higher K/Cs ratio of about 4300, but varying from 2000 to 14,000. Quite generally, therefore, while very high Cs concentrations in granites may be used as evidence for an origin by differentiation, a low Cs content does not by itself indicate a completely different history. This uncertainty unfortunately strongly limits the potential use of Cs as petrogenetic indicator. The George and Younger Saldanha Granites from the Hoedjies Bay Contact also show low Cs concentrations.

The Cs distribution in granites has often been found to be rather erratic (e.g. DELEON and AHRENS, 1957; BOWLER, 1959; BUTLER and THOMPSON, 1963) and HEIER (1962) suggested that Cs is easily leached out of the feldspar structure but strongly adsorbed on mineral (especially mica) surfaces in rocks affected by late stage hydrothermal solutions. The high mobility of Cs was demonstrated by EUGSTER (1955) who showed that at 800°C Cs was nearly equally partitioned between sanidine and water.

The Cs concentration of the Cape Granite plagioclases was found to be at the sensitivity limit of about 1 p.p.m., but Rb-Cs plots of the K-feldspars and micas are shown in Figs. 53 and 54. Cs in the K-feldspars ranges from 5 to 56 p.p.m. The average K-feldspar from the coarsely porphyritic granite has 12 p.p.m., almost identical to the Cs concentration of the total rocks, but the K-feldspars from the medium- and fine-grained granites average 18 p.p.m. and 31 p.p.m. respectively while the average Cs content of their total rocks actually falls slightly. This increase in the Cs content of the K-feldspars is therefore far stronger than in the case of Rb and again must be mainly ascribed to the very low mica content of the fine-grained, most strongly fractionated granites. For comparison, Fig. 53 also shows the average trend-line shown by TAYLOR and HEIER (1960) for alkali feldspars from Southern Norway. Their line would be roughly parallel to a mean line for all Cape Granite K-feldspars, although still displaced. This difference may be due to analytical error to some extent, but the Cape Granites

are obviously enriched in Cs. It may be noted, that again the K-feldspars from the George Granite (Samples 134, 135, 142 and 143) and from the Younger Saldanha Granite nearest the contact have relatively low Cs concentrations.

Fig. 54 shows a similar Rb-Cs plot for the granite biotites, with Cs ranging from 28 to 260 p.p.m. As expected, biotites 177 and 178 from the more basic intrusives are much lower at 23 and 13 p.p.m. respectively.

Because of the larger size, Cs is expected to be more strongly concentrated than Rb in the larger 12 coordinated K positions of micas. This is confirmed by Fig. 55 which shows an average of about 10 for the ratio $\frac{K/Cs \text{ in K-feldspar}}{K/Cs \text{ in biotite}}$, while the ratio $\frac{K/Rb \text{ in K-feldspar}}{K/Rb \text{ in biotite}}$ is close to 4. The relatively constant Cs distribution between K-feldspars and biotites also suggests that Cs is at least in approximate equilibrium between these two phases for the different granites. Therefore, marked Cs loss is unlikely to have occurred as a result of secondary processes. It seems more likely, that most of any Cs loss, especially from some of the most strongly differentiated border facies granites, occurred at the last stages of crystallization owing to high volatile pressure. However, the K-Cs plot of the minerals from the coarse Peninsula Granite 106 (Fig. 56) shows that within the limits of analytical precision the chlorite has the same K/Cs ratio of about 900 as the biotite from which it was derived by alteration. By contrast, Fig. 47 showed the same chlorite to have lost Rb preferentially

to K. Cs may be adsorbed on the chlorite surface to some extent as also on that of the secondary muscovite (sericite).

9-4. Thallium.

SHAW (1957), in a review of the geochemistry of Tl, gave it's crustal abundance as 1.3 p.p.m., but a more recent estimate by TAYLOR (1964) shows a lower average of 0.45 p.p.m. BROOKS and AHRENS (1961a) give a granite average of only 0.75 p.p.m. with a Rb/Tl ratio of about 200.

The method of analysis used in this study for the volatile elements Pb, Tl, Ga, Cu and Sn is a modified spectrochemical technique described in detail by KOLBE (1965). By arcing large amounts of sample in a constant stream of oxygen delivered through a Stallwood jet the sensitivity limit achieved for Tl is about .5 p.p.m. with a detection limit of .2 p.p.m.

Tl^{1+} (1.47A) substitutes for K^{1+} (1.33 A) in K silicates, but it's more covalent bond with oxygen also allows it to enter sulphides to some extent. Because of equality of charge and radii Rb and Tl should form a close association, but since the Rb-O bond is more ionic than the Tl-O bond, a general decrease of the Rb/Tl ratio is noted in the sequence from basic ($Rb/Tl > 300$) to acid rocks ($Rb/Tl \sim 200$) to pegmatites (< 150) (TAYLOR, 1965).

The Rb-Tl relationships of the Snowy granites are shown in Fig. 57. The granodiorites average 1.1 p.p.m. Tl, ranging from 0.6 to 1.6 p.p.m. The differentiated leucogranites are distinctly higher with an average of 2.1 p.p.m. (range, 1.5 to 3.2 p.p.m.).

The high-level Cape Granites, similarly plotted in Fig. 58, show an average of 1.8 p.p.m. (range, 1.1 to 3.1). This level may be compared with BROOKS and AHRENS' (1961b) result of 1.3 p.p.m. for Cape Peninsula Granite listed in Table 9.

Among the Cape Granites, showing a mean Rb/Tl ratio of about 150, the most differentiated finer-grained varieties cannot be readily distinguished on the basis of Tl concentrations because of the appreciable spread shown in Fig. 58. The Rb/Tl ratio of the Snowy granites actually increases from an average of about 110 for the granodiorites to 185 for the late-stage leucogranites (Fig. 57) in spite of the demonstrated concomittant decrease in the average K/Rb ratio from 220 to 100.

Tl and the Rb/Tl ratio are therefore not very reliable indicators of fractionation. Similarly, BUTLER (1962) found a fairly regular Tl increase with Rb for some high-level calc-alkali granites from Malaya and Cornwall, England but noted that in alkali granites from Northern Nigeria, Tl increases with Rb when Rb is below about 300 p.p.m., but fails to increase much for higher concentrations of Rb.

KOGARKO (1959) and VOSKRESENSKAYA (1959) demonstrated the greater mobility of Tl relative to Rb during metasomatism. The data presented here suggests that, as for Cs, some of the most differentiated members of the Snowy and Cape Granites have lost variable amounts of Tl during the last stages of their crystallization.

ZLOBIN (1958) suggested that Tl is concentrated in halogen-rich magmas by forming $TlCl$. This dissociates on crystallization Tl entering the K-positions. Some Tl in this form could presumably be easily lost due to the movement of volatiles into the intruded country rock. The probably higher volatile concentration might account for the apparent Tl (and Cs) loss mainly from the most differentiated granites. These also either form relatively smaller intrusive bodies or the border facies in the case of the Cape Granite Plutons. In the case of Tl an additional factor may be the earlier removal of even very small amounts of a sulphide phase.

Rb-Tl plots for all Cape Granite K-feldspars are shown in Fig. 59. One of the two dashed lines shown represents the relationship for pegmatite minerals found by AHRENS (1948); the other, due to TAYLOR and HEIER (1960), is also based mainly on K-feldspars from large pegmatites. As for Cs, the observed increase in the average Tl content of the K-feldspars (1.7 p.p.m. for K-feldspars from coarse granites to 3.6 p.p.m. for those of the fine-grained granites) and decrease in the Rb/Tl ratio (240 to 180) with increasing fractionation of the Cape Granites must again be attributed to the strong decrease in modal biotite with fractionation.

Because of its size, Tl enters biotite more readily than K-feldspars. The distribution factor relative to the major element K, viz. $\frac{K/Tl \text{ in K-feldspar}}{K/Tl \text{ in biotite}}$, averages about 10, almost identical with that of Cs, but more than twice as high as for Rb (~ 4).

Tl ranges from 5 to 16 p.p.m. in the Cape Granite biotites with an average Rb/Tl ratio of about 100. Compared with the biotites the primary muscovites (Samples 147, 171 and 172) have distinctly lower Tl concentrations (Rb/Tl about 360). This is in marked contrast to their apparently comparable Rb/Cs ratios. This may be due to an inherent greater difficulty of Tl entry into the muscovite lattice, although possibly some Tl may be present in the biotites as sulphides, but not in muscovites.

9-5. Barium.

Among the divalent trace elements only Ba^{2+} (1.34 Å) is of about the same size as K^{1+} (1.33 Å) and is captured in early formed K-minerals (e.g. HEIER, 1962) despite the slightly more covalent character of the Ba-O bond.

However, also partly due to the relatively late crystallization of the main K-minerals, NOCKOLDS and ALLEN (1953) found gradually increasing Ba concentrations and relatively constant K/Ba ratios in the calc-alkali igneous rock series examined. A sudden sharp decline in Ba was observed only in the very latest differentiation stages of the E. Sierra Nevada and Scottish Caledonian Series.

The sudden depletion of Ba only in the most fractionated Snowy leucogranites is illustrated in the Ba-Sr plot of Fig. 12. The Snowy granodiorites and gneisses show relatively little variation about an arithmetic mean of about 590 p.p.m. ($K/Ba = 45$ for the granodiorites), but Ba varies strongly in the leucogranites averaging 270 p.p.m. K/Ba varies from 49 to 1750 (Table 5). The three

least differentiated leucogranites (Samples 6, 11 and 12) are apparently not depleted in Ba. They also have relatively high Sr and low Rb and Cs.

The high-level, coarse Cape Granites (Fig. 60) average 650 p.p.m. Ba with a K/Ba ratio of 64, but the trend of their further strong differentiation with decreasing grain-size is indicated by the much lower Ba (and Sr) level of the fine-grained facies varying from 270 to 30 p.p.m.

The rather erratic sharp decline of Ba only at the end of strong differentiation makes estimation of the average Ba content of "granites" especially difficult. On the basis of two granitic composites analysed by GAST (1960), TUREKIAN and WEDEPOHL (1961) assigned values of 420 p.p.m. to high-Ca granites and 840 p.p.m. to low-Ca granites. This implies a two-fold Ba increase with differentiation, which does not seem to apply generally, especially since the quoted Sr level falls from 440 to 100 p.p.m. Thus, the averages quoted by Turekian and Wedepohl should be reversed.

Of all trace elements sought, Ba displays the strongest variation in the Cape Granite minerals. Fig. 61 shows the general inverse relation between Ba and Cs in the K-feldspars, which vary from 4500 p.p.m. Ba (no. 174 from the contaminated Darling Granite) to only 45 p.p.m. in K-feldspar 150 from the strongly differentiated, fine-grained Malmesbury Granite. The Ba/Cs ratio similarly declines with progressing differentiation of the granites from 900 to 2, a drop even more marked than that shown by the 100-fold decrease in

the Ba/Rb ratio (Table 22). Fig. 61 also shows that granite plagioclases 106 and 137 are lower in Ba relative to their coexisting K-feldspars by a factor of about 5, although their K/Ba ratios are comparable (Tables 22 and 23).

Fig. 62 shows the well developed inverse Ba-Cs relation of the Cape Granite biotites, which vary in Ba content from 1900 to 110 p.p.m. Coexisting primary muscovites (e.g. Sample 171) are somewhat lower. Data from NOCKOLDS and MITCHELL (1948) show Ba to be concentrated in K-feldspars relative to biotites by a factor of about 2. TAYLOR (1965) ascribed this to the greater difficulty of charge balance in the K^+ positions of the mica structure. The Ba distribution ratio between K-feldspars and biotites averages about 3, but varies rather more than, for instance, the Rb distribution ratio. This is mainly due to the relatively higher Ba levels of biotites 130, 131 and 141 from the Saldanha Granite, Slippers Bay Contact, and biotite 122 from Malmesbury Granite. These four biotites are also distinguished by relatively higher levels of Ca, Pb and Zr, higher Fe/Mg ratios and low Cr, Ni and trace alkalis, especially Cs.

In the diorite-gabbros (Samples 177 and 178), which contain little or no K-feldspar, Ba is more strongly concentrated in the biotites (Fig. 62) relative to their coexisting plagioclases (Fig. 61).

9-6. Sodium and Calcium.

The $Na_2O - SiO_2$ variation diagram shown in Fig. 17 indicates a slight increase in Na towards the most acid members of both Cape

and Snowy Granites. The relatively low Na content of the Snowy granodiorites probably reflects the strong contribution of shale-rich parent material; this applies especially to the Snowy gneisses which contain only 1.16% Na with the unusually high K/Na ratio of 3.0.

The observed Na and Ca concentrations in Cape Granite feldspars have been discussed in Chapter 8-4. Apparently no simple relation exists between their Na content and that of coexisting biotites which average only about 1400 p.p.m. (Table 24); but both sericite and the primary muscovites analysed show higher Na at about 5500 p.p.m.

The normally expected decrease in Ca with differentiation of granites is also illustrated in Fig. 17. The rather variable Ca concentration of the Cape Granite biotites (Table 24) must be largely due to small inclusions of apatite; primary muscovites are uniformly lower with only about 500 p.p.m. Ca.

9-7. Strontium.

	<u>Ca%</u>	<u>Sr p.p.m.</u>	<u>Ca/Sr</u>
Average Basalt*	7.6	465	163
Average High-Ca Granite*	2.53	440	58
Average Low-Ca Granite*	.51	100	51
<hr/>			
Snowy Mts. gneisses	.68	113	60
granodiorites	2.07	190	109
leucogranites	.51	42	121
<hr/>			
Cape coarsely porphyritic Granites	1.17	110	106
medium-grained Granites	.89	77	116
fine-grained Granites	.42	20	210
<hr/>			

* (TUREKIAN and KULP, 1956).

The average Sr levels of the corresponding main granite types from both areas are lower by a factor of about two, compared with the averages of TUREKIAN and KULP (1956). The Sr results shown here are well controlled by the primary standards listed in Table 29 and some additional isotope dilution values (Table 18). The low Ca and Sr concentrations of the Snowy gneisses reflect their origin from a shale-rich sediment.

Sr^{2+} (1.12 Å) is intermediate in ionic radius between K^{1+} (1.33 Å) and Ca^{2+} (.99 Å) and occurs principally in the Ca positions of plagioclase and the K positions of K-feldspar, but only to a very small extent in the Ca-bearing ferromagnesian minerals. During fractionation of basic magma the Ca/Sr ratio decreases towards a minimum at the granodiorite stage to increase again in highly differentiated granites because of the additional removal of much Sr by capture in the earlier K-feldspars.

The strong decrease of Sr (and Ba) in the K-feldspars with increasing fractionation of the Cape Granites is shown in Fig. 63. The observed simultaneous decrease in the Ba/Sr ratio from about 10 to nearly 1 is comparable to the range found by HEIER and TAYLOR (1959b) in alkali feldspars from large pegmatites. The preferential entry of Ba, despite its larger radius, is ascribed to the more ionic character of the Ba-O bond. Fig. 63 also demonstrates the very similar Sr levels of granite plagioclases 106 and 137 relative to their coexisting K-feldspars. A rather uniform Sr distribution ratio close to unity was also noted by HEIER (1962).

Compared with the strongly decreasing Ba/Sr ratios of the K-feldspars the total rock Ba-Sr plots of the Snowy granites (Fig. 12) and of the Cape Granites (Fig. 60) show much less change of the Ba/Sr ratio and only a slight decrease in the most differentiated granites. This relatively more constant rate of decrease of Ba and Sr is due to the strongly varying Ba/Sr ratios of the major minerals crystallizing: plagioclase removes Sr at a much faster rate than Ba, K-feldspar preferentially incorporates Ba, and the quantitatively less important mica contains virtually only Ba.

As can be seen from Table 24 the Sr level of the biotites averages only about 6 p.p.m., of which about 2.3 p.p.m. is radiogenic as indicated by Samples 104, 108 and 110. Apart from the valency difficulty TAYLOR (1965) ascribed the very low level of Sr in micas to the difficulty for the usually 8 or 10-coordinated Sr to occupy the larger 12-coordinated K positions of the micas.

Biotites 177 and 178 from the diorite-gabbro intrusions stand out with 11 and 20 p.p.m. Sr respectively. Their higher Sr levels relative to the granite biotites is expected from the greater Sr contents of their total rocks and plagioclases (Fig. 63). Primary muscovites have Sr levels comparable to the biotites, but the higher Sr content of 16 p.p.m. shown by muscovite 172 from the George Granite pegmatitic vein is also matched by similarly higher Sr of the coexisting K-feldspar. This vein, intruded into bordering schists, is clearly not a late-stage granite differentiation product and is strongly dis-

similar to the other small pegmatites whose minerals in most respects resemble those of the more differentiated, finer-grained Cape Granite facies.

9-8. Lead.

Despite the observed variation of Pb from 14 to 69 p.p.m., the averages of all main granite types, both from the Snowy Mts. (Table 4) and of the Cape Granites (Table 18) are close to about 30 p.p.m.. The low Pb content of the Snowy Amphibolite (no. 36, 8.6 p.p.m.) is consistent with an origin from basic rock and the Cape diorite-gabbro intrusions are also relatively lower with 16-18 p.p.m. Pb. The granite data does not show the expected increase of Pb in the most differentiated granites, although the Pb distribution, especially in the most fractionated granites, is too erratic for any firm conclusions. The Snowy leucogranites actually have a lower mean of 23 p.p.m., compared with the granodiorites. Among the Cape Granite the three samples of Paarl Granite (120, 139 and 140) stand out by significantly higher than average Pb values of 54, 54 and 53 p.p.m. respectively. (Paarl Granite also shows the highest U and Th concentrations encountered).

WEDEPOHL (1956) reported the average Pb contents of basic, granodioritic and granitic rocks as 6, 15 and 20 p.p.m. respectively. He used a spectrographic technique employing PbO standards diluted with quartz, and his reported analyses of G-1 and W-1 were 26 and 6 p.p.m. respectively. The more recent results reported in STEVENS

et al. (1960) and by FLEISCHER and STEVENS (1962), however, indicate 49 and 8 p.p.m. respectively. These values were used as primary standard points in the present study. Therefore, unless the earlier reported lower results are due to suggested inhomogenous distribution of Pb in different samples of G-1, older spectrographic Pb results based on the lower G-1 value will be systematically too low. WEDEPOHL's (1956) average for granitic rocks multiplied by a factor of 49/26 would be close to the overall average of about 30 p.p.m. obtained here for the Snowy and Cape Granites.

Divalent Pb^{2+} (1.20 Å) is very close in size to Sr^{2+} (1.12 Å) and therefore also intermediate between Ca^{2+} (.99 Å) and K^{1+} (1.33 Å). According to the classical Goldschmidt Rules it should therefore also be captured in early K positions. The much higher electronegativity and ionization potential (Table 26), however, indicate the strongly covalent character of the Pb-O bond. In spite of smaller radius and double charge, Pb is thus not expected to be concentrated in early K^{1+} positions, while both size and bond-effect would tend to exclude it from early Ca^{2+} positions (TAYLOR, 1965).

Although GOLDSCHMIDT (1954, p.399) maintained that Pb was concentrated in early K minerals, data presented by WEDEPOHL (1956) and by HEIER and TAYLOR (1959a) show Pb enrichment in the most fractionated pegmatite K-feldspars. It is therefore of interest to note that Pb in the Cape Granite K-feldspars (Table 22), although not very uniform in its distribution, shows a slight but definite decrease with increasing differentiation of the granites:

<u>K-feldspars from</u>	<u>Range, p.p.m.</u>	<u>Average.</u>
Coarsely porphyritic Cape Granite	23 - 60	41
Medium-grained Cape Granite	16 - 58	34
Fine-grained Cape Granite	< 6 - 43	28
Small granite pegmatites	19 - 26	22

Furthermore, the highest Pb values recorded were in K-feldspar 174 (67 p.p.m.) from the contaminated Darling Granite and in K-feldspar 172 (64 p.p.m.) from the George Granite pegmatite vein; both feldspars are also least differentiated with respect to other trace elements, e.g. they contain high Ba and Sr, but low trace alkalis.

Available data on the distribution of Pb between K-feldspars and coexisting plagioclases presented by HEIER (1962) is also not very conclusive, but on an average the distribution ratio is close to unity. In general the concentration of Pb is here found to decrease in the order, K-feldspar > total rock > plagioclase > biotite > primary muscovite > sericite. In granites 106 and 137 the ratio Pb in K-feldspar/Pb in plagioclase is about 1.8.

The Pb concentration of the biotites averages about 15 p.p.m., half the level of K-feldspars, but in the three samples of Saldhana Granite from the Slippers Bay Contact (nos. 130, 131 and 141) the biotites are strongly enriched in Pb, with up to 95 p.p.m. in biotite 141. Their K-feldspars appear normal and, as a result of the high Pb concentration of the micas, these three total rocks contain higher Pb than the K-feldspars. The higher Ca level of these

three biotites suggests the presence of apatite inclusions (Table 24); these may be particularly enriched in Pb, here substituting for Ca in 9-fold coordination with oxygen. However, the highest Pb value of 130 p.p.m. obtained from pegmatitic biotite 171 is not accompanied by similarly high Ca. K-feldspar 171 shows a normal and much lower Pb concentration of 26 p.p.m.

TAUSON and KRAVCHENKO (1956) found that about 10-20% of the total Pb in K-feldspars and 30-50% of the total Pb in granites was extractable with HCl. As suggested by TAYLOR (1965) the observed somewhat erratic distribution of Pb may be due to the presence of some Pb in the sulphide phase as galena. Thus earlier formed minerals could be expected to contain more sulphide inclusions, while the erratically high Pb concentration of only a few late-stage biotites may be metasomatic. With some increase in sensitivity and precision a number of such problems of trace element distribution in minerals should be attempted by the use of an electron microprobe.

9-9. Yttrium.

Average values and ranges observed (in brackets) of Y and the rare earths, La and Nd, in the main granite types are summarised below from Tables 4 and 18:

<u>Snowy Mts.</u>	<u>Y p.p.m.</u>	<u>La p.p.m.</u>	<u>Nd p.p.m.</u>
Granodiorite	37 (17-56)	41 (< 15-65)	-
Gneiss	33 (25-41)	38 (34-41)	-
Leucogranite	26 (19-36)	~ 30 (< 15-54)	-
<u>Cape Granite</u>			
Coarsely porphyritic	26 (21-42)	40 (24-65)	33 (< 15-54)
Medium-grained	24 (16-36)	34 (< 15-60)	28 (< 20-50)
Fine-grained	26 (8-39)	~ 15 (< 10-26)	< 20 (< 15-35)

Y figures given by EDGE and AHRENS (1963) for a sample of Cape Peninsula Granite (22 p.p.m.) and for quartz porphyry (30 p.p.m.) from Hoedjies Bay, are closely similar to the values found here. The most recent general data survey by FLEISCHER (1965) showed averages of 34 p.p.m. for granodiorites and 52 p.p.m. for granites and quartz porphyries.

While the average Snowy granodiorite is very close to the average granodiorite quoted, the strongly differentiated Snowy leucogranites actually contain less Y, as do the high-level Cape Granites. Average La and Nd concentrations also apparently decrease in the most strongly differentiated granites of both areas. NOCKOLDS and ALLEN (1953) similarly noted a decrease in Y at the extreme acid end of the E. Central Sierra Nevada Series. The generally rather uniform Y concentrations from basic to acid igneous rocks noted by FLEISCHER (1965) is also shown here by the analyses of the Snowy Amphibolite (Sample 36, 42 p.p.m.) and the Cape diorite-gabbros (Samples 177, 178; 34 and 27 p.p.m.).

The data on the Cape Granite minerals, given in Tables 22, 23 and 24, indicate a decrease of Y in the order: biotite > (total rock) > plagioclase > K-feldspar, muscovite, sericite, chlorite.

	<u>Y p.p.m.</u>
Biotite	48 (32-90)
Plagioclase	11, 30
K-feldspar, coarse granite	< 5
medium-grained granite	~ 5
fine-grained granite	9.2 (5.4 - 20)
small pegmatites	< 5
Muscovite, sericite, chlorite	< 8

However, summation of the Y contents of the major minerals indicates that more than half of the total Y in the granites is not accounted for and therefore must be concentrated in accessory minerals not analysed.

In spite of smaller radius and higher charge Y^{3+} (.92 A), is preferentially excluded from early Ca^{2+} (.99A) positions, presumably due to the more covalent character of the Y-O bond relative to the Ca-O bond. In granites Y is known to be concentrated strongly in apatite, and also in other accessory minerals such as sphene, zircon, monazite, allanite and the yttrium mineral xenotime, YPO_4 . All these minerals have been observed in the Cape Granite. Since the Ca concentration of granites is determined largely by the plagioclase, no simple Ca-Y relationship can be expected — nor was it observed in the granites here investigated.

The high Y concentration of the biotites must, to a considerable extent, be due to the ubiquitous inclusions of accessory minerals. It is difficult to decide whether Y is present in feldspar lattice sites. The higher level of Y in plagioclase relative to K-feldspar could be explained by the larger number of Ca sites available in plagioclase. But submicroscopic mineral inclusions could well occur in granite feldspars. This might also explain the observed Y increase in the K-feldspars from the fine-grained, more rapidly cooled granites. An apparent Zr-Y relation also exists for K-feldspars and biotites for all cases where these two elements were present above their detection limits.

It is noteworthy that in marked contrast to the biotites from the granite, biotite samples 177 and 178 from the diorite-gabbro intrusions have no detectable Y (< 5 p.p.m.), much less than their plagioclases with 11.2 and 17.5 p.p.m. respectively. In these rocks much of the Y may be contained in the relatively abundant euhedral apatite crystals scattered throughout the rock.

9-10. Lanthanum and Neodymium.

The observed concentration of these two rare earths in the main granite types is given in the previous section. Nd especially was never far above the spectrographic sensitivity limit; it was not determined in the Snowy granites and sought, but not detected, in the Cape Granite minerals.

The La and Nd figures obtained by EDGE and AHRENS (1963) for two samples of Cape Granite (Table 9) are rather higher than the levels quoted here, but are more nearly comparable when the lower values for standards G-1 and W-1 used here are considered (Table 29).

Both elements show strong variations in different granite samples, but averages again appear lower in the most differentiated granites of both areas. There is a general coherence of Zr and La for all granites indicating that Zr similarly decreases (as Y to a lesser extent) in the final differentiates. Thus either a greater part of the accessory minerals, such as zircon, was removed by slightly earlier crystallization, or a considerable proportion of the rarer elements was lost, possibly as complexes, during the final

stages of differentiation. Fig. 64 shows a La-Nd plot of all Cape Granites in which these two elements were above their detection limits. The average La/Nd ratio is about 1.1. Sample 175, the dark band of the Clifton Xenolith, shows by far the highest concentration: 105 p.p.m. La and 95 p.p.m. Nd.

The ionic radii of La^{3+} (1.14 Å) and Nd^{3+} (1.04 Å), members of the lighter and larger "cerium earths", are slightly bigger than that of Ca^{2+} (.99 Å), the common cation closest in size with which the rare earths are known to display diadochy. Apart from the additional size effect in the case of the larger R.E. ions the generally observed enrichment of the whole R.E. group in residual melts is ascribed to the slightly more covalent character of the R.E.-O bond in comparison with the Ca-O bond (RINGWOOD, 1955a; TAYLOR, 1965). But, as for Y, no clear Ca-La or Ca-Nd relationship was found in the granites.

Data on granite minerals given by CHASE et al. (1963) indicate that La is concentrated in mica relative to the total rock while K-feldspar contains levels comparable to that of the host granite. But, apart from the unusual xenolithic biotite 176 (78 p.p.m. La) and biotite 173 from the Sea Point migmatite zone (85 p.p.m.), La was not detected (< 25 p.p.m.) in the granite micas or occurred as trace in a few (Table 24). The observed La concentration of biotite, muscovite, sericite and chlorite is thus generally lower than that of the total rocks. Similarly only a few feldspars

showed a trace of La (< 15 p.p.m.); in the bulk of feldspar samples it was not detected (< 10 p.p.m.).

The observed distribution of the "cerium earths", La and Nd, is thus in strong contrast to that of Y which was found to be enriched in biotite to some extent (or in accessory minerals occurring in the biotites). Previous data on the differential enrichment of the "cerium group" and "yttrium group" in different accessory minerals is discussed by TAYLOR (1965).

9-11. Thorium and Uranium.

The average Th, U and K (γ -ray) concentrations obtained for the principal granite types are summarized below from Tables 4 and 18. Mean values of collected analyses given by CLARK, PETERMAN and HEIER (1965) for granodiorites, silicic igneous rocks and "common" shales are included for comparison:

	<u>Th (range)</u>	<u>U (range)</u>	<u>Th/U (range)</u>	<u>K%</u>
Snowy Mts. Gneiss	19.9(19-22)	4.0(3.4-4.4)	5.0(4.3-6.4)	3.26
granodiorite	17.0(8.7-27)	3.8(1.4-5.1)	4.5(2.0-7.9)	2.60
leucogranite	17.2(8-27)	8.0(2.7-15)	2.2(0.7-6.7)	3.82
Cape Granite, coarse	21.6(14-59)	6.5(2.3-20)	3.3(1.3-9.9)	3.93
medium & fine	29.6(4.8-62)	12 (4.3-21)	2.5(0.3-5.4)	4.28
Av. granodiorite	9.3	2.6	3.6	(2.55)
Av. silicic igneous	20	4.7	4.3	
Av. "common" shale	12 (2-47)	3.7 (1-13)	3.8 (1-12)	

Fig. 65 shows a Th-U plot for all rocks analysed. The Snowy Amphibolite (Sample 36) and the Cape diorite-gabbros (Samples 177 and

178) plot close to the crustal average Th/U ratio of about 3.5 (ADAMS et al., 1959), but the granitic rocks show a very considerable scatter. Th and U in the granites show no apparent correlation with any other element.

Compared with the average granodiorite given above the Snowy granodiorites and gneisses have generally higher Th and U levels. In both Snowy and Cape Granites U is distinctly enriched in the most fractionated rocks. Rather surprisingly, the Snowy leucogranites are not similarly enriched in Th. The strongly differentiated fine-grained Cape Granites also show only a relatively slight Th increase. As a result the average Th/U ratio decreases in the most fractionated granites of both areas. In view of the spread of results, the number of samples may be rather limited for a firm conclusion, especially for the Snowy leucogranites. For instance, the average for the Snowy leucogranites is strongly affected by the exceptionally low Th/U ratios (about 0.7) of the two samples of Eucumbene Granite (Fig. 65, nos. 8 and 9). The lowest Th/U ratio observed is 0.26 for the fine-grained Cape Granite 147. Unfortunately this represents the only sample from Kloof Quarry analysed radiometrically.

IMMELMAN (1934) determined the radium content of 14 selected samples of Cape Granite by the fusion method. The average, recalculated from Ra²²⁶ as U²³⁸, is 7.7 p.p.m. U (range 4.7-10.1), remarkably close to the results obtained here, but the values of 7.6 and 4.4 p.p.m. U for two samples of Yzerfontein Diorite are considerably

higher than those obtained here for the Malmesbury diorite-gabbros (1.0 and 2.1 p.p.m.). On the basis of the published Cape Granite results SCHOLTZ (1946) suggested that the finer-grained, more acid varieties might be distinguished by lower radioactivity. Data of this study show the reverse to be the case.

One distinctive regional feature among the Cape Granites is the high and very similar Th (60 p.p.m.) and U (16-21 p.p.m.) concentration of all three samples of Paarl Granite (nos. 120, 139 and 140). These granites are also distinguished by high Pb and slightly higher than average Be.

Studies by WHITFIELD et al. (1959), ROGERS and RAGLAND (1961) and others indicate a general increase in both Th and U with differentiation of granitic rocks. The more erratic U distribution and a slight increase in the Th/U ratio of later-stage granites is usually explained as due to selective removal of soluble $(\text{UO}_2)^{2+}$ formed under oxidising conditions. LARSEN and GOTTFRIED (1960) found no increased loss of U relative to Th during later stages of crystallization.

On the basis of melting point data the $\text{Th}^{4+}\text{-O}$ bond is stronger than the $\text{U}^{4+}\text{-O}$ bond and the Th/U ratio should decrease during fractionation (TAYLOR, 1965). But the large, quadrivalent Th^{4+} (1.02 Å) and U^{4+} (.97 Å) ions do not enter lattice sites of the common rockforming minerals. Data presented by ADAMS et al. (1959) show that accessory monazite and allanite concentrate Th, while zircon, apatite, sphene and xenotime contain relatively more U.

Acid leaching studies by PLILLER and ADAMS (1962) indicate that most of the Th and U of granodiorite is situated in acid soluble minerals or in interstitial materials, e.g., along grain boundaries or fractures.

All accessory minerals mentioned above have been observed in the Cape Granite, but no quantitative data are available. The most feasible explanation of the decreasing Th/U ratio in the most differentiated, fine-grained Cape Granites of the border facies may lie in the outward migration of late-stage hydrothermal fluids. Being more soluble, U would be preferentially moved to the periphery of the granite plutons.

9-12. Zirconium.

Published Zr averages of the major igneous rocks (DEGENHARDT, 1957; CHAO and FLEISCHER, 1960; TAYLOR, 1965) show relatively small variations: ultrabasic 50 p.p.m., basalt 150, granodiorite 140, and granite 180 p.p.m. The averages of the major granite types here investigated are:

Snowy Mts. gneiss	221 (range: 200-245)
granodiorite	195 (97-350)
leucogranite	88 (52-138)
Cape, coarse granite	216 (115-330)
medium-grained granite	170 (115-300)
fine-grained granite	107 (28-235)

In spite of some erratic fluctuations Zr obviously decreases in the most differentiated rocks of both areas by a factor of about 2.

This decrease is similar to that observed for La and Nd and leads to a direct Zr-La relationship for the granites. The granites also show a general inverse Zr-Cs relationship; but this is most definite in the case of the Snowy leucogranites, plotted in Fig. 66.

NOCKOLDS and ALLEN (1953) also found the Zr content in general to rise gradually from the low basic end of each of the rock series examined by them, then stay more or less constant, and fall again at the extreme acid end. According to CHAO and FLEISCHER (1960) regional variations of the Zr distribution indicate possible inhomogeneity in the mantle. But regional variations of essentially undifferentiated gneisses and granodiorites probably rather reflect the erratic Zr distribution of original sedimentary source materials. Due to the marked resistance of zircon to weathering, strong local accumulations could be expected in some resistate sediments. However, the strong variations observed in highly differentiated granites must be due to magmatic processes.

As a free ion Zr^{4+} (.79 Å) may substitute for Fe^{3+} (.64 Å) to some extent following Ti^{4+} (.68 Å); it is known to enter pyroxenes and also apatite (TAYLOR, 1965). RINGWOOD (1955b) considered that, due to the high ionic potential, Zr should occur mainly as ZrO_4^{-4} complexes in magma. Because of their larger size relative to SiO_4^{-4} these should become concentrated in residual melts. The granite data from both areas here considered indicates that, unless a substantial part of the Zr is lost completely from the most highly fractionated

granites, any Zr complexes do not accumulate to the very last stages of differentiation but probably break down to form zircon, $ZrSiO_4$, throughout crystallization of the granites.

The granite biotites and chlorite (Table 24) average about 150 p.p.m. Zr, with a range from 85 to 275 p.p.m., but only a trace (here < 15 p.p.m.) was found in muscovites or sericite. Probably most of the Zr found in the biotites is due to the small, microscopically observed zircon inclusions; no Ti-Zr coherence can be seen.

Most K-feldspar analyses (Table 22) from the normal Cape Granite also show traces of Zr (4-6 p.p.m.) with somewhat higher levels averaging 12 and 9 p.p.m. for the K-feldspars from the fine-grained facies and the Younger Saldanha Granite respectively. The recalculated granite plagioclases, (Table 23, 106 and 137) show the surprisingly high Zr level of 100 p.p.m.. But plagioclases 177 and 178 from the diorite-gabbro intrusion are even higher with 470 and 330 p.p.m. respectively. (Their biotites have only 70 and 50 p.p.m., considerably lower than the granite biotites). NOCKOLDS and MITCHELL (1948) similarly found high Zr in some plagioclases, but not in K-feldspars. This must be due mainly to very small mineral inclusions.

9-13. Tin.

Due to an ionic potential slightly higher than that of Zr^{4+} , Sn^{4+} will also tend to form complexes (SnO_4^{-4}) in silicate melts (RINGWOOD, 1955b). Because of size difficulties these again will not readily be accepted in silicate lattices and should therefore accumulate in residual melts. Apart from occurring as

cassiterite, however, tin as the free ion Sn^{4+} (.71 A) may also display some diadochy with Fe^{3+} (.64 A), Ti^{4+} (.68 A) or Zr^{4+} (.79 A) and is further known to occur in sulphides (TAYLOR, 1965). Data by ONISHI and SANDELL (1957), BARSUKOV (1957), and HAMAGUCHI et al. (1964) indicate averages of about 1 p.p.m. Sn for basic rocks, 3.5 p.p.m. for granites, but up to 30 p.p.m. for tin-bearing granites.

The Sn results discussed here were obtained by the modified spectrochemical technique described in KOLBE (1965). The detection limit achieved, 1 p.p.m., is probably just adequate for a study of Sn in granitic rocks.

The concentration range of 2.0 to 4.2 p.p.m. observed for all granite samples is remarkably small, and no relationship was observed between Sn and other elements, such as Ti. In marked contrast to the behaviour of Zr, Sn in the granites of both areas increases slightly with increasing fractionation. The Snowy granodiorites average 3.0 p.p.m., increasing to 3.5 p.p.m. in the Snowy leucogranites (Table 4). The coarsely porphyritic granites forming the bulk of the Cape Plutons also average 3.0 p.p.m., while the marginal, more leucocratic, fine-grained facies show a mean of 3.4 p.p.m. (Table 18). Three previously published Sn figures on samples of Cape Granite, due to Ahrens and coworkers, are listed in Table 9.

The Younger Saldanha Granite at Hoedjies Bay (Samples 163, 166 and 167) may generally be slightly higher in Sn (average obtained: 4.1 p.p.m.), but apparently normal levels were recorded from three

samples of the Kuils River Granite (nos. 119, 137 and 149) which is cut by the NW trending, cassiterite-bearing zone of mineralization (see Chapter 6-2).

However, the Sn concentration of the K-feldspars from the three latter samples (4.0, 4.0 and 5.3 p.p.m.) is rather higher than the observed mean for the K-feldspars generally: 2.7 p.p.m. for those from the normal coarse granites and 3.7 p.p.m. for the K-feldspars from the fine-grained leucocratic varieties (Table 22). No significantly different Sn concentration was found in the K-feldspars from the small pegmatites, contaminated granite or xenolith, but K-feldspars 110 and 145 from the Peninsula Granite have apparently anomalously high Sn values of 11 and 10 p.p.m. respectively, although not significantly different in other respects. It thus seems most likely that Sn in these feldspars occurs as very small inclusions of cassiterite. This may also account for the Sn values obtained for the plagioclases (Table 23).

In a study on micas, mainly from pegmatites, AHRENS and LIEBENBERG (1950) found SnO_2 concentrations varying from $<.0005\%$ to nearly $.5\%$. Two of their muscovites (Table 1, nos. 29 and 30) from George and Sea Point, Cape Province are listed as containing $.011$ and $.09\%$ SnO_2 respectively. Unfortunately no further locality data are given for these two samples. The Sn concentration of the Cape Granite biotites found here (Table 24) is only slightly higher than that of the K-feldspars and total rocks. They average about 4.5 p.p.m. (range: 3.2-6.5 p.p.m.), and the few specimens of

muscovite, sericite and chlorite examined also show no more than 7.3 p.p.m. No correlation is evident in the micas between Sn and other elements, e.g. Ti. It is thus again difficult to decide whether Sn actually occupies lattice sites in the mica structure, although this seems more likely than in the case of the feldspar lattice. AHRENS and LIEBENBERG (1950) concluded that in the micas containing lower concentrations of Sn, it is all held octahedrally in the mica structure, but in those with high Sn concentrations cassiterite is present as well.

9-14. Iron and Magnesium.

The strong decrease of both these major elements with progressive differentiation of the granitic rocks is illustrated in the FeO and MgO silica variation diagrams shown in Fig. 16. A comparison of the FeO-MgO plot for the Snowy granites (Fig. 7) and an Fe-Mg plot for the Cape Granites (Fig. 67) with similar plots of the previously published (chemical) granite analyses (e.g. Fig. 8) demonstrates the much smaller spread of the spectrographic results of this study, especially at lower concentration levels.

Figs. 7 and 67 also illustrate the increasing Fe/Mg ratio with differentiation: from an average of 2.8 for the Snowy granodiorites to 8 for the Snowy leucogranites; and from 4.6 for the average coarse Cape Granite to 17 for the most fractionated fine-grained varieties. This is mainly due to the well known increase of the Fe/Mg ratio of biotites with differentiation — illustrated

in Fig. 68 for the Cape Granite biotites by use of the percentage Mg of the total rock as a sensitive measure of fractionation. Apart from relatively unimportant contributions from occasional accessory hornblende, cordierite or tourmaline, the Mg concentration of the granites is controlled by their biotites. A plot of the Fe/Mg ratios of the biotites relative to their total rocks (Fig. 69) shows that the ratio $\frac{\text{Fe/Mg in total rock}}{\text{Fe/Mg in biotite}}$ is greater than one, about 1.3. This is a measure of iron ore present in the granites.

HEIER (1962) discussed the evidence for some substitution of Si and Al in the tetrahedral positions of feldspars by Fe^{3+} , Ti^{4+} etc.. He suggested that hematite flakes, often present in certain feldspars, may be exsolution products of a ferric compound corresponding to K-feldspar formed in the ternary system $\text{K}_2\text{O}-\text{Fe}_2\text{O}_3-\text{SiO}_2$. The Cape Granite K-feldspars (Table 22) have an average Fe (total Fe) content of about 500 p.p.m.; Mg in the same K-feldspars varies from an average of about 110 p.p.m. for the coarse granites to 35 p.p.m. for the fine-grained granites. That the distribution of these two elements in the feldspars is not random is shown by the sympathetic variation of the Fe/Mg ratio for feldspars and their host rocks (Fig. 70). This is best explained by the presence in the feldspars of very small amounts of biotite or sericite. Thus all Mg in the K-feldspars from the normal coarse granite could be accounted for by about .2% biotite, possibly present as minute inclusions. But the higher Fe/Mg ratio of K-feldspars relative to their biotites (~ 1.3) suggests that additional small amounts of Fe are present

in the K-feldspars, although it is not certain whether this is present in lattice positions or not. (Muscovites and sericite have even lower Fe/Mg ratios than biotite — e.g. no. 106, Table 24). Ti and Mn are similarly calculated to be in "excess" in K-feldspars.

Although the K-feldspars investigated generally appear little altered, sericitisation was especially noted in Samples 124, 125, 126 and 127 from the Older Saldanha Granite at the Hoedjies Bay Contact. They are probably hydrothermally altered and are conspicuous by high Fe, Mg, Pb and especially Cu.

9-15. Titanium.

The high ionic potential of Ti^{4+} would suggest that it forms complexes in silicate melts as does Zr^{4+} (RINGWOOD, 1955b), but the well developed Fe-Ti and Mg-Ti relationships observed for the Cape Granites (Fig. 71) suggest that Ti is predominantly present in silicate structures as are Fe and Mg. The rate of decrease with differentiation of these three elements is seen to be $Mg > Ti > Fe$. A similar trend is observed for the Snowy granites, for which a Fe-Ti plot is shown in Fig. 10.

The similar Mg/Ti ratios of the normal, coarse Cape Granites and their biotites (av. 2.4) suggest that almost all Ti in these rocks is present in the biotites. Rutile, TiO_2 , has only been observed in the Clifton Xenolith (Sample 175, Ti=1.1%), but some Ti is also contributed by the very small amounts of sphene, $CaTiSiO_5$, found in a few granites (e.g. Sample 122). As expected from the high

Ti content of diorite-gabbros 177 and 178, their biotites also are higher in Ti (3.1% and 2.95%) than any of the granite biotites which range from 1.43-2.46% (Table 24). It is noteworthy that Ti in chlorite 106 (1.45%) is significantly lower than in the biotite (1.93%) from which it formed, despite the normal higher Fe and Mg concentration of the chlorite.

Ti was found to be present in all feldspars analysed (Tables 22 and 23). The mean of the 35 K-feldspars from the normal, coarse Cape Granite is 63 p.p.m.; this decreases to an average of only 25 p.p.m. for fine-grained granites and pegmatites. K-feldspars from the Younger Saldanha Granite (Samples 158-166) rather surprisingly average just over 100 p.p.m., despite the low Ti of the total rocks (Fig. 71). Although apparently "normal" in Fe and Mg, these nine feldspars are also higher than average in Zr. The average ratio $\frac{\text{Mg/Ti in biotite}}{\text{Mg/Ti in K-feldspar}}$ for pairs of these two minerals is nearly 2. Therefore, as considered in the case of Fe, if all Mg of the K-feldspars is due to biotite contamination, about half of the Ti cannot be thus accounted for. Nor can it be due to contamination by either muscovite, sericite or chlorite, since these show even higher Mg/Ti ratios than coexisting biotites. Possibly Ti may be present in the feldspars as tiny inclusions, such as rutile, although these were not observed. But despite the relatively large size of Ti^{4+} (.68 Å) some may occupy tetrahedral lattice sites, as suggested for Fe^{3+} . But this question, as the related problem of the distribution of

some chalcophile elements, must await further investigation by micro-probe.

9-16. Scandium.

The Sc concentration of the granites investigated here is essentially in agreement with the figures of 14 p.p.m. for high Ca granites and 7 p.p.m. for low Ca granites suggested by TUREKIAN and WEDEPOHL (1961) from data by AHRENS (1954).

Snowy Mts. gneiss	13 (range: 11.6-17)
granodiorite	13 (6.4-21)
leucogranite	5 (2.7-7.8)
Cape Granite, coarsely porphyritic	6.6 (5-11)
medium-grained	4.1 (3.5-6)
fine-grained	2.3 (<1-4)

The highest Sc concentration observed, 46 p.p.m. for Snowy Amphibolite, Sample 36, indicates an origin from a basic rock.

The observed Fe-Sc relationship for the granitic rocks is closer than for Mg and Sc. This is as expected since Sc^{3+} (.81 Å) should be captured in Fe^{2+} (.74 Å) positions, aided by the more ionic character of the Sc-O bond; Mg^{2+} (.66 Å) and also Fe^{3+} (.64 Å) are considerably smaller (TAYLOR, 1965).

Sc was not detected (< 1 p.p.m.) in any of the Cape Granite feldspars. The biotites show a rather constant level of about 50 p.p.m. and therefore contain virtually all the Sc of the granites. However, biotites 177 and 178 (18 and 19 p.p.m.) are considerably lower than

their diorite-gabbro host rocks (30 and 37 p.p.m.). In these Sc must be concentrated mainly in the other ferromagnesian minerals, principally hornblende and some pyroxene. Similar preferential entry of Sc into these minerals and also sphene and apatite has been noted by a number of previous workers.

Among the granite biotites only the otherwise chemically similar biotite 135 (Table 24) has a drastically lower Sc concentration of 5.2 p.p.m., almost identical to the normal level of the total rock (5.0 p.p.m.). Unfortunately this is the only biotite analysed from the strongly deformed, gneissic George Granite. It is possible that Sc was lost from the biotite during deformation and redistributed. On the other hand, the similar Sc concentration of Chlorite 106 (45 p.p.m.) relative to biotite 106 (48 p.p.m.) shows that Sc is not normally strongly lost from biotite during probable late-stage hydrothermal alteration.

As expected from their low Fe content, sericite and muscovites (Table 24) contain much less Sc than coexisting biotites. The higher level of 45 p.p.m. of pegmatitic muscovite 172 must be due to the absence of biotite, which has more favourable lattice sites.

9-17. Manganese.

The averages of the granite types investigated here agree generally with the mean values of 540 p.p.m. for high-Ca granite and 390 p.p.m. for low-Ca granite given by TUREKIAN and WEDEPOHL (1961).

	<u>Mn</u>	<u>Range</u>	<u>Fe/Mn</u>
Snowy Mts. gneiss	570	380-680	72
granodiorite	635	445-980	59
leucogranite	325	130-510	28
Cape Granite, coarse	450	290-560	57
medium	360	200-590	40
fine	175	16-280	42

Manganese is present in igneous rocks predominantly as Mn^{2+} (RANKAMA and SAHAMA, 1950). It has a very similar electronegativity to Fe^{2+} , but the observed decrease in the Fe/Mn ratio with fractionation may be explained by the larger ionic radius of Mn^{2+} (.80 Å) compared with Fe^{2+} (.74 Å). Mg^{2+} (.66 Å) and Fe^{3+} (.64 Å) are even smaller than Fe^{2+} , and Mg^{2+} forms more ionic M-O bonds. The observed rate of removal from fractionating magmas is therefore $Mg > Fe > Mn$.

The granite data show a general decrease of the Fe/Mn ratio with differentiation. The Mn distribution is seen to be erratic, especially at the lower concentrations of Fe, i.e., in the most differentiated granites. The variation of the Fe^{3+}/Fe^{2+} ratio must be a contributory cause. Due to its low ionic potential divalent Mn^{2+} is also more easily leached even by very weakly acid solutions than other divalent elements of the iron family (GOLDSCHMIDT, 1954). It may therefore be more easily transported by late-stage hydrothermal solutions from one part of a rock, to become fixed in another, after oxidation to the highly insoluble trivalent or quadrivalent state. Such a process would be most marked in the latest-stage granites. In these some redistribution of Mn would also be more apparent because of their lower overall Mn level.

The biotites from the coarse Cape Granite average about .26% Mn (Table 24). Mn in the biotites increases with differentiation of the granites as does Fe. The highest observed value is .4% for biotite 149. Biotites 177 and 178 (.21% and .155% Mn) from the diorite-gabbro intrusions are distinctly lower than the granite biotites although their total rocks (.135% and .15%) have a 3-fold higher level than the granites. Mn in these more basic rocks must therefore be concentrated preferentially in other ferromagnesian minerals. Data by NOCKOLDS and MITCHELL (1948) show a similar Mn enrichment in hornblende and pyroxenes relative to coexisting biotites.

Muscovites and sericite from normal granite are low in Mn (about 200 p.p.m., Table 24). K-feldspars (Table 22) average only about 10 p.p.m.. Recalculated granite plagioclases 106 and 137 have <40 p.p.m..

Substitution of Mn^{2+} for either Ca^{2+} or Na^{1+} in the feldspar lattice seems unlikely in view of the much greater electronegativity of Mn. If all Mg in the K-feldspars is considered as due to the presence of submicroscopic mica inclusions, comparison of the Mg/Mn ratio of the micas and feldspars shows that a variable proportion (about 1/2 on an average) of the Mn observed in the feldspars cannot be accounted for by such inclusions. This is especially marked in the case of a few K-feldspars from the finer-grained granites (e.g. Samples 144-147) which have >30 p.p.m. Mn without concomitant increase of Mg or Fe. Probably Mn is present as insoluble oxides or

hydroxides in mineral fractures or coating mineral grains. Some Mn in this form may also occur finely disseminated throughout the rock. Summation of the Mn contents of the major minerals analysed here only accounts for an average of about 75% of the total Mn in the granites. Data by NOCKOLDS and MITCHELL (1948) and RANKAMA and SAHAMA (1950) suggest that it is unlikely that all remaining Mn is contained in the relatively small amount of accessory sphene, apatite, tourmaline and iron ore present in the Cape Granites.

9-18. Copper.

Recent estimates of the average Cu concentration of basalts, dioritic rocks and granitic rocks are: 85-90 p.p.m., 25-30 p.p.m. and 8 p.p.m. respectively (WEDEPOHL, 1962). The strong decrease of Cu with increasing fractionation is especially marked for the granitic rocks of the Snowy Mts.:

		<u>Average Cu</u>	<u>Range</u>
Snowy Mts. (Table 4)	gneiss	27	13-35
	granodiorite	22	1.7-73
	leucogranite	<2	1-4.6
Cape Granites, coarse (Table 18)		9.9	2.5-16
	medium	~7	1.1-29
	fine	~5	1.4-17

The observed ranges attest to the extreme variability of the Cu distribution in all granite types. This contrasts with the behaviour of Mn which shows strong variations mainly in the most strongly differentiated rocks.

The general level of major and trace elements of the Snowy Amphibolite (Sample 36) is consistent with an origin from basic rock, but compared with a basalt average of 90 p.p.m. Cu, the concentration of only 22 p.p.m. is decidedly low. HEIER (1960) explained similar low Cu levels of metabasalts as due to the loss during strong metamorphism of volatile Cu, especially from sulphides. The erratic behaviour of Cu in granitic rocks may also be due to a large extent to late-stage hydrothermal redistribution.

The arithmetic mean of Cu in all 26 samples of Cape Granite micas is 13 p.p.m. (Table 24). By comparison with most other trace elements the observed range of 5.6-28 p.p.m. is small, since analyses of all biotites, muscovites, sericite and chlorite are included from sources as diverse as the different granite types, migmatite zone, pegmatites and xenoliths. Biotites 177 and 178 from the diorite-gabbros are lower with 3.8 and 5.4 p.p.m..

Cu was detected in all K-feldspars. They average just over 2 p.p.m. with a range of <1 (trace) to 5 p.p.m. (Table 22). (Only K-feldspars 124 to 127 from the Older Saldanha Granite at the Hoedjies Bay Contact are conspicuously higher with 12-20 p.p.m.. But these feldspars are somewhat sericitized and are also distinguished by higher Fe, Mg and Pb). Plagioclases from granites 106 and 137 show a 4-fold increase in Cu relative to their coexisting K-feldspars (Table 23). The Cu contents of the micas and feldspars are not apparently related to the concentration of any other element present.

The low Cu concentration of the micas rules out the possibility that inclusions of mica are responsible for the observed Cu levels of the normal feldspars.

As free ion Cu^{2+} (.72 A) substitutes for Fe^{2+} (.74 A) in ferromagnesian minerals. Purely from size considerations the quantitatively less important Cu^{1+} (.96 A) might be expected to replace Ca in apatite and both Ca^{2+} (.99 A) and Na^{1+} (.97 A) in plagioclase. But the Cu-O bond is far more covalent than either the Fe-O, Na-O or Ca-O bonds (TAYLOR, 1965). This results in the strongly chalcophile character of Cu. The low Cu level of the biotites reflects the difficulty of any Cu^{2+} - Fe^{2+} substitution. The similar Cu levels of biotites and muscovites actually suggest that Cu is not dependent on the Fe concentration in the micas, but may be at least partly present as sulphide inclusions. Even assuming that all Cu in the granite micas is present in the structure, at most 20% of the total rocks Cu is accounted for. Data from granites 106 and 137 indicate that feldspars (and quartz) account for another 30%. The rest of the total Cu, 50% or more, must be sought in sulphides outside the rock-forming minerals. It probably occurs as chalcopyrite, the main primary mineral of Cu.

HEIER (1960) tentatively suggested that enrichment of Cu in plagioclases relative to K-feldspars might be explained by the substitution of Cu for Na or Ca. But the plagioclase analyses here given in Table 23 show that plagioclases are also enriched relative

to K-feldspars in other elements such as Mg, Fe, Mn, Ti, Zr and Y. (See also data by NOCKOLDS and MITCHELL, 1948). It is not likely that all these elements occur in lattice positions. The relatively higher concentration of some of these elements and Cu in the plagioclases may be due rather to a greater amount of very small mineral inclusions. Submicroscopic sulphide inclusions may also account for the very low levels of Cu in the K-feldspars.

9-19. Vanadium.

This element occurs principally as V^{3+} (.74 Å) and is captured in Fe^{2+} (.74 Å) positions, aided by the more ionic character of the V^{3+} -O bond. The virtual exclusion of the trivalent cations, V^{3+} and Cr^{3+} , from olivines is due to the difficulty of maintaining electrical neutrality (TAYLOR, 1965). V^{3+} also forms a more ionic bond with oxygen than does Fe^{3+} and should therefore be able to substitute for it to some extent, despite the smaller size of Fe^{3+} (.64 Å). Data by NOCKOLDS and MITCHELL (1948), WAGER and MITCHELL (1951) and SEN, NOCKOLDS and ALLEN (1959) show that the V concentration in minerals generally decreases in the order: magnetite » ilmenite » biotite » hornblende and pyroxenes » olivine.

The Fe-V and Mg-V plots for the Snowy granites (Fig. 9) and the Cape Granite (Fig. 72) demonstrate the strong, regular decrease of V and the increase of the Fe/V ratio with fractionation. The range of V observed (~1- >100 p.p.m.) makes it difficult to give averages for rock types. On the basis of data by AHRENS (1954),

TUREKIAN and WEDEPOHL (1961) suggested averages of 88 p.p.m. and 44 p.p.m. for high-Ca and low-Ca granites respectively. The arithmetic mean of the Snowy granodiorites and gneisses lies between 60 to 65 p.p.m., somewhat lower than that suggested for granodiorites generally. The normal, coarsely porphyritic types, which form the bulk of the highlevel Cape Granite Plutons have a mean of 40 p.p.m.. But the most strongly fractionated granites of both areas average only about 5 p.p.m. (Tables 4 and 18).

The analysed biotites of the Cape Granite average 260 p.p.m. (Table 24). Biotites from the contaminated granites are highest with 430 p.p.m. and those from the most highly fractionated granites much lower; e.g. biotite 149 has only 45 p.p.m.. V is thus concentrated in the earlier, Mg-rich biotites. This results in a general Mg-V relationship for the micas, which also contain the bulk of the V found in the granites. These facts, together with the sharp decrease of modal mica with progressive differentiation (Table 21, Fig. 40) explain the apparently very close Mg-V relationship of the total rocks seen in Fig. 72. (The V level of muscovites, about 10 p.p.m., is too low to be of any effect). It is doubtful whether V^{3+} substitutes to any extent for Mg^{2+} (.66 Å). Although Mg^{2+} is actually slightly larger than Fe^{3+} , the much smaller difference in ionization potentials (Table 26) between V and Mg may not be sufficient to offset the size effect due to the 12% larger ionic radius of V^{3+} . The electro-negativity data for the pair Mg^{2+} and V^{3+} actually suggests that Mg forms the more ionic bond with oxygen.

V was not detected in most of the K-feldspars (< 1 p.p.m.). The plagioclase-quartz mixture of Cape Granites 106 and 137 showed only a trace, but plagioclases 177 and 178 from the diorite-gabbro have about 5 p.p.m. (Table 23). The coexisting biotites from these two basic rocks are also higher in V than granite biotites. The high V content of 1800 p.p.m. for biotite 178 shows that in this basic rock V is concentrated in biotite relative to the coexisting hornblende, which constitutes about 1/3 of the total rock.

The mica data show that on an average about 80% of the V in the normal, coarse Cape Granites is contained in the mica. This proportion may decrease somewhat in the more leucocratic types. The remainder of the V must be sought in the observed traces of iron ore, especially in magnetite, $\text{FeO} \cdot \text{Fe}_2\text{O}_3$. Too few biotite samples from the most leucocratic granites were analysed to reach a firm conclusion on the V distribution in these rocks. The biotite and total rock data from the normal, coarse Cape Granite show clearly that a separate magnetite phase in these granites cannot contribute most of the V to the composition of the whole rock as implied by the data of SEN, NOCKOLDS and ALLEN (1959) for the granitic rocks of the Southern California batholith.

9-20. Chromium.

Trivalent Cr^{3+} (.63 A) is much smaller than V^{3+} . It preferentially enters early Fe^{3+} (.64 A) positions because it forms a more ionic bond with oxygen (TAYLOR, 1965).

CARR and TUREKIAN (1962) reported a close relation between Cr and Mg in 30 granitic rocks analysed for Cr by neutron activation. They found that Cr did not correlate well with either Ca or Fe. Their Cr average for high-Ca and low-Ca granites is 16-22 p.p.m. and 3-4 p.p.m. respectively. Arithmetic means of the granite types here investigated are:

		<u>Cr</u>	<u>Range</u>
Snowy Mts. (Table 4)	gneiss	55	47-65
	granodiorite	34	5.3-84
	leucogranite	3.8	2.8-5.0
Cape Granite, coarse (Table 18)	medium	22	10-34
	medium	7.8	3.0-14.5
	fine	3.8	3.2-5.0

A Mg-Cr plot for the Snowy and Cape Granites is shown in Fig. 73 together with the statistical line of best fit calculated by CARR and TUREKIAN (1962) for their data. It can be seen that relative to Mg the Cr concentration of the bulk of Snowy and Cape Granite samples is higher by a factor of 2-3. This factor should even be higher because Carr and Turekian reported 30 p.p.m. Cr in G-1, while the value used here for G-1 as primary standard was only 17 p.p.m. (Table 29). Moreover, there is a distinct departure from an approximately 45° straight line relationship in the most fractionated granites, which have a lower Mg/Cr ratio. This "toe" could possibly be due to contamination of all granite samples by about 2-3 p.p.m. Cr. But this is considered unlikely. Some Cape Granite feldspars showed

a trace of Cr (1-2 p.p.m.). This amount can be explained by the presence of minute mica inclusions. But Cr was not detected (< 1 p.p.m.) in other feldspars which had been treated identically to all other feldspar and total rock samples. The upper limit of any general Cr contamination during preparation is therefore below 1 p.p.m.. The two samples of CARR and TUREKIAN which show the lowest Mg concentration actually plot distinctly off their calculated line of best fit, possibly suggesting a trend similar to the one observed here. RINGWOOD (1955b) pointed out that ions of intermediate ionic potentials, such as Ni^{2+} , V^{3+} , Sc^{3+} and Cr^{3+} , could form MO_4 complexes in volatile rich magma and be concentrated in this form in some residual magmas during the latest stages of magmatic crystallization. It is noteworthy that of the four ions mentioned only Cr^{3+} does not show a regular decrease in the most strongly differentiated granites; Cr^{3+} also has the highest ionic potential (Table 26).

The mica analyses of Table 24 show that muscovites contain very little Cr (up to 8 p.p.m.). Both Cr and V seem to be lost easily during strong alteration of biotite to chlorite (see Sample 106). The observed Cr variation of the Cape Granite biotites (330 - 11 p.p.m.) is even stronger than that observed for V. Cr is also concentrated in the earlier Mg-rich biotites. Electronegativity data (Table 26) suggest that Mg forms a much more ionic bond with oxygen than does Cr. It is therefore doubtful whether Cr

substitutes for Mg to any extent. Correlations of Mg in granitic rocks with either V or Cr (as well as with Ni and Co) may therefore not have any fundamental crystal-chemical significance, but be due largely to modal variations. The granite data show a general increase of the Fe/Cr ratio during fractionation.

The mica data show that in the normal, coarse Cape Granites virtually all Cr is contained in the biotites. But in some of the most highly fractionated, leucocratic granites the micas can only account for a small part of the total Cr present in the rock (about 25% in Samples 141 and 149). This trend is therefore more pronounced than in the case of V. The "toe" observed in the Mg-Cr plot of Fig. 73 is a reflection of this trend in the Cr distribution because Mg in the granites is virtually all contained in the micas. In the more leucocratic Cape Granites traces of accessory magnetite probably become the most important sites of Cr in the rock. SEN, NOCKOLDS and ALLEN (1959) showed that both Cr and V were concentrated largely in the magnetites of the acidic rocks from the S. California batholith.

Viewed against the general high Cr level of basic igneous rocks the concentration of 97 p.p.m. Cr observed for the Snowy Amphibolite, Sample 36, confirms its basic rock parentage. But no explanation can be offered for the surprisingly low Cr concentration of only 5 and 28 p.p.m. in the Malmesbury diorite-gabbros (Samples 177 and 178, Table 18). For rocks of their chemistry they also have anomalously low Ni levels, 3.3 and 9.7 p.p.m. respectively.

9-21. Cobalt and Nickel.

Evidence summarized by TAYLOR (1965) indicates that Co and Ni preferentially enter early Fe^{2+} positions rather than Mg positions. Although electronegativity and ionization potential data do not in this case give a very clear picture, it may be predicted from ionic radii and oxide melting point data that the sequence of entry into crystal lattices should be Mg^{2+} (.66 Å), Ni^{2+} (.69 Å), Co^{2+} (.72 Å), Fe^{2+} (.74 Å).

Fig. 74 shows a Ni-Co plot of Snowy and Cape Granites in which Co and Ni were above their spectrographic sensitivity limits of 1 and 2 p.p.m. respectively. Both elements are strongly depleted during granite fractionation. Ni falls at a slightly greater rate than Co, so that the average Ni/Co ratio decreases from about 1.5 to 1. The following two diagrams, Figs. 75 and 76, show plots of Co and Ni versus Fe and Mg for the Cape Granites. Co shows better correlation with Mg and Fe than does Ni. From the slopes of the trend lines shown it can be inferred that depletion of these elements during granite fractionation follows the predicted order Mg, Ni, Co, Fe.

Averages for the granite types are given below from the data presented in Tables 4 and 18. For comparison the latest estimates taken from TUREKIAN and CARR (1960) and CARR and TUREKIAN (1961) are also included.

	<u>Co</u>	<u>Ni</u>	<u>Ni/Co</u>	<u>Ca%</u>	<u>Fe%</u>	<u>Mg%</u>
Snowy Mts. gneiss	16	27	1.7	.68	4.09	1.43
granodiorite	13.5	15	1.1	2.07	3.72	1.35
leucogranite	< 2	< 2	-	.51	.92	.12
Cape Granite, coarse	6.6	8.9	1.3	1.17	2.58	.56
medium	~ 3	~ 3.3	1.1	.89	1.44	.19
fine	< 2	< 2	-	.42	.74	.043
<hr/>						
Basalt	48	130	2.7	-	8	4
Shale	19	71	3.7	-	3.9	1.4
High-Ca granite	7	14	2	2.53	2.96	.94
Low-Ca granite	1	.4	< 1	.51	1.42	.16

Relative to the major elements Ca, Fe and Mg, the Snowy granodiorites and gneisses are high in Co. The gneisses also are rich in Ni. The high level of elements such as Co, Ni and Cr in these rocks is a reflection of their shale-rich sedimentary parent material. The dashed line shown in Fig. 75 represents the Mg-Co regression line calculated for their granite data by CARR and TUREKIAN (1961). Their Co data was obtained from the same suite of 32 granitic rocks used for the Cr determinations (see Fig. 73). Relative to Mg the Cape Granites are also higher in Co by an average factor of about 2. It is not thought likely that this difference can be ascribed to analytical error of the Co determinations. Normal background corrections were applied to the Co line read (see Appendix). The Co values used here for the primary standards G-1 and W-1, 2.4 and 50 p.p.m. respectively, correspond to CARR and TUREKIAN's (1961)

figures of 2.4 and 52 p.p.m.. Nor is it likely that samples have been generally contaminated to the degree necessary. Neither Co nor Ni were detected in identically prepared samples of the most fractionated granites or in any of the granite feldspars examined. (The detection limit here was estimated as <1 p.p.m.).

It would be an interesting fact if both the Snowy and the typical high-level Cape Granites proved to be significantly higher in Cr and Co (and Ni to some extent) than average granitic rocks of comparable major element composition. However, the Cr and Co averages given by Carr and Turekian may not be representative of granitic rocks in general. For example, their sample YCR 5, a composite of western N. American Granites with .67% Mg, 21 p.p.m. Cr and 7.8 p.p.m. Co, plots very close to the Mg-Cr line of the Snowy and Cape Granites (Fig. 73) and falls virtually on the Mg-Co line for the Cape Granites (Fig. 75). Earlier granite data also support somewhat higher Cr and Co figures (e.g. SANDELL and GOLDICH, 1943 and AHRENS, 1954).

Co and Ni in the Cape Granite muscovite micas was less than 5 p.p.m. in all samples (Table 24). In the biotites examined Co averages 41 p.p.m. (range 14-57 p.p.m.). As expected from the total rock data Ni in the biotites shows a greater spread of values than Co, ranging from 6-105 p.p.m. with an average of 62 p.p.m.. As in the case of V and Cr the lowest Co and Ni results are found in biotites from the most strongly fractionated granites. The

Ni/Co ratios of individual biotites generally agree well with the Ni/Co ratio of their host rock (Tables 19 and 24). The Co and Ni levels of biotites from the normal, coarse Cape Granite show that these two elements are virtually confined to the biotites of these rocks. CARR and TUREKIAN (1961) have shown that in granites containing <1 p.p.m. Co the contribution of Co disseminated through the non-ferromagnesian minerals may become significant. The data presented for V and Cr show that in the most leucocratic Cape Granites modal mica cannot, in fact, account for a major portion of the rock's V and Cr as it does in the case of the normal granites. Unfortunately this cannot be also shown for Co and Ni since they proved too low for determination in the most strongly fractionated, leucocratic granites (<2 p.p.m.).

9-22. Lithium.

In their survey of the geochemistry of the alkali metals HEIER and ADAMS (1963) gave general averages of 20 and 30 p.p.m. Li for granodiorites and granites respectively. The snowy granodiorites and gneisses average 30 p.p.m. (range 17-36 p.p.m.), but the erratic variation (6-65 p.p.m.) found for the differentiated Snowy leucogranites makes their similar mean of 29 p.p.m. very uncertain (Table 4). A parallel position exists for the Cape Granites. The normal, coarse granites are somewhat higher than the Snowy granites averaging 42 p.p.m. (range 27-52 p.p.m.), but the fine-grained, most leucocratic and differentiated Cape Granites again show a stronger variation (14-64 p.p.m.) and average only about 28 p.p.m. Li (Table 18).

Because it is much smaller in size, Li^{1+} (.68 Å) is unable to occupy the lattice positions of other alkalis. Instead this univalent ion is admitted into 6 fold coordination positions, (with oxygen) substituting for divalent Mg^{2+} (.66 Å) and possibly Fe^{2+} (.74 Å) especially in late stage ferromagnesian minerals (HORSTMAN, 1957; HEIER and ADAMS, 1963; TAYLOR, 1965).

The now well-documented strong decrease in the Mg/Li ratio with differentiation was noted by STROCK (1936). Fig. 77 shows the Mg/Li ratios of all rocks here analysed plotted against their Mg concentration as index of granite differentiation. The Mg/Li ratio of the granitic rocks plotted decreases from 1500 to 3.

Li in the Cape Granite biotites varies from 35-480 p.p.m. (Table 24). As in the case of Cs, but to a less marked extent for Rb, the highest concentrations of Li are found in the biotites from the leucocratic, most strongly differentiated granites. Muscovites, sericite and chlorite have considerably lower Li contents than coexisting biotites and range between 50 and 70 p.p.m.. The observed Li variation of the K-feldspars is from 2.1-14 p.p.m., but most Li analyses fall close to the average of about 5 p.p.m.. The two plagioclase-quartz mixtures (Table 23, Samples 106 and 137) with 14 and 10 p.p.m. Li are higher than their respective coexisting K-feldspars.

The Mg/Li ratio of the feldspars is far lower than that of coexisting micas. Therefore, contamination or inclusions of mica

in the feldspars cannot account for most of their Li. HEIER (1960) questioned LUNDEGARDH's (1947) suggestion that Li^{1+} replaces Al^{3+} in the plagioclase structure and thought it more likely that limited substitution of Li^{1+} takes place for Na^{1+} in the feldspar lattice. The variation of Li and Na in the granite feldspars is too small to demonstrate any clear relationship between them, but the K-feldspars from the most strongly fractionated, leucocratic Cape Granites, as also those from the Younger Saldanha Granites are higher than average in both Li and Na. These rocks are also particularly low in modal mica (Table 21) and Li here appears to be forced to a greater degree to take up the structurally much less favourable feldspar sites. The Li data on all Cape Granites and their major minerals suggest that even in the normal granites a significant proportion of the total Li is contained in the feldspars.

The erratic distribution of Li in the latest stage Snowy and Cape Granites strongly resembles the behaviour of Cs. There is a suggestion of a relation between Cs and Li in these highly differentiated granites in that some samples showing abnormally low Cs are also low in Li. It is argued that both these volatile elements were strongly lost from some of the rest magmas during the last stages of crystallization. The possibility of strong selective loss of some mobile trace elements such as Li, Cs, Rb, Pb, Tl and also Nb and Be is neatly demonstrated by DIETRICH and HEIER (1965) for a miarolitic sample of alkali granite (ekerite) from the Oslo

Series. The greater spread of Mg/Li ratios and a possible steepening of the curve at the low Mg portion of Fig. 77 is probably also largely due to varying loss of Li. As for Cs, extremely high levels of Li, of the order of a few hundred p.p.m., as found for instance by BOWLER (1959) for some high-level granites of Devon and Cornwall, are indicative of extreme fractionation. But the very low concentration of such highly mobile trace elements in other granites obviously is not in itself evidence against a similar origin. Whether some mobile trace elements are lost from late stage granite magma or not must depend strongly, among other factors, on volatile pressure and the particular geological environment, which determines to what extent the system is an open one.

9-23. Silicon and Aluminium.

The increase in average silica concentration of the different granitic rock types, from granodiorites to most strongly fractionated leucogranites, is shown in Tables 4 and 18. Fig. 16 demonstrates the general inverse variation of Al_2O_3 (16.3-12.0%) with SiO_2 (63-78%) for all granitic rocks analysed.

9-24. Gallium.

The concentration range of Ga in common igneous rocks is rather small. Estimates of the average Ga concentration of granitic rocks given by various workers (e.g. BELL, 1955; SHAW, 1957; BURTON et al. 1959; BORISENOK and SAUKOV, 1960) depart only slightly from the figure of 17 p.p.m. for both high-Ca and low-Ca granites

given by TUREKIAN and WEDEPOHL (1961). Averages for the granite types here investigated are:

	<u>Ga</u>	<u>Range</u>	<u>Ga/Al x 10⁴</u>
Snowy Mts. gneiss	17	14-19	2.2
(Table 4) granodiorite	20	16.5-22.5	2.6
leucogranite	13.5	12-14.5	2.0
Cape Granite, coarse	21.5	16.5-27.5	2.8
(Table 18) medium	17.5	15.5-19.5	2.5
	18	16.5-22	2.6

Considering the overlap of concentration ranges for the Cape Granite types the apparent slight decrease in both the Ga concentration and the Ga/Al ratio in the most fractionated, fine-grained granites may not be significant. But the strongly differentiated Snowy leucogranites show a more definite decrease of Ga and the Ga/Al ratio.

The figure of 22 p.p.m. reported by EDGE and AHRENS (1963) for a sample of Cape Peninsula Granite (see Table 9) is in good agreement with the average for the coarse Cape Granite reported here. The lowest value (8 p.p.m., $Ga/Al \times 10^4 = 1.3$) was here obtained for the Sea Point Aplogranite (Table 18, Sample 156) which contains <.5% mica and the highest for the extremely mica rich Clifton Xenolith (Sample 175, 37 p.p.m., $Ga/Al \times 10^4 = 4.7$).

Analyses of the Cape Granite minerals show the expected increasing Ga concentration in the order K-feldspar, plagioclase, biotite (=chlorite), muscovite and sericite. Ga in the 35 K-feldspars from the normal, coarse Cape Granite varies from 10.5

to 16.5 p.p.m. and averages 13.2 p.p.m.. The 23 K-feldspar samples from the more leucocratic fine-grained and Younger Saldanha Granites as well as from pegmatites show a slightly higher mean of about 16 p.p.m.. Biotites (Table 24) range from 22-55 p.p.m. Ga (average 35 p.p.m.) and also show slightly higher Ga concentrations in samples from the most leucocratic granites. Whether a similar trend exists for plagioclases is not clear since only two recalculated plagioclase analyses (Table 23, 25 and 23 p.p.m. Ga) are available.

A small drop in the Ga concentration of late-stage leucogranites can be explained by the decrease of mica and plagioclase which just overshadows the effect due to the small increase in modal K-feldspar and the slightly higher Ga level of the late-stage minerals.

Ga^{3+} (.62 A) is usually held to show close coherence to Al^{3+} (.51), but it is considerably larger and forms a more covalent bond with oxygen. A strong increase in the Ga/Al ratio with differentiation would be predicted. The Ga/Al ratio does show a general increase from about 1.7×10^{-4} in basic rocks to about 2.2×10^{-4} in granites (e.g. BELL, 1955), but in many igneous rock series studied the Ga/Al ratio does not vary significantly (BORISENOK and SAUKOV, 1960). These authors also state that granite pegmatites are not generally enriched in Ga compared with granite. According to TAYLOR (1965) Ga^{3+} should enter Fe^{3+} (.64 A) positions more readily than Al^{3+} positions. A close association between Ga and Fe^{3+} is easily masked by the large amount of Al

present. In a granite differentiation series the removal of some Ga in Fe^{3+} (and also possibly in Cr^{3+} and Ti^{4+}) positions at the granodiorite stage would occur at the expense of later formed differentiates. The Ga/Al ratio is further upset by the entry of Ga into sulphides, especially zinc sulphide. A small additional factor in some very late-stage magmas may be a slight loss of Ga. Due to the relatively high ionic potential (4.83) it may form complexes in volatile-rich magma (RINGWOOD, 1955b). According to BORISENOK and SAUKOV (1960) enrichment of Ga, e.g. in alkaline pegmatites, is found only in cases where volatile components such as water vapour, fluorine and chlorine play an important role. This and the general enrichment of Ga in greisens demonstrate the mobility of this element. Preferential loss of Ga may be due to the known greater solubilities and volatilities of some Ga halides and halide complexes relative to their Al counterparts.

9-25. Beryllium.

According to the detailed study of BEUS (1956, 1961) the average Be content of diorites is 2 p.p.m., rising to 4.5 p.p.m. in biotite granites and 10 p.p.m. in some muscovite and two-mica granites. The level of Be in normal granites is thus only little higher than the spectrographic sensitivity limit of about 2 p.p.m. attained here and the results must be treated with some caution.

Be was determined in only six samples of Snowy granodiorite, gneiss and porphyry (Table 4). They range from <2-4.0 p.p.m. and average 3.0 p.p.m.. A further six samples of Snowy

leucogranites showed a slightly higher mean of 4.5 p.p.m. (range 3.5-6.5). A similar higher average of 4.7 p.p.m. was obtained for 41 samples of Cape Granite (Table 18). The variation observed here was from 2.7-7 p.p.m. but the Be level does not vary significantly in different facies. The results given agree well with the world averages and indicate a Be increase from granodiorite to fractionated, high-level granite. Be was not detected in the Snowy Amphibolite or in the Cape diorite-gabbros.

Data by BEUS (1956, 1961) show that in normal granite the bulk of Be (85-98%) is bound in the feldspars although the order of increasing Be concentration is usually K-feldspar, plagioclase, biotite, muscovite. Only in muscovite granites and albitized muscovite granites, which are the result of strong metasomatism, a substantial part of the Be is contained in the mica or in accessory beryl.

In most of the K-feldspars from the normal, coarse Cape Granite Be was not detected (< 1 p.p.m.); only a few showed a trace (< 2 p.p.m.). But as observed for a few other elements such as Sn, Zr and Y, the K-feldspars from the fine-grained, leucocratic Cape Granite are higher in Be. They range up to 3.8 p.p.m. and average about 2.3 p.p.m. (Table 22). The Cape Granite biotites (Table 24) may show a similar trend. In most biotites analysed Be was only recorded as trace (here estimated as about 3 p.p.m., which may be rather too low). The highest level recorded was

13 p.p.m. for biotite 149 from a fine-grained, leucocratic Kuils River Granite. Muscovites and sericite have a higher average of about 5 p.p.m. and the two recalculated plagioclase analyses (Table 23, Samples 106 and 137) gave 4.9 and 7 p.p.m.

Be^{2+} (.35 A) may be expected to exist in magma partly as $(\text{BeO}_4)^{6-}$ complex which can substitute for $(\text{SiO}_4)^{4-}$ in silicate lattices (RINGWOOD, 1955b). Such substitution will, however, lead to charge balance difficulties unless counterbalanced by the presence of free cations of high valency, such as Ti^{4+} , Zr^{4+} , Y^{3+} etc., or by anions such as F^- or OH^- substituting for oxygen (BEUS, 1956; GANEEV, 1961). In this connection it is probably significant that the plagioclase and those K-feldspars which contain the highest Be also show a definite increase in their levels of Zr, Sn and Y.

9-26. Boron.

B^{3+} (.23 A) exists in magmas as $(\text{BO}_3)^{3-}$ or $(\text{BO}_4)^{5-}$ complexes (RINGWOOD, 1955b). $(\text{BO}_4)^{5-}$ may be expected to substitute for $(\text{SiO}_4)^{4-}$ or $(\text{AlO}_4)^{5-}$ tetrahedra in silicates. Thus Reedmergerite, NaBSi_3O_8 , a natural boron analogue of albite has been discovered by MILTON et al. (1960). But $(\text{BO}_3)^{3-}$ is not accepted into silicates and may accumulate in residual magmas. Under high volatile pressure (e.g. pegmatitic or very late-stage granitic stage) boron may also concentrate in the form of BF_4^{1-} or $\text{B}(\text{OH})_4^{1-}$ complexes (RINGWOOD, 1955b).

Such strongly diverse processes go some way towards explaining the relatively uniform B content of basic rocks (~ 5 p.p.m., HARDER, 1960) compared to the concentration variation over almost 2 orders of magnitude observed in acid rocks. TAYLOR (1965) considers 10-20 p.p.m. a reasonable B average for granites.

The generally high B concentration of shales (average 100 p.p.m., TAYLOR, 1965) should make it possible to distinguish anatectic granites formed from such material, but the extremely mobile B must be very easily lost during metamorphic and igneous processes. Very high B contents could therefore indicate a sedimentary origin or be the result of extreme fractionation, but a low concentration cannot be taken as evidence against either of these processes (cf. Cs). This may be illustrated by the results of Table 4 which show that B does not exceed 25 p.p.m. in any of the 12 Snowy granite samples in which this element was sought. (Due to line interference difficulties mentioned in the Appendix, section 8, quantitative B results are not given for samples containing < 20 p.p.m.).

The B analyses of Cape Granite (Table 18) reveal strong regional differences. B was not detected or is not present at levels higher than 20 p.p.m. in any of the 41 samples except for:

- (1) All analyses of the coarsely porphyritic Peninsula Granite showed B ranging from 25-125 p.p.m.. The fine-grained marginal leucocratic facies exposed at Kloof Quarry shows even higher concentration of up to 190 p.p.m..

(2) One sample of the Younger Saldanha Granite (no. 163) from the Hoedjies Bay Contact has 50 p.p.m.

(3) The highest figure of 240 p.p.m. was recorded for Sample 149, the fine-grained marginal of the Kuils River - Stellenbosch Pluton.

Table 9 lists some previously published B analyses on Cape Granites from WASSERSTEIN (1951). These are in good agreement with the levels recorded here for equivalent Cape Granites.

The Cape Peninsula Granite is not in other respects uniquely different from other Cape Granites, and the much higher B content cannot be due to particularly strong differentiation. According to data by ERLANK (1965) the intruded Malmesbury Sediments average about 75 p.p.m. B, which is normal for a shale (see Table 7, nos. 3, 4 and 5). The granite samples showing high B are all relatively near to the sedimentary contact and B was probably introduced by late-stage hydrothermal activity. SCHOLTZ (1946) noted the relative abundance of accessory tourmaline in the Peninsula and Stellenbosch Plutons and in these samples much of the B present must be present in this mineral.

In granitic rocks which do not contain tourmaline B is mainly concentrated in plagioclase (GETLING and SAVINOVA, 1958; STAVROV and KHITROV, 1960; BARSUKOV, 1961). The Cape Granite plagioclase- (+ quartz) samples (Table 23) are estimated to contain ~ 20 p.p.m., but B was not detected in any K-feldspar or biotite samples. The observed B content of about 35 p.p.m. for muscovites and sericite (Table 24) is consistent with the hydrothermal introduction of this element.

IV CONCLUSIONS.The Snowy Mts. Granites.

(1) Using both major and trace elements data the granitic rocks of the Snowy Mts. area can be broadly divided into "gneisses" (corresponding to Joplin's gneissic granites, Ordovician type), "granodiorites" (corresponding to both foliated Silurian and massive post-Silurian types granites) and "leucogranites".

(2) On the basis of the geochemical evidence the Snowy Mts. gneisses are considered to have formed entirely from the Upper Ordovician psammo-pelitic, clay-rich sediments with which they are associated, without differentiation or addition of any significant amount of magmatic material.

(3) The "granodiorites" varying in comp. from adamellites almost to tonalites form the bulk of the batholiths and show a limited but continuous variation in both major and trace elements. Their geochemistry is consistent with an origin by mobilization and melting at depth, without significant magmatic differentiation, of varying proportions of geosynclinal sediments that can be represented on an average by equal parts of normal shale, greywacke and Upper Ordovician clay-rich psammo-pelites. With the available data the granodiorites cannot be generally subdivided into "foliated" and "massive" types, although this may be possible for any particular smaller area, as shown, for instance, by the massive, cross-cutting Island Bend granite. This mass is chemically distinctive and may have originated from a

sedimentary mixture containing a greater proportion of greywacke and less clay-rich shale. The apparent overlap in chemical composition between foliated and massive types finds a parallel in their K-Ar ages, which also showed no real distinction between foliated and massive types on a broad regional basis, although the gneisses appeared slightly older in any one area.

(4) Chemical variations within bathyliths appear to be larger than overall variations between different bathyliths. Therefore a very much larger number of samples would be needed to detect any significant differences in chemical composition between the bathyliths, if such differences exist. The number of samples taken is, however, considered adequate for the calculation of an "average granodiorite" representing all bathyliths in the area.

(5) The somewhat younger, crosscutting leucogranites associated with the granodiorite bathyliths are strongly differentiated granites and on present limited sampling may be subdivided into three groups showing varying degrees of magmatic fractionation. They did not originate by fractionation of basic magma but probably formed by partial melting and magmatic differentiation from pre-existing geosynclinal sediments.

(6) Samples of three quartz-feldspar porphyry dykes examined indicate that they are chemically quite dissimilar to one another but neither represents strongly differentiated material. One is chemically similar to the gneisses, another resembles some massive type

granodiorites, while the third may possibly be related to Lower Devonian rhyolite lavas in the area.

(7) Comparison of the major element data presented here from the strategically placed Snowy Mts. area with previously published analyses from a wider region indicates that the new trace element data, and other conclusions of this study, may be applicable to the granitic rocks of a similarly wider region of the Lachlan Geosyncline.

The Cape Granite.

(1) In contrast to the essentially undifferentiated granodiorites of the Snowy Mts. batholiths the Cape Granite plutons formed from a typical "high-level" fractionated granite magma as shown by the geochemical evidence of the total rocks and minerals. The cores of the plutons are formed of coarsely porphyritic biotite granite which grades outwards into medium and fine-grained granites. The data confirms the view of SCHOLTZ (1946) that these represent even more strongly fractionated magma, presumably chilled against the country rock.

(2) Variable loss of some trace elements, either volatile or otherwise mobile due to the formation of complexes, has occurred from some of the most strongly differentiated members of the Cape Granites and also Snowy leucogranites. These trace elements include especially Li, Cs and Tl and possibly to some extent Pb, Cu, Mn, Y, La, Nd, Zr, B and Ga.

- (3) The only distinct chemical differences observed between any of the granite plutons examined are the uniformly high concentrations of Th, U and Pb of the Paarl Granite and apparently higher than average B levels of the Cape Peninsula Pluton.
- (4) Minerals from pegmatitic phases of the Cape Peninsula Granite indicate a degree of fractionation comparable to that of the fine-grained granites of the border facies. A pegmatitic vein from the George area, in contrast, is not a late-stage granite differentiation product.
- (5) Trace element analyses of coexisting minerals from different granites, e.g. Rb, suggest that K-feldspars and biotites crystallized at least in approximate chemical equilibrium. This makes it unlikely that K-feldspar phenocrysts in the Cape Peninsula Granite formed by a general late-stage potash enrichment.
- (6) The Rb-Sr age of the coarse Cape Peninsula Granite and its finer-grained, more differentiated border facies is 553 ± 8 m.y. with a primary $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of $.710 \pm .003$. This is assumed to be the age of emplacement of all "older" south-western Cape Granite plutons.
- (7) The isotopic data, K-Ar ages on two biotite samples, as well as some apparently anomalous obliquity values of K-feldspars and low calculated temperatures of formation all suggest that a mild but widespread metamorphism affected the granites after their formation.
- (8) Preliminary data on a crosscutting mass of aplogranite at Sea Point suggest that it was derived from the same source as the granites, but intruded 500 ± 15 m.y. ago. This event may be

associated with the metamorphism of the main granite body and possibly mark the intrusion of "younger" granites in the south-western Cape generally.

(9) The apparent "isochron" observed for the intruded Malmesbury sediments, which shows an unexpected and remarkably strong colinearity, indicates an age of 595 ± 46 m.y. with an Ri ratio of $.712 \pm .003$.

This age accords with the view of SCHOLTZ (1946) that the Cape Granite was intruded only shortly after the deposition of the Malmesbury. The indicated age of the Malmesbury Formation rules out its correlation with the pre-Cape and pre-Nama rocks in the Bitterfontein-Van Rhynsdorp area which must represent a formation considerably older than the Malmesbury.

(10) On the observed Sr isotope and geochemical data it appears possible, but unproven, that the Cape Granite was formed entirely by mobilization of Malmesbury sediments at depth with subsequent differentiation and intrusion.

"Granite" averages

The granitic rocks examined from both areas form a continuous series ranging almost from tonalites to strongly leucocratic alkali granites. To date the most useful approach to establishing an "average granite" composition, especially for trace elements, is the chemical subdivision used by TUREKIAN and WEDEPOHL (1961). Such compilation should be revised from time to time in the light of newer and/or better data. For most major and trace elements their high-Ca granites

correspond well with the average Snowy granodiorite, forming the bulk of the batholiths in that area. The normal coarsely porphyritic granite of Cape plutons is similarly matched by their low-Ca granites.

Significant differences are the overall lower Sr figures of the granitic rocks here analysed. Ba averages assigned by TUREKIAN and WEDEPOHL (1961) to their two granite types may best be reversed. Co and Cr may be generally higher in granites by a factor of about 2 compared with averages quoted by CARR and TUREKIAN (1961, 1962).