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A SULPHUR ISOTOPE STUDY
OF THE CALEDONIAN GRANITES OF
BRITAIN AND IRELAND

by

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Submitted for the Degree of Master of Science

UNIVERSITY OF GLASGOW

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I dedicate this thesis to my mother and father, brothers
and sisters

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ABSTRACT

The Caledonian fold belt is thought to have formed as a result of the closure of the 'Iapetus' ocean basin during Lower Palaeozoic times. Granitic magmas were intruded into Precambrian and Lower Palaeozoic country rocks between approximately 640 and 390 Ma. Most important, spatially and volumetrically, are the late Caledonian granites, the 'Newer' and 'Last' granites of Read (1961). In general, the late Caledonian granites have the calc-alkaline characteristics typical of plutonic rocks emplaced at destructive plate margins. They range in composition from diorite and tonalite, through granodiorite, to peraluminous granite with chemical variation continuous among the various rock types. Petrographically and chemically, the granitoids span the range from S 'sedimentary' to I 'igneous' types as defined by Chappell and White (1974) with no discernible geographical pattern to their distribution.

There have been few sulphur isotope studies on primary sulphides in granites; yet such data have considerable potential in understanding the petrogenesis; that is in terms of granites derived either from igneous or metasedimentary protoliths. From about 50 British and Irish Caledonide granites, including both 'Newer' and 'Older' intrusions, conventional separation techniques have yielded sulphide separates from only 19 granites for $\delta^{34}\text{S}$ analyses. Mineralogically, the

sulphides consist of mainly pyrite and pyrrhotite, although chalcopyrite is present in a few intrusions. It was noticeable that granites with high $\delta^{18}\text{O}$ and high initial $^{87}\text{Sr}/^{86}\text{Sr}$ yielded very little sulphides.

The $\delta^{34}\text{S}$ analyses proved most informative when compared with the following: mol $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$, K/Na, $\text{Fe}_2\text{O}_3/\text{FeO}$ ratios, initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$. Granites with high to intermediate $\delta^{18}\text{O}$ (11 to 10‰) and high initial $^{87}\text{Sr}/^{86}\text{Sr}$ (> 0.709) are accompanied by $\delta^{34}\text{S}$ from +5.0 to +16.0‰ and are indicative of crustally derived granites (S-types). These are mainly 'Older' Caledonian granites (e.g. the Oughterard granite and the Cashel microgranite sill in Connemara, Ireland; the Aberdeen granite in Scotland). Intermediate to low $\delta^{18}\text{O}$ (10 to 6‰) and low initial $^{87}\text{Sr}/^{86}\text{Sr}$ (0.703 to 0.708) correspond to $\delta^{34}\text{S}$ values between -4.5‰ and +4.4‰ indicative of granites derived from the mantle or lower crust; these intrusions are mainly 'Newer' Caledonian granites. $\delta^{34}\text{S}$ analyses also confirm the diverse protolithic derivation of zoned granites; a good example being the Strontian granite in the northwest Highlands of Scotland with a variety showing $\delta^{34}\text{S}$ value of -0.1‰ and, therefore, considered to be derived from a basic igneous protolith, and a more leucocratic member showing a spread $\delta^{34}\text{S}$ values between +5.6 and +8.4‰ which is considered to be derived from a crustal component.

Sulphur isotope analyses of coexisting sulphide minerals are also useful as a geothermometer as long as the sulphide-bearing phases are in equilibrium. The putative temperature of formation of two coexisting mineral pairs from the Oughterard granite has been calculated; 418°C from a pyrite-pyrrhotite pair and 441°C from a pyrite-chalcopyrite pair.

The results of sulphur isotope analyses coupled with the above geochemical and isotopic parameters have proved useful in understanding granite genesis, and hence distinguishing the Caledonian intrusions in terms of precursor protolith.

CHAPTER 1

INTRODUCTION

1.1 Introduction

A major advance in igneous petrology during the last decade or so has been the realization that much of the variety of igneous rocks, including granitoids, result from separate partial fusion events involving different source rocks. In Southeastern Australia, for instance, Chappell and White (1974) have recognised granites derived from source rocks of igneous composition (I-types) and those derived from the partial melting of metasedimentary source rocks (S-types). Each type can be distinguished by chemical, mineralogical, field and isotopic criteria.

The British Caledonian granites comprise a compositionally diverse group of intrusive rocks ranging from diorite to leucogranite, which were emplaced across the British Isles in and adjacent to the Caledonian metamorphic belt. A small number of plutons were emplaced prior to the polyphase deformation and metamorphism of the Grampian Orogeny while another group was contemporaneous with it, but the largest volume of the Caledonian magmatic activity postdate the main orogenic event and is Lower Devonian in age, about 400 Ma ago.

Petrographically and chemically, the British Caledonian intrusions range from I-type to S-type as defined by Chappell and White (1974) with no discernible pattern to the distribution of different types; many are composite and zoned.

1.2 Aim of the Project

The aim of this piece of work is to examine the sulphur isotopic composition of some Caledonian granitoids of Ireland, Scotland and Northern England, in order to ascertain whether S isotopes systematically differ in I-type and S-type granites.

In addition to sulphur isotope chemistry, existing field evidence, trace and major element geochemistry and other already available stable isotope data (oxygen and initial strontium isotope ratios) have been considered in this study in order to distinguish between the two types of granites.

1.3 Geological Setting

The Caledonian orogeny is widely considered to be related to the subduction and plate collision associated with the closure of the Iapetus Ocean during Early Paleozoic times. Caledonian magmatic activity in Britain largely postdates the polyphase deformation and metamorphism of the Grampian Orogeny (Late Cambrian to Early Ordovician) and the main volume of activity also postdates the traditional Caledonian tectonism of end-Silurian age. The Caledonian belt of

Britain lies between the Precambrian Lewisian Foreland of northwestern Scotland and the Upper Paleozoic cover of the Variscan Foreland of Central England. This belt can be divided into three distinct structural-stratigraphic provinces (Fig. 1.1). Northwest of the Great Glen Fault, a marginal zone of parautochthonous nappes is developed within a highly deformed basement of Archean granulites and gneisses (the Lewisian Gneisses), and the thick sequence of Proterozoic sediments (the Moinean Granulites) which forms an uncomfortable cover. Between the Great Glen Fault and the Highland Boundary Fracture Zone in south-central Scotland lie the orthotectonic Caledonides, a structurally complex alpinotype metamorphic fold belt of highly deformed and variably metamorphosed Late Proterozoic to Early Paleozoic supercrustal rocks (mostly Dalradian Schists). Southeast of the Highland Boundary Fracture Zone, in the Southern Uplands of Scotland, in northern England and Wales, and in eastern Ireland is a wide, low grade to non-metamorphic region of weakly deformed pelitic rocks, the paratectonic Caledonides, which were deposited during Early Palaeozoic sedimentation. The Midland Valley of Scotland lies between these two main Caledonian tectonic provinces.

More than 100 granitoid intrusions, ranging in size from small sheets, vein complexes, and stocks to large plutons are exposed in the British Caledonides; the majority are concentrated in the Grampian Highlands. In general, there is a lack of extensive hydrothermal alteration of the Caledonian intrusions, a fact mostly attributed to the anhydrous nature of the pre-Caledonian crust through which many of the British Caledonian granitoid magmas were emplaced (Plant et al, 1983).

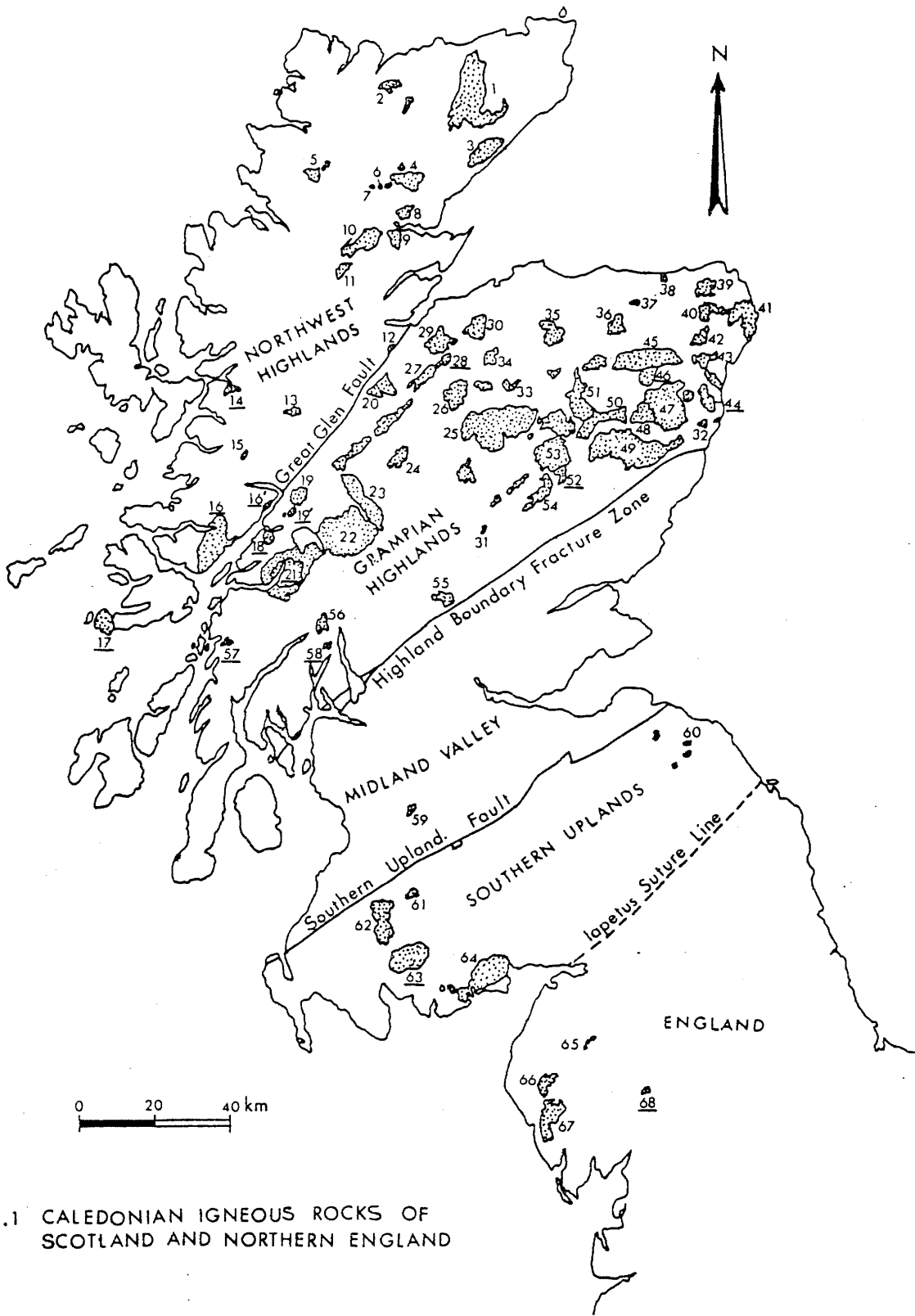


Fig.1.1 CALEDONIAN IGNEOUS ROCKS OF SCOTLAND AND NORTHERN ENGLAND

Fig. 1.1 Partial outline map of the British Isles showing: 1) major geographic provinces in Northern England and Scotland; 2) the distribution of Caledonian granitoids; and 3) the location of important structural features. The numbers assigned to the following intrusions:

- | | |
|--------------------------------|--------------------------------|
| 1. Strath Halladale | 43. Ardlethen |
| 2. Ben Loyal | <u>44.</u> Aberdeen |
| 3. Helmsdale | 45. Insh |
| 4. Lairg-Rogart | <u>46.</u> Kemnay |
| 5. Borrolan | 47. Skene |
| 6. Loch Shin | 48. Hill of Fare |
| 7. Grudie | 49. Mount Battock |
| 8. Migdale | 50. Bellater |
| 9. Fearn | 51. Morven-Cabrach |
| 10. Carn Chuinneag | <u>52.</u> Glen Doll |
| 12. Abriachan | 53. Lochnagar |
| 13. Cluanie | 54. Ben Vuirich |
| <u>14.</u> Ratagain | 55. Comrie |
| 15. Glen Dessary | 56. Garabal Hill |
| <u>16.</u> Strontian | <u>57.</u> Kilmelford |
| <u>16'</u> Corran | <u>58.</u> Arrochar |
| <u>17.</u> Ross of Mull | 59. Distinkhorn |
| <u>18.</u> Ballachulish | 60. Cockburn Law |
| 19. Ben Nevis | 61. Cairnsmore of Carsphairn |
| <u>19'</u> Mullach nan Coirean | 62. Loch Doon |
| 20. Foyers | <u>63.</u> Cairnsmore of Fleet |
| <u>21.</u> Etive | 64. Criffell |
| 22. Rannoch Moor | 65. Skiddaw |
| 23. Strath Ossian | 66. Ennerdale |
| 24. Strathspey | 67. Eskdale |
| 25. Cairngorm | <u>68.</u> Shap |
| 26. Monadhliath | |
| 27. Glen Kyllachy | |
| <u>28.</u> Findhorn | |
| 29. Moy | |
| 30. Ardlach | |
| 31. Dunfallandy Hill | |
| 32. Auchlee | |
| 33. Dorback | |
| 34. Grantown | |
| 35. Ben Rinnes | |
| 36. Huntly | |
| 37. Aberchirder | |
| 38. Longmanhill | |
| 39. Strichen | |
| 40. Maud | |
| 41. Peterhead | |
| 42. Haddow House-Arnage | |

NB: Underlined numbers refer to plutons which have been analysed for their sulphur isotopic composition.

The Caledonian intrusions of Scotland, northern England and Ireland were emplaced in and adjacent to the Caledonian metamorphic belt in a variety of different geological environments from about 555 to 390 Ma. Compositionally, the Caledonian granites range from diorites and tonalites, through granodiorites, to peraluminous granites.

The earliest phase of Caledonian magmatism in Scotland was the emplacement of small migmatitic and sheeted complexes of biotite or muscovite granite dating from 555 ± 10 Ma (Long, 1964) to 491 ± 5 Ma (Pankhurst and Pidgeon, 1976). Subsequently, during the main phase of structural deformation and metamorphism of the Grampian Orogeny which occurred over a very short interval from about 490 to 470 Ma, these older granites were largely converted to foliated augen gneiss or schistose granite. The main phase of Scottish Caledonian magmatism occurred from 463 ± 4 Ma (Pankhurst, 1974) to 390 ± 6 Ma (Pidgeon and Aftalion, 1978) with the emplacement of younger undeformed post-tectonic granites.

In Ireland, the oldest of the discrete acid plutons (though not the oldest granite) exposed is the Oughterard granite in the Dalradian schists of Connemara, Co. Galway. It forms two large, roughly circular, plutons, each six km in diameter joined by an irregular dyke of granite, in addition to many minor intrusions. The granite is situated to the west of Lough Corrib, between Oughterard and the Corcogamore mountains. It is intruded into the Connemara schists and migmatites which include K-feldspar gneisses (Leake, 1970b), the oldest granite in the area. The Oughterard granite has suffered shearing, chloritization and sericitization

but there is no evidence of forceful intrusion. The age relations of the Oughterard granite have been discussed in detail (Leggo et al, 1966; Pidgeon, 1969). Rb - Sr isochron studies have dated the granite at 469 ± 7 Ma (Leake, 1978).

Most of the Irish Caledonian granites (e.g. Donegal and Galway Granite suites; Leinster Granite (Fig. 1.2)) are about 400 Ma old (Leake, 1978). The Galway Granite (Fig. 1.3) is one of the largest of these bodies and lies on the assumed direct extension of the Southern Upland Fault across Ireland, a major splay of which probably passed through the ground now occupied by the batholith to emerge in the Skerd Rocks, southwest of the granite where a major pre-granite fault brings the south Connemara series of supposed Ordovician age against the Connemara basic and ultrabasic rocks (Leake, 1963; Max and Ryan, 1975). In addition to some small satellite bodies, e.g. Omev, Roundstone and Inish granites, the Galway batholith involves a number of distinct intrusion centres (Leake, 1978). The Errisbeg Townland Granite, a porphyritic orthoclase-microcline-adamellite; the Carna dome granodiorite, and the Galway Kilkieran dome. Murvey Granite is a late marginal variety of more acidic albite granite. The whole batholith has been dated at 407 ± 12 Ma by a Rb - Sr isochron (Leggo et al, 1966) and 415 ± 15 Ma by U-Pb measurements on zircons (Pidgeon, 1969).

1.4 History of Previous Work

The systematic study of the geochemistry of the Caledonian granites was severely hampered by the difficulty of obtaining large

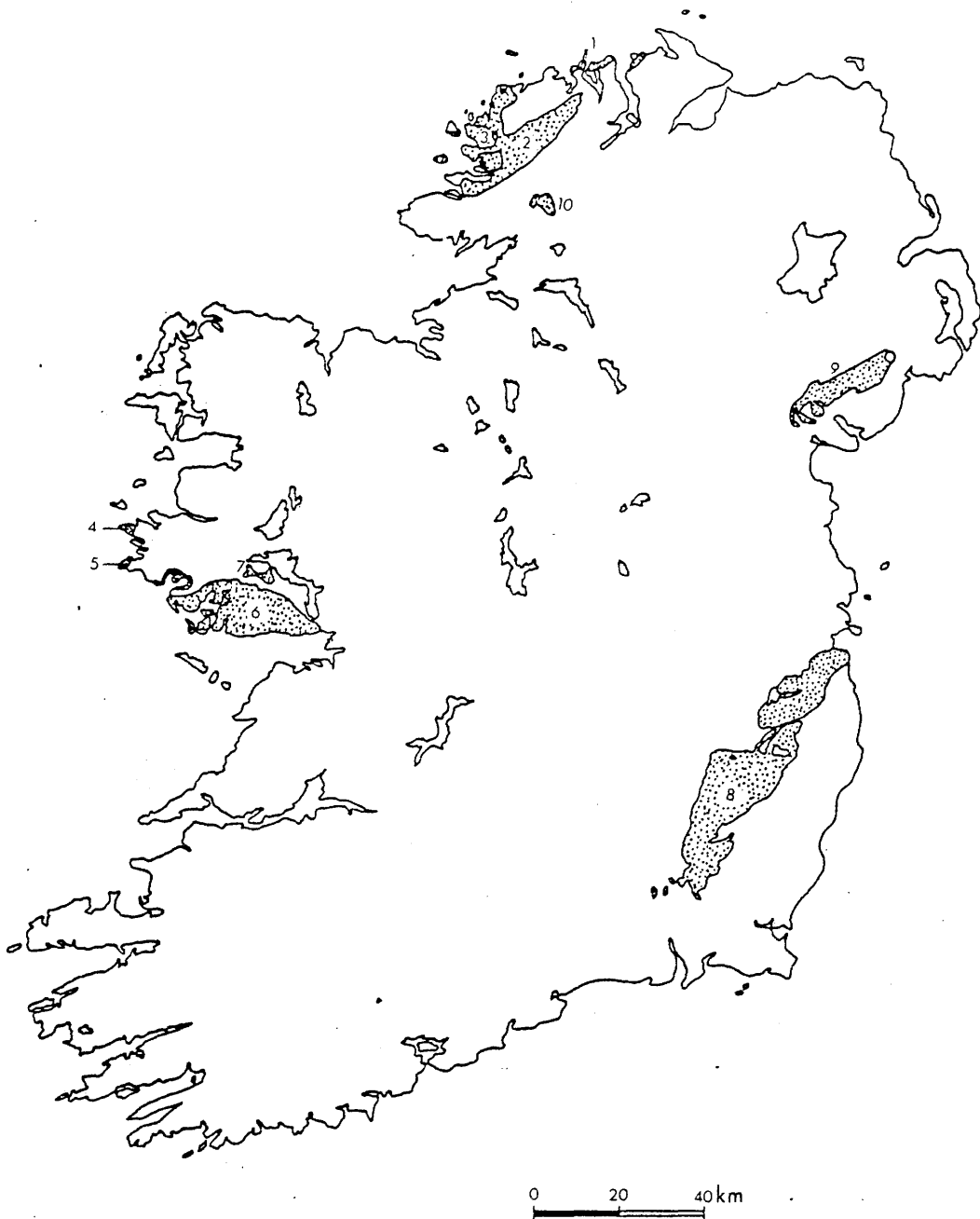


Fig. 1.2 Sketch map of Ireland showing the distribution of Caledonian granitoids. The numbers assigned to the following intrusions:

- | | |
|-----------------|---------------|
| 1. Fanad | 6. Galway |
| 2. Main Donegal | 7. Oughterard |
| 3. Rosses | 8. Leinster |
| 4. Omey | 9. Newry |
| 5. Inish | 10. Barnsmore |

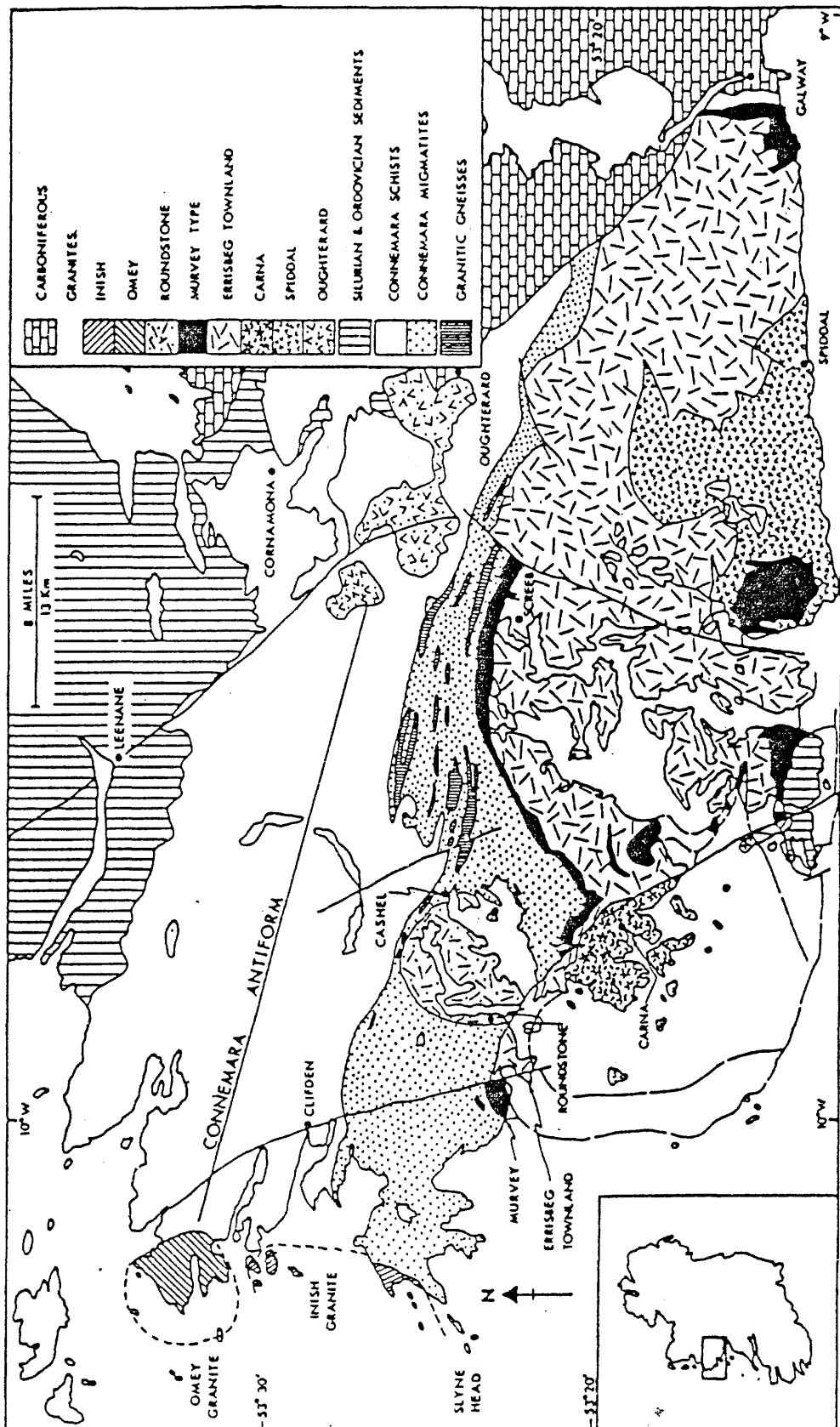


Fig. 1.3. The Connemara Granites with the central part of the Galway Granite adapted from Max *et al.* (1978).

numbers of analyses until automatic methods became available about 20 years ago. Nockolds (1941) presented and discussed major element analyses of rocks and minerals in relation to the petrogenesis of the Garabal Hill Complex in Scotland. This work was extended by Nockolds and Mitchell (1948) to include trace elements and data for a number of other intrusions. Little else had been published by the time that Read (1961) wrote his classic synthesis. Read (1961) classified the British Caledonian Granites into two temporal groups, the 'Older', pre-tectonic granites and the 'Newer' post-tectonic granites, which he further subdivided on the basis of intrusive style into 'Forceful' and 'Last' intrusions.

More recent classifications have attempted to differentiate and subdivide the British Caledonian granites on the basis of geochronological, geochemical and geophysical differences. Van Breemen and Bluck (1981), and Pankhurst and Sutherland (1982) offer satisfactory temporal classifications which do not, however, describe clearly the petrogenesis of the Caledonian granites. Brown and Locke (1979) recognized that many of the Older and Newer 'Forceful' granites had chemical compositions, as well as density and aeromagnetic expressions, that were similar to the Moinian and Dalradian country rocks into which they had been intruded. These similarities contrast markedly with the large negative gravity anomalies, significant aeromagnetic anomalies, higher Sr contents, higher K/Rb ratios, and lower U contents typical of many Newer 'Last' granitoids. According to Brown and Locke (1979)

the Older and Newer 'Forceful' granites were largely derived from the upper crust, whereas the Newer 'Last' granitoids were primarily subduction zone derived. These authors also argue that the two classes were separated in time, the former being pre-Silurian in age and the latter, Siluro-Devonian. This classification which postulates a genetic relationship, as well as temporal difference between the Older and Newer 'Forceful' granites, and Newer 'Last' granitoids is incorrect; for example, the Sr- isotopic composition of the Newer 'Forceful' Ballachulish, Moor of Rannoch and Strontian granitoids is the same as that of the Newer 'Last' Cruachan and Ben Nevis igneous complexes, and is indicative of an origin in the mantle or lower crust rather than upper crust (Pankhurst, 1979; Halliday et al., 1980; Hamilton et al., 1980; Harmon and Halliday, 1980). Likewise, the Newer 'Forceful' Fleet and Foyers complexes are clearly Devonian in age, post-dating such newer 'Last' granitoids as Lochnagar, Hill of Fare and Cairngorm (Halliday et al., 1979; 1980).

Since isotope studies have proved to be helpful in understanding the origin and evolution of plutonic igneous rocks, there has been an extensive amount of Sr- isotopic data and lesser amounts of O-, Pb- and Nd-isotopic data for representative populations of granitoids from all Caledonian provinces over the past few years, see Halliday et al. (1979); Pankhurst (1979); Harmon and Halliday (1980); Hamilton et al. (1980); Harmon (1984); Harmon et al. (1984); and Halliday et al. (1985). From such studies a fundamental division of the British Caledonian granites has been made. The 'Older' granites are considered to be derived from metasedimentary upper crust. Among the 'Newer' intrusions, S-types predominate south of the Iapetus suture and I-types predominate to the north of the

Southern Uplands and a mixture in the Southern Uplands prism.

Although there has been such extensive work on isotope geochemistry, there has been no sulphur isotope data relating to the British Caledonian granites and their origin despite the fact that Coleman (1977) pointed out that sulphur isotopes and variations in sulphur-bearing lithologies can provide constraints on the source of the sulphur, and hence can give information on the origin of the host rocks. There is little data on S isotopic compositions in granites and most S isotopic data being on sulphide minerals in, or associated with ore bodies. However, Dr. S.E. Shaw of Macquarie University (in Coleman, 1977) was able to distinguish the 'I' and 'S' type granites in New England batholith of SE Australia showing that I-type samples have $\delta^{34}\text{S}$ in the range of -3.6‰ to +5‰, while the S-types give -9.4‰ to +7.6‰. Sasaki and Ishihara (1980) have also published data on sulphur isotope characteristics of granitoids in Japan; the magnetite-series being I-types and the ilmenite-series being S-types.

CHAPTER 2

PETROGRAPHY

2.1 GENERAL PETROGRAPHY OF THE SCOTTISH CALEDONIAN GRANITES

2.1.1 Old, Pre-Tectonic Granites

Most of the early intrusions of the Scottish Caledonides are distinguished by their gneissose texture, and locally the rocks of their aureoles show primary sedimentary textures. The Carn Chuinneag and neighbouring Inchbae (Harker, 1962) are examples of the augen-gneiss rock type, originally porphyritic granite. Potassium feldspar phenocrysts are generally set in an aggregate of quartz, cloudy oligoclase and albite, myrmekite, biotite and muscovite with accessory apatite, sphene, garnet, zircon, epidote, allanite, ore minerals, and rare fluorite. As the rocks become more sheared, microcline increases at the expense of orthoclase. More basic rocks present at Cairn Chuinneag include gabbro, augite-diorite quartz-diorite, tonalite, and hornblende-granite. They have mainly been metamorphosed to amphibolite, hornblende-schist, and hornblende-gneiss. Among the isotopically dated 'older' granites of the Dalradian of Tayside (Perthshire), the Ben Vuirich granite (Pidgeon and Aftalion, 1978) has a well developed foliation. It is a uniform K-feldspar, oligoclase, quartz, biotite, gneiss with accessory

sphene and garnet. The augen are composed of microcline and quartz wrapped around by biotite and muscovite.

2.1.2 Post-tectonic Granites

Many of the Newer Caledonian granites of Scotland have a relatively simple structure but some show more or less concentric arrangement of different granitic rock-types, notably the Helmsdale, Rogart, Strontian, Foyers, Etive, and Ben Nevis complexes in the NW and Grampian Highlands of Scotland, and Loch Doon, Cairnsmore of Fleet, Criffell- Dalbeattie, and Cairnsmore of Carsphairn in the Southern Uplands. There is only a moderate degree of mineralogical variation but the rock-types commonly range from biotite-granite through adamellite, and granodiorite to tonalite, and more basic rocks may also be present as inclusions or major members of complexes. Many of the great masses of the Grampian Region, especially those of Aberdeenshire, are formed of biotite-granite; those of Dumfries and Galloway are typically granodiorites or tonalites. Where there is variation within a single mass, the more basic rocks generally occur at the margins.

Biotite-granite or adamellite occurs in many of the intrusions, e.g. Lairg, Helmsdale, Migdale, Fearn, Ratagain, Ross of Mull, and Strontian in Northwest Scotland, and Cairngorm, Lochnagar, Glen Tilt, Moy, Monadhliath, Foyers, Strichen, Ben Nevis, Ballachulish, and Stratav in the Grampian Highlands. The Strontian granite complex, the largest and one of the better known of these masses in the

Northern Highlands, illustrates the nature of many of the varieties (Sabine, 1963). The inner part of the complex is a biotite-adamellite which cuts the other main components. The rock is pale-pink or pale-grey, medium-grained, composed of hypidiomorphic oligoclase, subordinate orthoclase or microperthite, and allotriomorphic quartz. Dark minerals usually constitute 5% or less. Greenish-brown biotite is the main ferromagnesian mineral and is often moulded upon feldspar. Accessory myrmekite, iron ore, apatite, sphene, allanite, and epidote occur. The biotite is commonly altered to chlorite, opaque ore, and leucoxene, and plagioclase may be altered to clay minerals with scattered sericite.

The granodioritic member of the Strontian Complex is a grey or pink porphyritic mass, distinguished from the tonalitic member by the abundant pink microperthite megacrysts up to 2.5cm long, and some phenocrysts of oligoclase. Green hornblende is, in places, in aggregates with or inclosed by greenish-brown to yellow biotite. Sphene and apatite are common accessory minerals. The tonalitic granodiorite, however, is a medium- to coarse-grained grey, well foliated rock composed of hypidiomorphic feldspar typically amounting to about 50% of the rock. The principal dark minerals are hornblende (up to 9%) and biotite (up to 11%) with chloritic pseudomorphs after diopside. Sphene is common, and apatite, calcite, zircon, muscovite, and iron ore are accessory minerals.

Dioritic rocks are a feature of a number of the complexes (e.g. Etive complex, Garabal Hill, Ratagain, Glen Doll, Arrochar,

and Glen Tilt). At Garabal Hill, pyroxene-mica-diorite occupies only a small outcrop in a complex notable for a wide variety of rock types from peridotite to granodiorite but is of importance according to Nockolds (1941) as representing the original magma. The rock consists of medium- to fine-grained hypidiomorphic augite hypersthene partly converted to fibrous amphibole, olivine largely altered and surrounded by coronas of pyroxene and plagioclase, clouded plagioclase zoned from labradorite (An_{55}) towards oligoclase (An_{30}), irregular flakes of biotite moulded upon plagioclase, accessory iron ore, apatite and zircon, and interstitial quartz and microperthite.

2.2 THE GALWAY BATHOLITH

The petrography of the Galway Granite has been described in detail by Wright (1964), and a summary is given by Leake (1978). Within the 14 square miles of outcrop of the Galway batholith, several varieties of granite are recognised, the most extensive of which is a porphyritic orthoclase-microcline-adamellite (Errisbeg Townland Granite) and an inner Spiddal Granodiorite. A transition occurs between the Carna Granodiorite and the Errisbeg Townland granite in which K-feldspar phenocrysts are more abundant, hornblende less so, and there is well-marked primary magmatic layering with variation in proportions of biotite and hornblende to feldspar and quartz, current-bedding and graded bedding (Wright, 1964). Satellite plutons of the Galway batholith include the Roundstone (Wager, 1932) Omev and Inish adamellites (Townend, 1966). The Inish mass has

a marginal zone of aplite and pegmatite containing abundant displaced blocks of country-rock passing out into closely veined rock, the veins gradually becoming less frequent over a distance of 1 km (Leake, 1978).

The Galway granite suite possesses a hypidiomorphic inequigranular texture. Tabular perthitic K-feldspars frequently enclose biotite, plagioclase, sphene, zircon, and hornblende. The K-feldspar is generally intermediate between microcline perthite and orthoclase microperthite with grain size ranging from a few mm in the Murvey and Carna granites to large pink phenocrysts of 4cm in the Errisbég Townland granite. Biotite is generally altered to green chlorite, or prehnite, or epidote. Hornblende is a common green prismatic variety present in most of the granites except in the Murvey type. It alters either to chlorite or to chlorite and epidote. Allanite is euhedral with dark brown inner and light brown outer zones. It occasionally attains a size of 0.5mm in diameter. When enclosed by K-feldspar it is the centre of the cracks which radiate out into the surrounding feldspar. Sphene is universally present, except in the Murvey variety, and tends to be associated with magnetite which it often mantles. Granular magnetite, and prismatic apatite and zircon are present throughout the granites. Pale pink garnet occurs only in the Murvey Granite.

2.3 THE CASHEL MICROGRANITE SILL

Leake (1970) proposed that the Cashel-Lough Wheelaun body of basic and ultrabasic rocks was displaced, within the mobilized

metasediments, along a curved surface of decollement. This suggested plane is represented by a thin microgranite sill which occurs within these mobilized metasediments, a few meters away from the contact with the Cashel intrusion. The sill can be traced from the north-west corner of the Cashel body, for over a kilometer in a north-easterly direction, gradually separating further and further from the intrusive contact. The outcrop varies in width, from a few meters to over 10 meters and is displaced in places by subsequent faulting. In thin sections, the rock can be seen to be composed of approximately equal proportions of quartz, plagioclase, and microcline. The quartz forms euhedral grains up to 5mm in diameter, that occasionally display strained-extinction. The plagioclase is of albite composition and forms euhedral to subhedral grains up to 4mm in diameter that display microcline twinning, and occasionally simple twinning. In addition, small quantities of chloritized biotite are present. Accessory minerals are apatite, zircon, epidote and muscovite.

2.4 THE OUGHTERARD GRANITE

The granite is quite unlike the remaining Caledonian granites of Ireland for being aphyric, considerably sheared, and for appearing in numerous unconnected pods and veins and in two connected, roughly circular, main bodies: the Tullaghboy mass in the west, now much displaced by faulting, and the Oughterard mass in the east (Bradshaw et al., 1969). The two bodies are joined by a most irregular dyke. The Tullaghboy mass, which is often xenolithic with country rock fragments, passes into a swarm of small granite pods, veins, sills

and dykes that extend for several km to the west in the Connemara Schists and also in the Migmatitic Quartz Diorite Gneiss. The intrusions largely lie astride the F_4 Connemara antiform being clearly later than both the F_3 and F_4 folds which they truncate (Leake, 1978). There are no pushing or distension structures and the granite has been emplaced partly by dissolving its way into the country rock and partly by dilation. There is no detectable contact aureole and it seems as if the magma was emplaced before the regional metamorphism had completely declined (Leake, 1978).

The petrography, geochemistry, and field relations of the Oughterard granite have been described by Bradshaw et al., (1969). Petrographically, the granite is massive with white or pink K-feldspar, slightly greenish plagioclase, glassy quartz, and green chlorite. In thin sections, it has a hypidiomorphic granular texture with about 30-50% quartz, 30-40% plagioclase, 15-30% K-feldspar, generally less than 7% chlorite, mostly after biotite, and a little muscovite. The grain size is generally uniform (1-2mm) and phenocrysts are rare. Exceptions are a small body of finer grained granite within the main mass of the Oughterard, and a local coarser facies on Lackavrea and east of Townaghbeg. Quartz occurs as sutured aggregates with undulose extinction and occasionally replaces both feldspars. Sericitized and kaolinised plagioclase is subhedral, and is partly replaced by quartz and K-feldspar. The potash feldspar is variably microperthitic, has patchy extinction, and is often microcline. Biotite is usually completely chloritized. Traces of muscovite replace chlorite. Spene, apatite, magnetite, epidote, pyrite,

prehnite, and calcite are irregularly present. Garnet is rare and hornblende is restricted to a small intrusion.

CHAPTER 3

GEOCHEMISTRY

3.1 GEOCHEMISTRY OF THE BRITISH CALEDONIAN GRANITES

3.1.1 Major Elements

The British Caledonian granitoids are a group of calc-alkaline to alkalic plutonic rocks, falling largely within the fields of high-K calc-alkaline magmas defined by Peccerillo and Taylor (1976), which cover the compositional spectrum from ultramafic rocks with less than 40% SiO₂ to extremely leucocratic rocks with more than 70% SiO₂ (Pankhurst and Sutherland, 1982). Overall and within individual complexes, there is a steady decrease in Al, Fe, Mg, Ti, P, and Ca with an increasing acidity (Fig. 3.1 to Fig. 3.7), and an increase in Na and K (Fig. 3.8 and Fig. 3.9). The lack of iron-enrichment in intermediate compositions is a distinguishing feature of the calc-alkaline series to which orogenic granites throughout the world belong. In fact, Mercy (1963) showed that, from diorite to granite, the Caledonian igneous rocks had a remarkably constant mol Fe/Mg ratio very close to 1. Fig. 3.10 shows variation in major elements as established by Nockolds and Mitchell (1948) and confirmed by all later work. Below about 55% SiO₂ there is considerable scatter, but above this level the trends are particularly

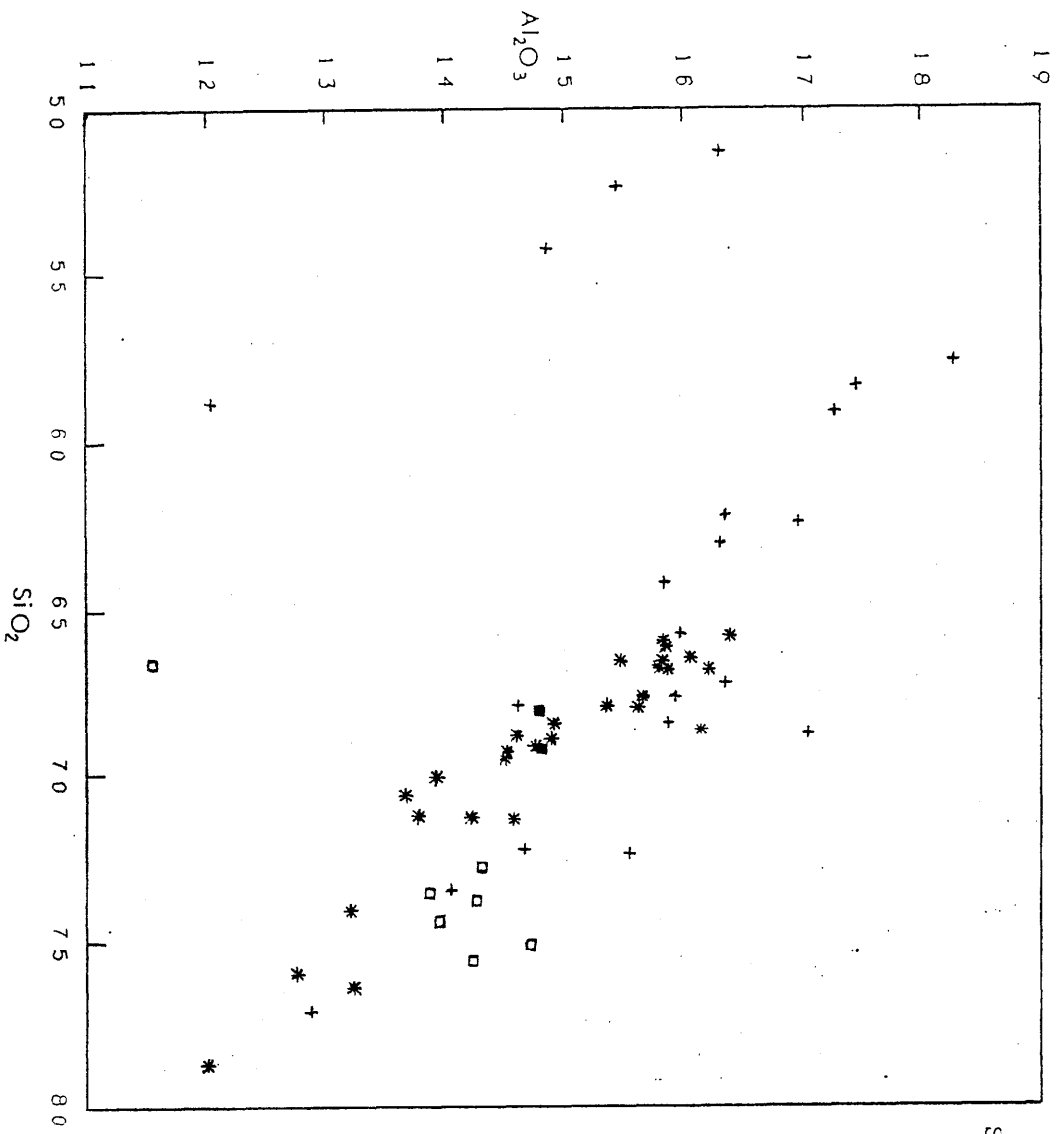


Fig. 3.1 Plot of SiO₂ (wt %) versus Al₂O₃ (wt %)

Symbols: + Scottish granites
 * Galway granites
 □ Oughterard granite
 ■ Cashel microgranite sill

Fig. 3.3 Plot of SiO_2 (wt %) versus Fe_2O_3 (wt %)

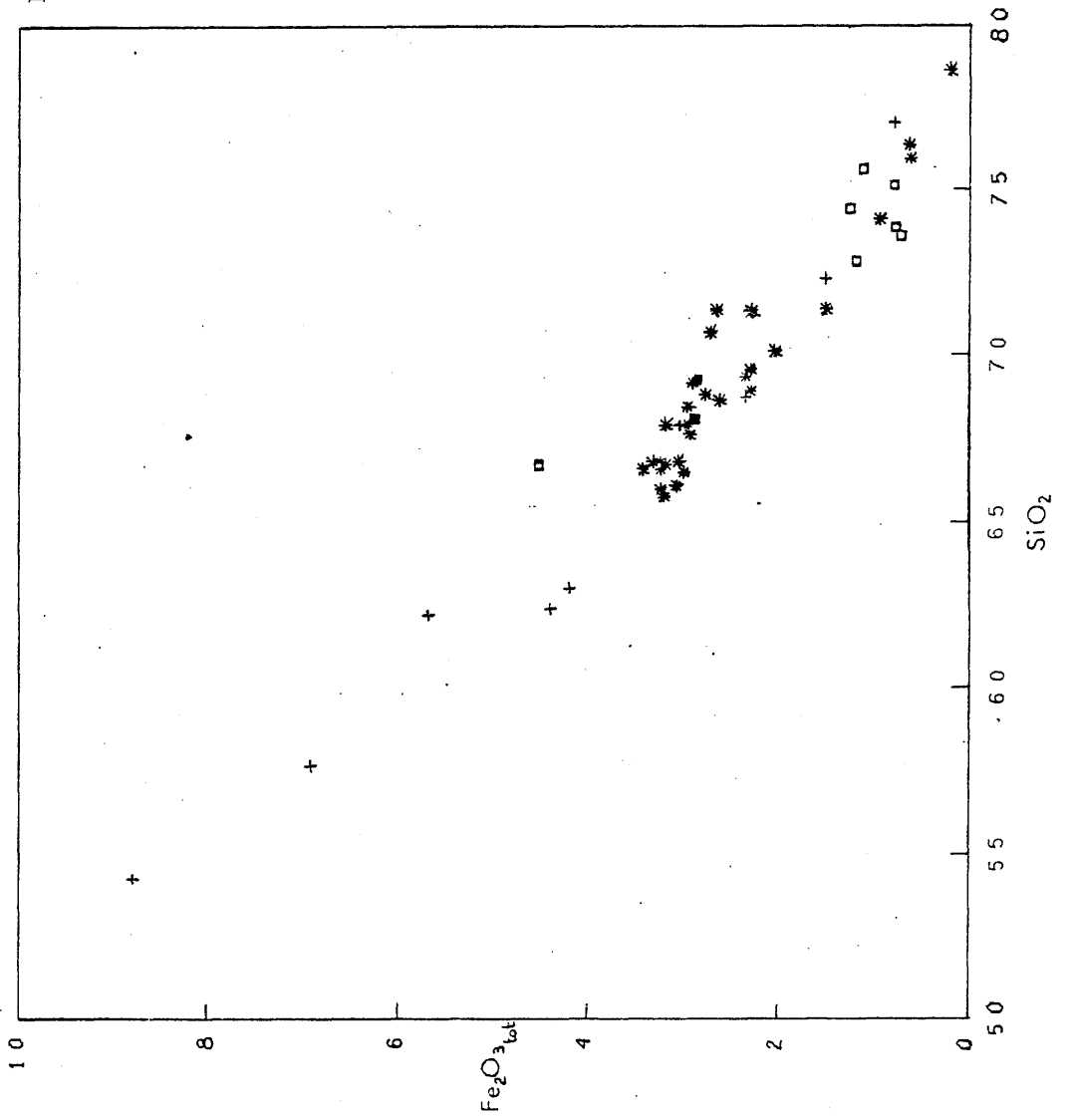


Fig. 3.4 Plot of SiO₂ (wt %) versus MgO (wt %)

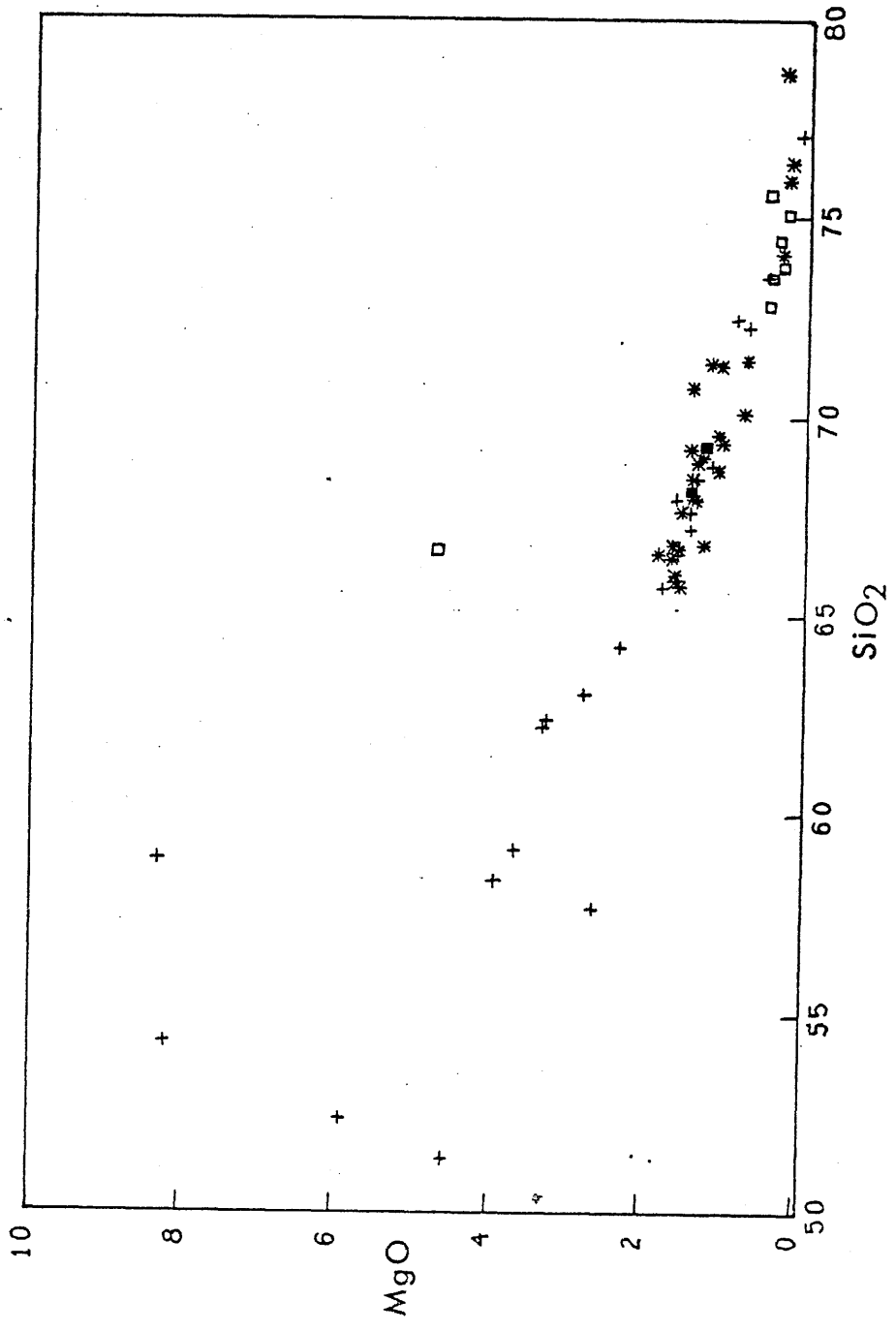


Fig. 3.5 Plot of SiO_2 (wt %) versus TiO_2 (wt %)²

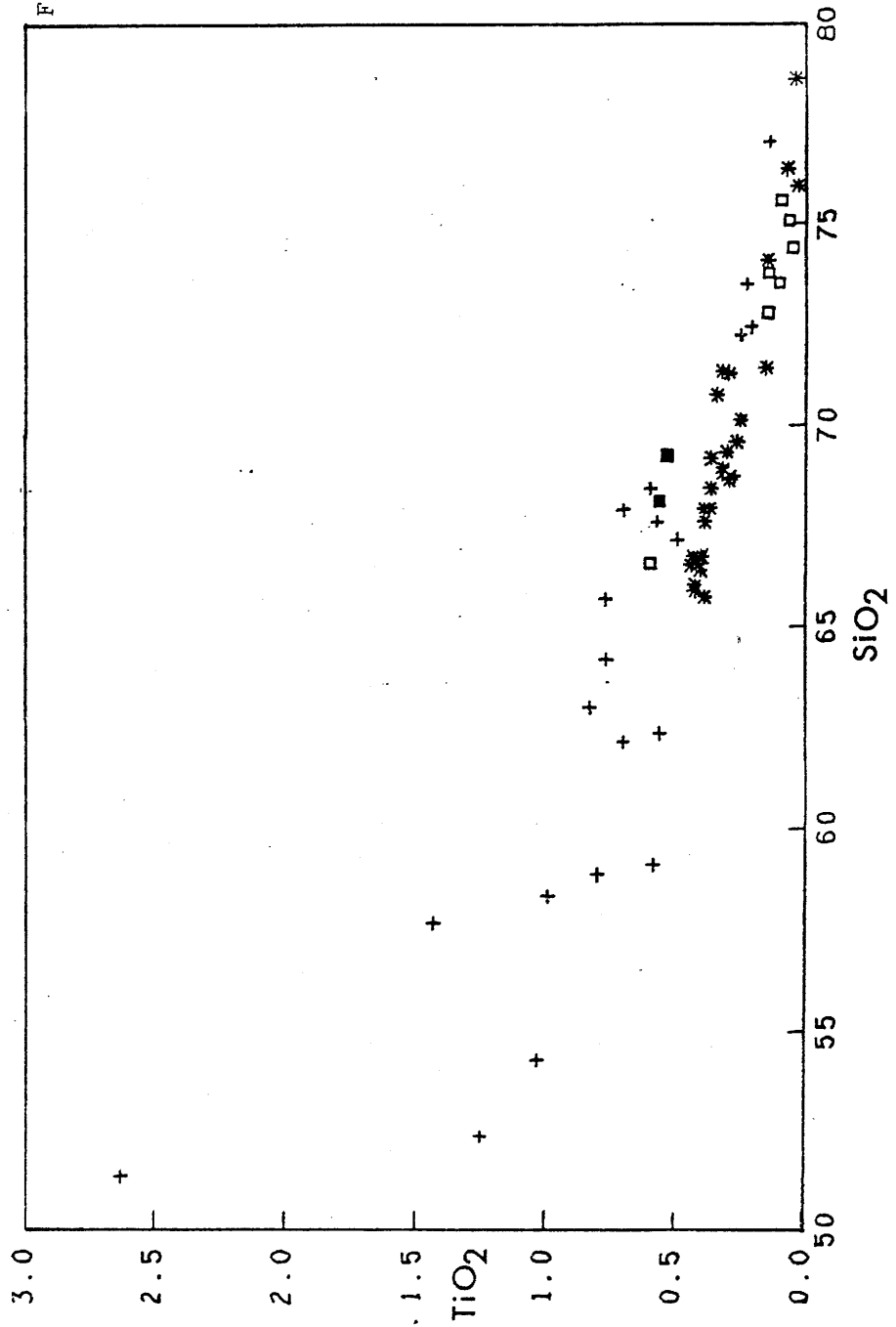


Fig. 3.6 Plot of SiO_2 (wt %) versus P_2O_5 (wt %)

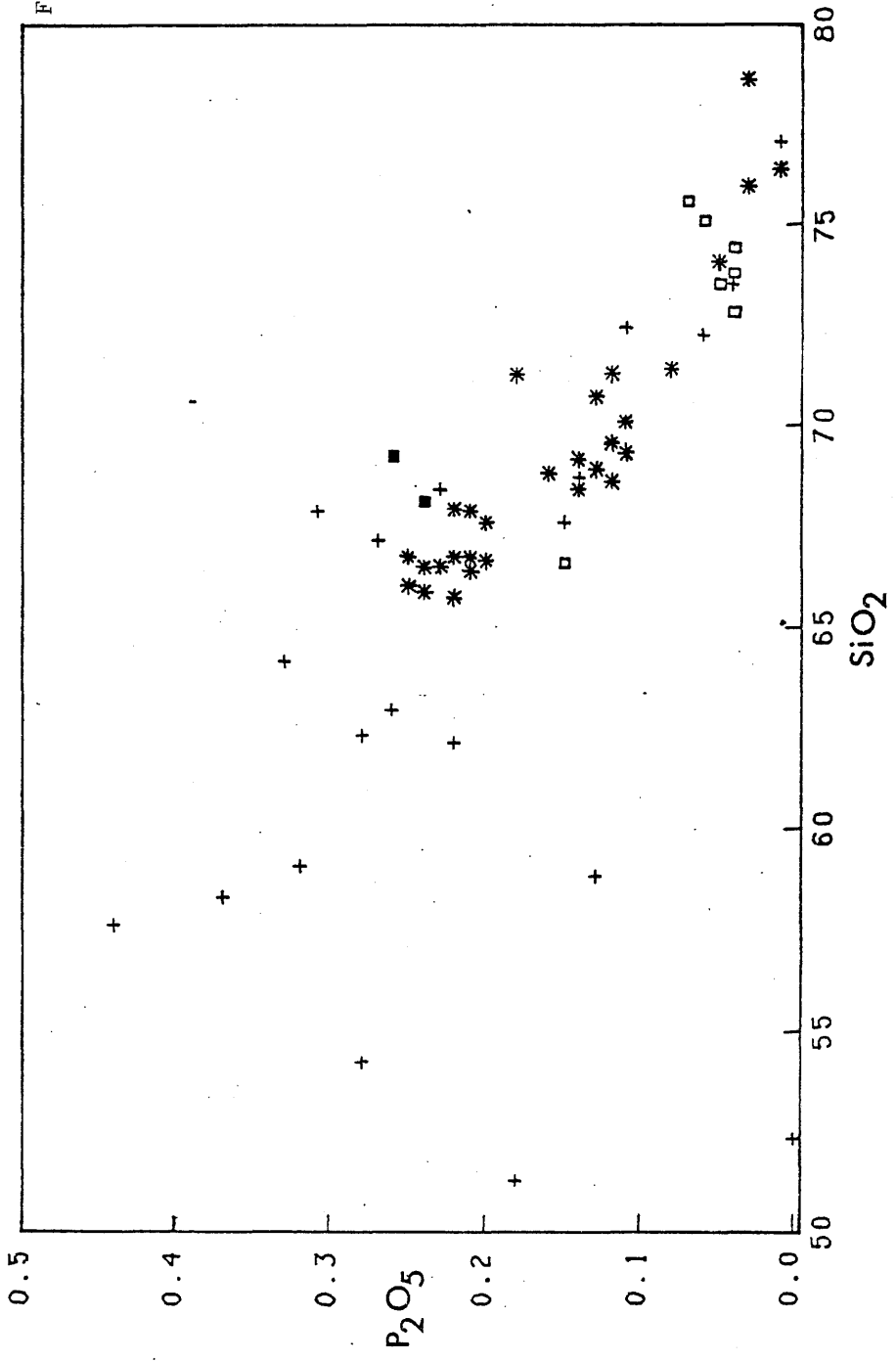


Fig. 3.7 Plot of SiO₂ (wt %) versus CaO (wt %)

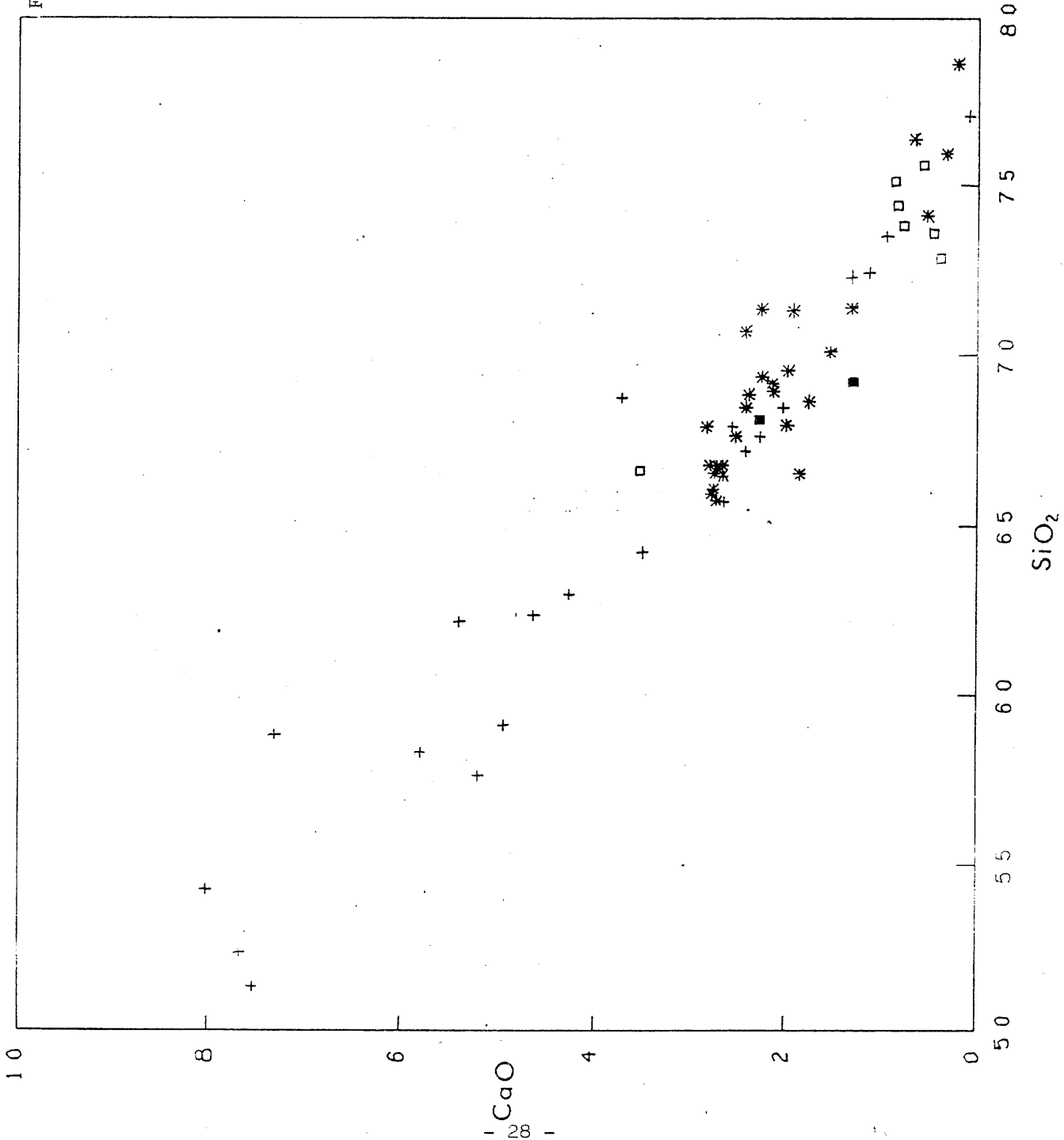


Fig. 3.8 Plot of SiO_2 (wt %) versus Na_2O (wt %)

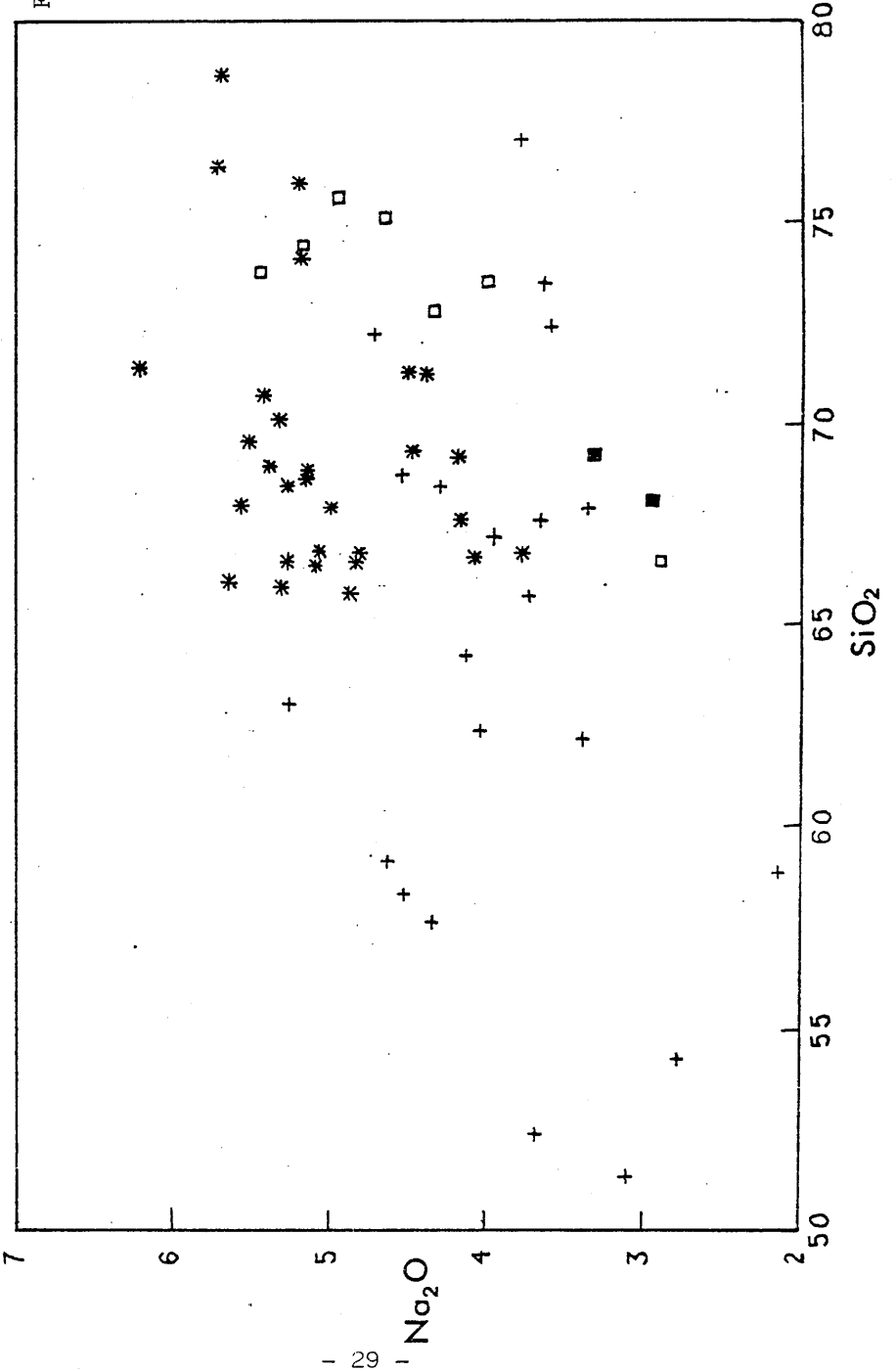
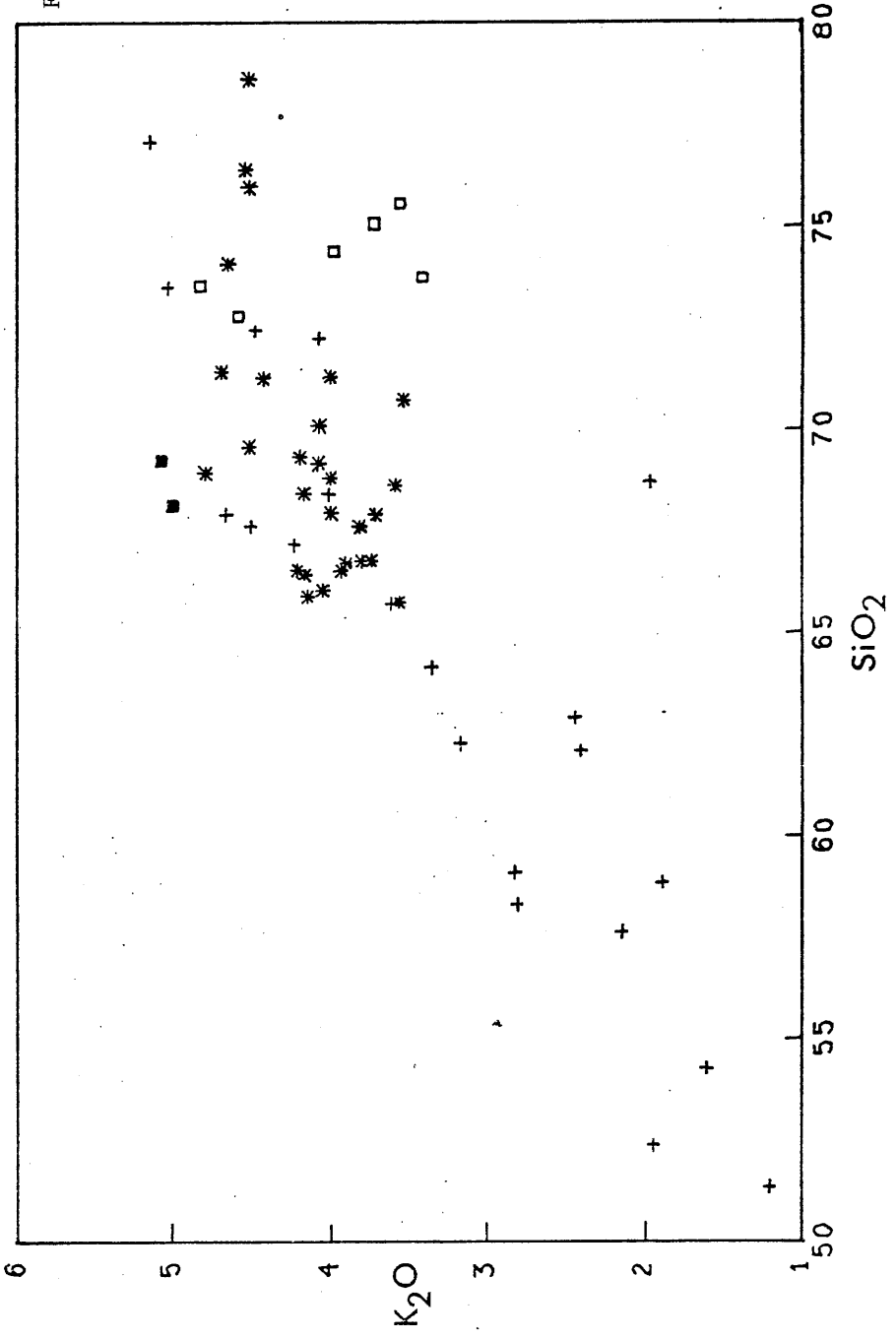


Fig. 3.9 Plot of SiO_2 (wt %) versus K_2O (wt %)



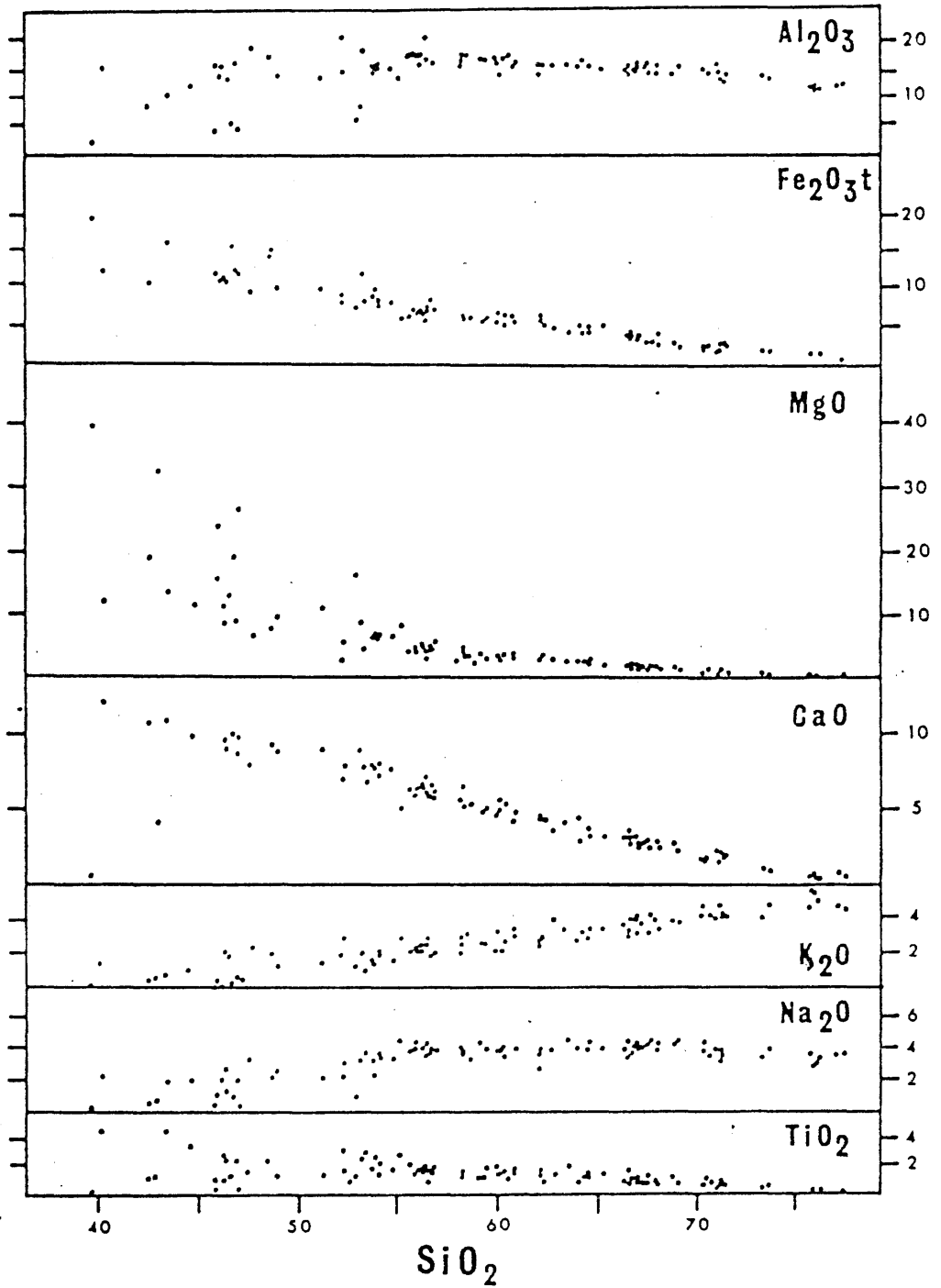


Fig. 3.10 Major-element variation in Caledonian calc-alkaline igneous rocks. (After Nockolds and Mitchell (1948)).

smooth and continuous. By considering chemical balances between the rock series and separated mineral phases, Nockolds (1941) demonstrated that the variations were consistent with removal of phenocrysts from a primary magma equivalent to the pyroxene-mica-diorite. Initially these crystals would be olivine, augite, and orthopyroxene, but soon hornblende, biotite, and plagioclase would dominate, with potassium feldspar ultimately becoming important (Nockolds and Mitchell, 1948). He, therefore, proposed that the sequence pyroxene-mica-diorite \rightarrow diorite \rightarrow granodiorite \rightarrow adamellite was a liquid line of descent related by crystal fractionation. However, this is unlikely to be the main derivative mechanism of most of the granites as the proportion of granite greatly exceeds what could be produced by fractionation from a pyroxene-mica-diorite magma.

In terms of granite classification, Chappell and White (1974) have classified granitic rocks into two primary groups based upon mineralogy and geochemistry. Those hornblende-bearing granites with accessory sphene and normative diopside and high Na_2O and low (less than 1.1) molecular $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ ratios are termed I-type. By contrast, those predominantly biotite- or muscovite-bearing granites having accessory monazite and normative corundum and low Na_2O and high (greater than 1.1) molecular $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ ratios are designed S-type. The I-type granites are considered to have been produced by melting of an igneous protolith, whereas the S-types are attributed to the anatexis of reworked meta-

pelitic crustal material that has been through a cycle of chemical weathering and sedimentation at the Earth's surface.

The 'Older' Caledonian granitoids of Britain are small plutons that tend to be internally homogeneous but compositionally variable as a group. Chemically they tend to be peraluminous with a narrow range of SiO_2 of 69 to 76%, and low Na/K and K/Rb ratios. Compositionally, they are mainly two-mica granites, although andalusite may replace muscovite on rare occasions (e.g. at Moy granite; Zaleski, 1982). Cordierite has not been recorded in any of the older granites. In most respects, the 'Older' granites have the characteristics of S-type granitoids, which are considered to be primary features inherited from a metasedimentary protolith.

The 'Newer' British Caledonian granitoids, by contrast, have a wide range of SiO_2 (54 to 77%) and a high Na at a given K concentration. Hall (1967) attributed the high Na content to melting at higher H_2O pressures. He cited as supporting evidence the apparent relationship between high normative albite and association with appinites (hydrous mafic intrusions). In Fig. 3.11, the ratio of molecular $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ is plotted against SiO_2 for the Caledonian granites of mainland Britain and Ireland (after Halliday and Stephens, 1984). Compositions above the line $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}) = 1$ are peraluminous. Samples with $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}) > 1.1$ are S-types according to the definition of Chappell and White (1974). These are

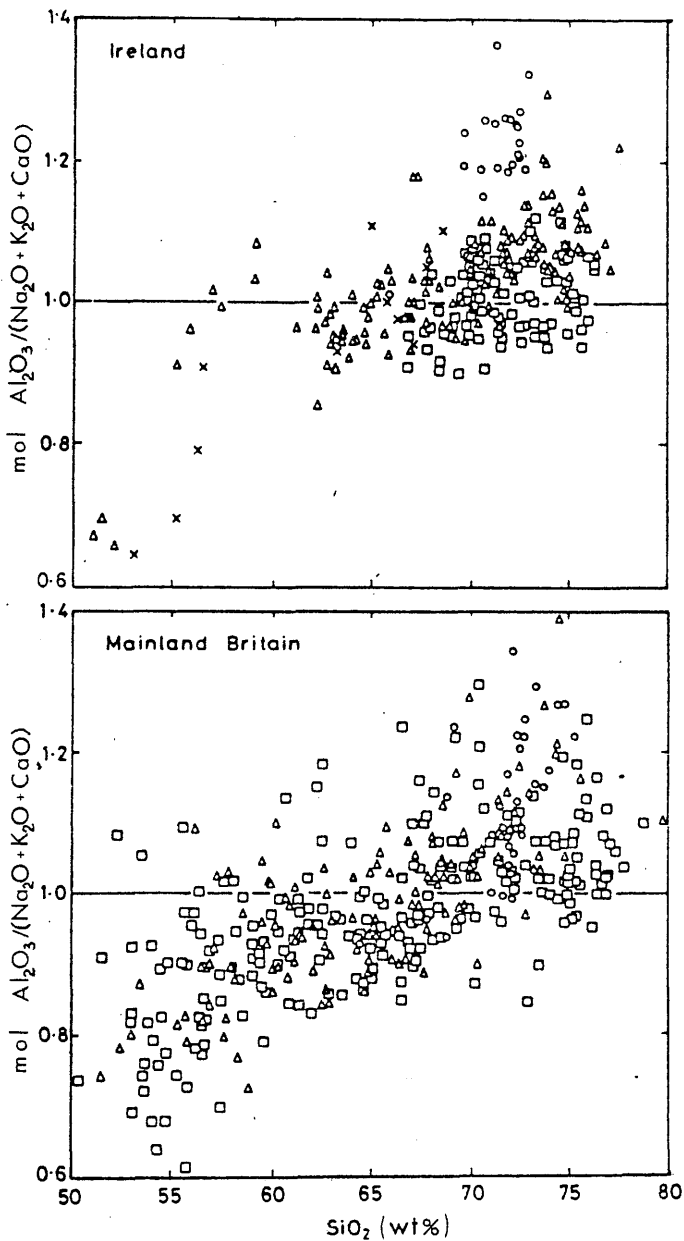


Fig. 3.11 Plot of mol Al₂O₃ / (Na₂O + K₂O + CaO) versus SiO₂.

(After Halliday and Stephens, 1984). Data points above horizontal line define peraluminous composition. For Ireland symbols are: crosses - Newry, triangles - Donegal squares - Connemara, circles - Leinster. For Mainland Britain symbols are: circles - England, triangles - Southern Uplands and Midland Valley, squares - Scottish Highlands.

mainly from English granites and Leinster (Ireland) all south of the Iapetus suture and are of high SiO_2 content. An exception is the Shap Granite in Northern England which is a high-K with I-type mineralogy. The $\text{K}_2\text{O} - \text{Na}_2\text{O}$ plot (Fig. 3.12), however, shows that none of the late granitoids falls within the field of S-type granites from the Lachlan fold belt, SE Australia (White and Chappell, 1983); all fall within the ranges of the Lachlan I- and A-types. In bulk terms, therefore, the late granitoids are largely metaluminous of high-K and calc-alkaline affinities and have the major oxide compositions of I-type granites.

3.1.2 Trace Elements

Concentrations of a wide range of trace elements in the British Caledonian granites are given by Nockolds and Mitchell (1948); Haslam (1968); Coats and Wilson (1971); Brück and O'Connor (1977); and Stephens and Halliday (1984). In general the pattern is what would be predicted from major element geochemistry. The transition metals: Ni, Cr, Co, V, Mn and Zn fall with increasing SiO_2 throughout the range of variation. Sr, Ba, and Zr increase at first, reaching very high concentrations (over 1000 p.p.m.) in the tonalites and granodiorites, but then decrease sharply in the more acid rocks. Only Rb, U, and Th have been shown to increase continuously with SiO_2 . K/Rb ratios are rather variable, ranging from 400 or more in some diorites down to about 100 in the most silicic granites and aplites. Differences in K/Rb ratios between different plutons

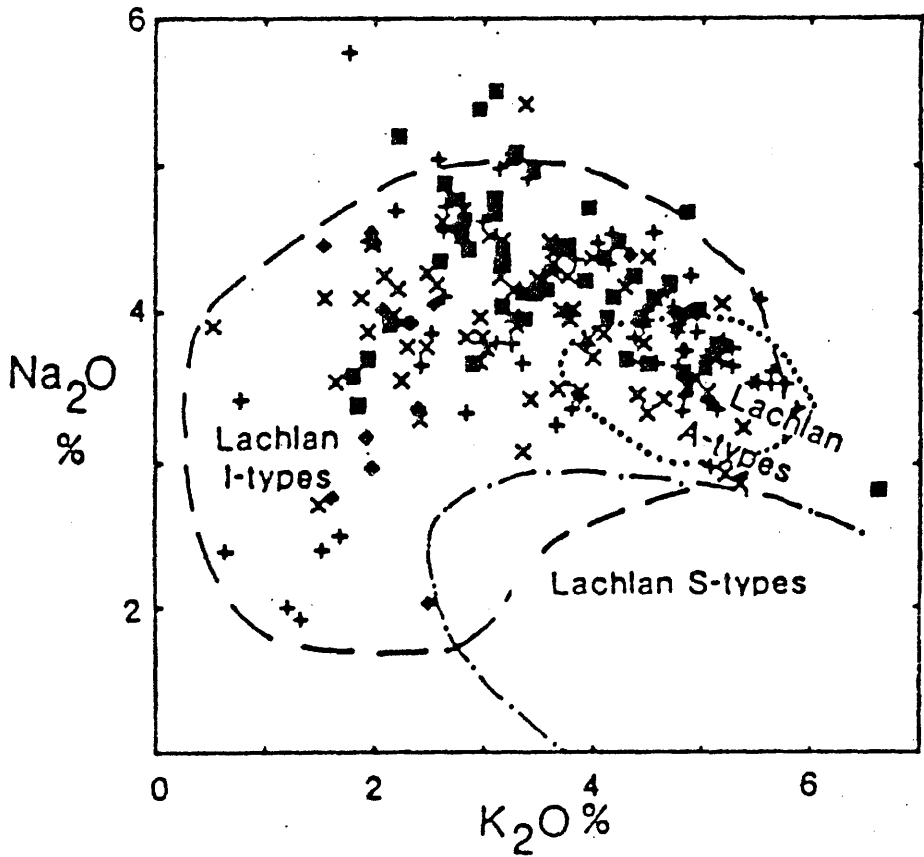


Fig. 3.12 Plot of Na_2O versus K_2O with fields for I-, S- and A-type granites of the Lachlan Fold Belt, Australia (White and Chappell, 1983) shown for comparison. (After Stephens and Halliday 1984).

Symbols are:

- + NE Highlands
- SW Highlands
- ◆ S Highlands
- * Midlands Valley
- x Southern Uplands

are also apparent and must have genetic significance. There is some indication that ratios such as Sr/Ca and Ba/Sr remain essentially constant, at least within the main sequence of individual complexes. Fig 3.13 shows the Rb versus Sr fields of the British Caledonian granites (after Halliday and Stephens, 1984). Some points arise from these data:

- (a) The English granites are low in Sr compared with those of Scotland.
- (b) Shap granite is anomalously rich in Rb for its Sr content.
- (c) The Southern Uplands granites (Doon, Criffell, and Fleet) are enriched in Rb and Sr relative to the Scottish Highland granites of the same Rb/Sr ratio.
- (d) All the granites exhibit trends of increasing Rb with decreasing Sr.
- (e) Sr rich magmas (>500 p.p.m.) are the norm in Scotland and Northern Ireland.

The most important aspects of the data are that the British Caledonian granites are represented by a high Sr province north of the Iapetus suture and a low Sr province to the south. The Sr rich granites are also commonly Ba rich and the Ba/Sr ratio is of the order of unity (Meighan and Neeson, 1979; Wright and Bowes, 1979; Plant et al, 1980). Halliday and Stephens (1984) pointed out that the high Sr magmas are almost certainly a product of a particular province maintained by a particular process. They argued that mantle-derived liquids are enriched in Ba and Sr as a result

Fig. 3.13 (See Overleaf)

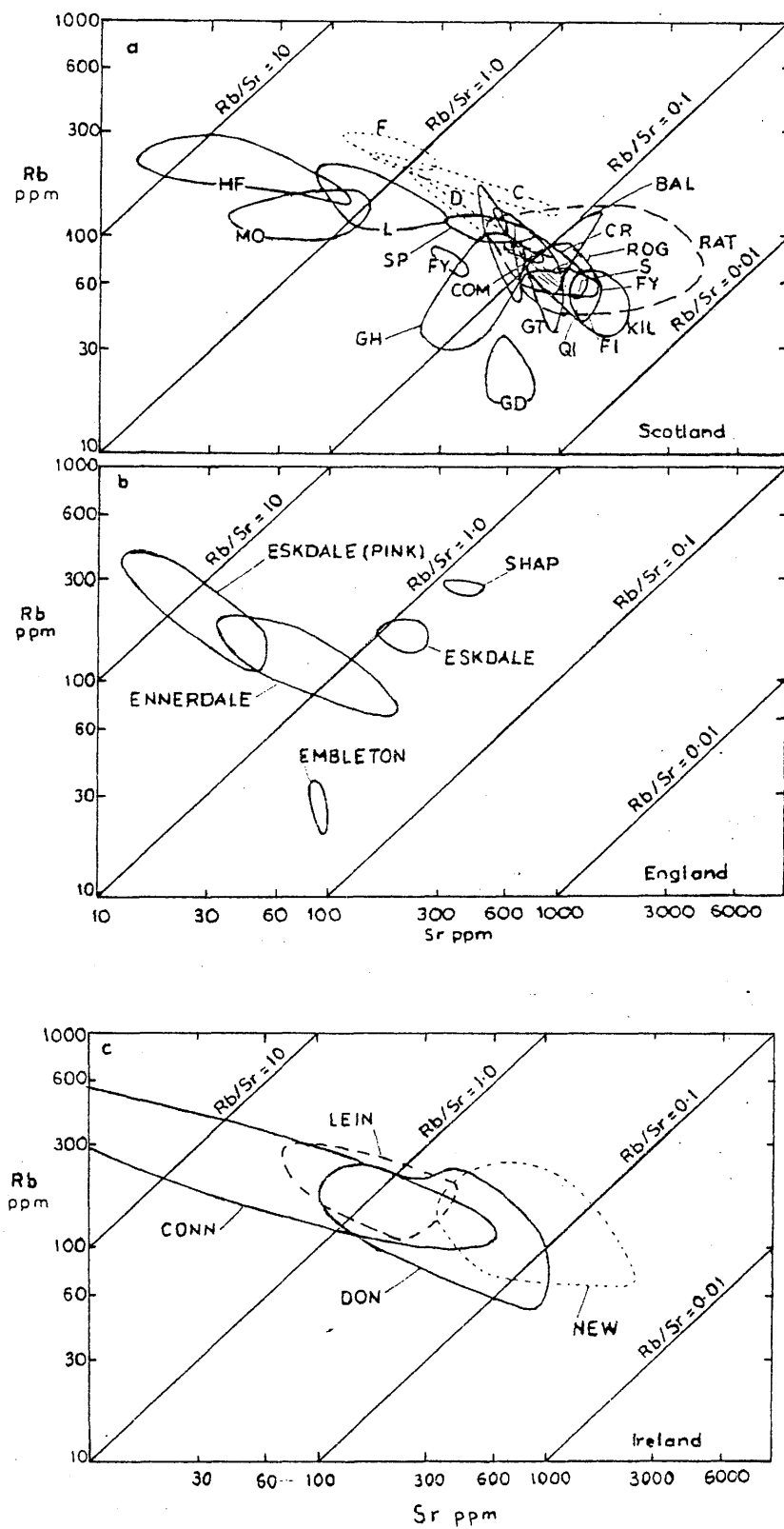


Fig. 3.13 Plot of Rb versus Sr for c.400 Ma granitoids. (After Halliday and Stephens, 1984).

- (a) Scotland: HF - Hill of Fare, L - Lochnagar,
S - Strontian, FY - Foyers, F - Fleet,
C - Criffell, D - Doon, GD - Glen Doll,
GH - Garabal Hill, RAT - Ratagain, COM-
Comrie, QI - Quarry Intrusion, FI - Fault
Intrusion, CR - Cruachan, SP - Stratav
Porphyry, MO - Meall Odhar, BAL -Ballachulish,
KIL - Kilmelford, ROG - Roggart.
- (b) England,
- (c) Ireland: CONN - Connemara, DON - Donegal,
LEIN - Leinster, NEW - Newry.

of partial melting of (probably metasomatized) peridotite without plagioclase as a stable phase possibly followed by high pressure fractionation. If such magma interacted with the lower crust (granulite), this serves to maintain Ba and Sr at high levels and lower the Rb/Ba ratios.

3.1.3 Rare Earth Elements

Rare-earth data are also useful for the petrogenesis of the British Caledonian granites, but the quantity of data available is rather limited. Pankhurst (1979) has shown that the 'Newer' granites of the Scottish Highlands are characterized by LREE enrichment with relatively constant Ce/Yb ratios, which are enriched by a factor of 2-3 over calc-alkaline magmas from modern destructive plate margin environments (Thorpe and Francis, 1979). It is clear from Fig. 3.14 that individual intrusive centres are characterized by distinct REE patterns which reflect their different histories. The lack of Eu anomaly in the more mafic phases of Etive, Strontian, and Foyers complexes indicate that the source region, be it mantle or crust, must have been feldspar-free, or had a very high oxygen fugacity, thus providing a mechanism for producing the extremely high Ba and Sr observed in these intrusions (Halliday and Stephens, 1984).

3.2 GEOCHEMISTRY OF THE GALWAY BATHOLITH

Tables 3.3 and 3.4 present the major and trace element analyses

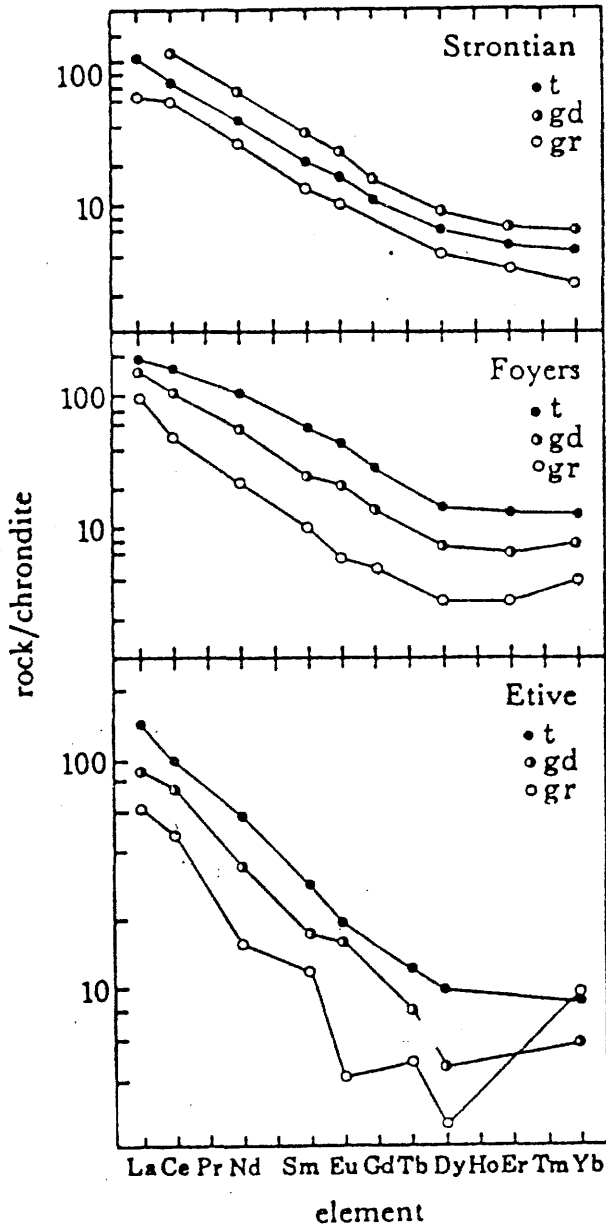


Fig. 3.14 Representative chondrite-normalized rare earth element abundance for the Strontian, Foyers and Etive intrusions of the Scottish Highlands. (After Harmon *et al.*, 1984).

t = tonalite; gd = granodiorite; gr = granite

of the samples collected from different types of granites of the Galway batholith including the Roundstone, Inish, and Omev satellites. Care was taken to use the samples which are not affected by weathering. All erosion surfaces were removed before crushing to a fine-grained homogeneous powder. X-Ray fluorescence was employed for the analyses, and prepared pressed pellets were analysed for the oxides of ten major elements in addition to sixteen trace elements. The methods of Harvey et al., (1973) were used in the case of major elements and that of Leake et al., (1969) for the determination of trace elements. The CO₂ and H₂O contents of each sample were determined by wet chemical analysis. This method was also employed for the determination of ferrous oxide (FeO) contents of each sample.

The objectives of geochemical analysis are to establish any possible relationship between the analysed elements and to compute the mineralogical compositions of the rocks and from this information reconstruct the history of the studied rocks. Several plots have been made to establish correlations between different major and trace elements (see Fig. 3.1 to 3.9 and 3.15 to 3.20).

3.2.1 Major Element

The major element variations as shown in Fig. 3.1 to Fig. 3.9 illustrate clearly that the granites form one continuous sequence and show the trends usually associated with magmatic differentiation;

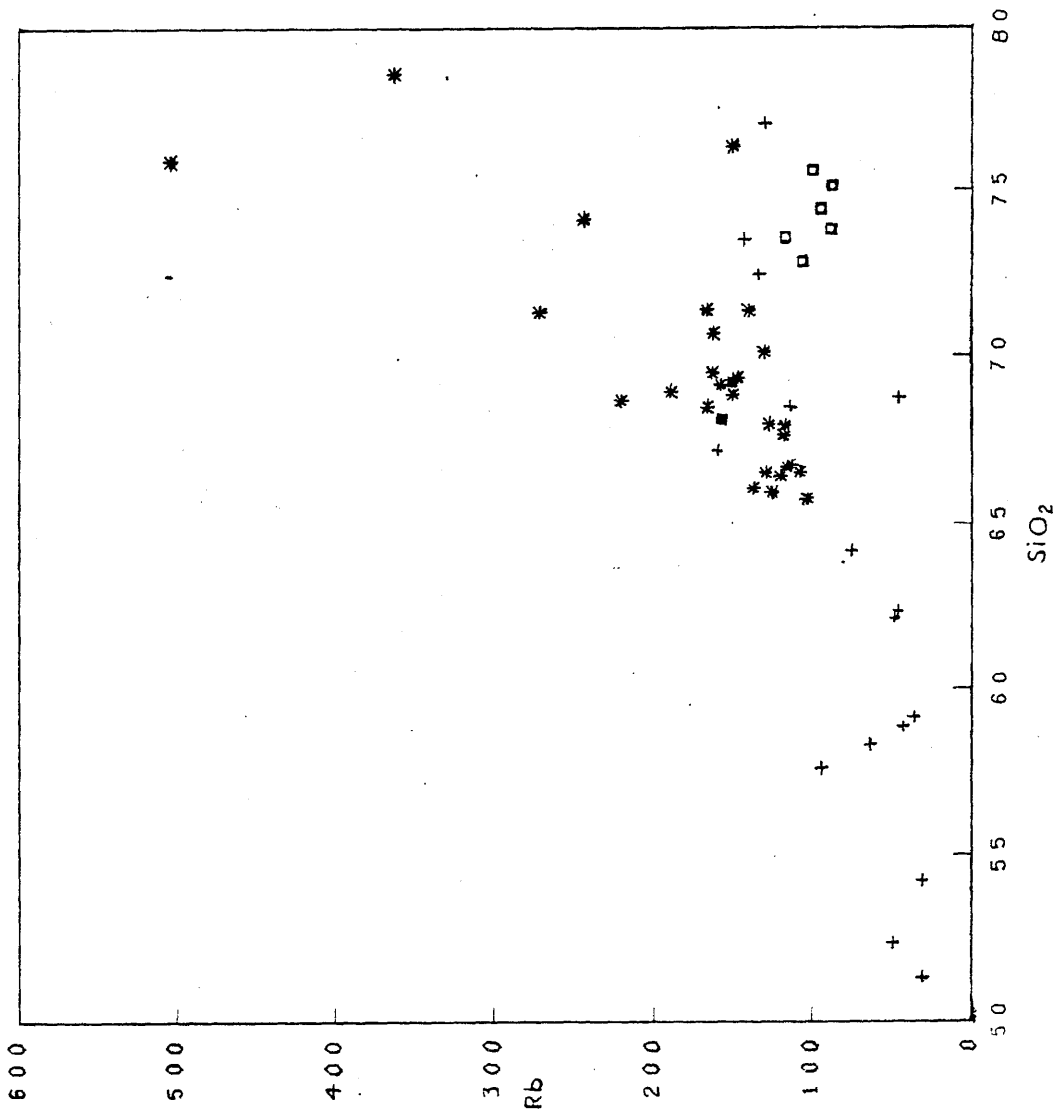


Fig. 3.15 Plot of SiO₂ (wt%) versus Rb (ppm)

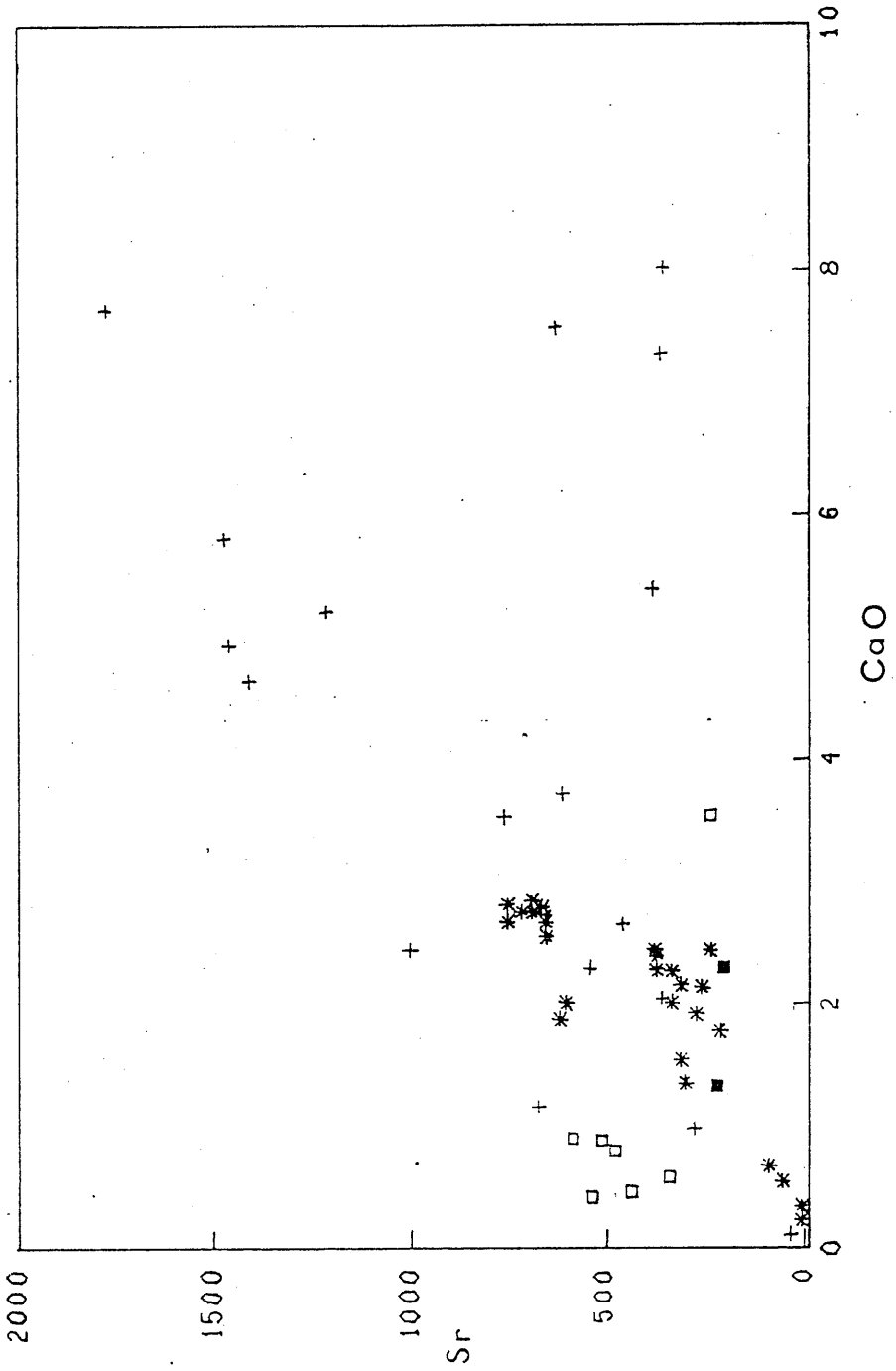


Fig. 3.16 Plot of CaO (wt %) versus Sr (ppm)

the increase in SiO_2 being accompanied by increases in K_2O and Na_2O while CaO , Fe_2O_3 , P_2O_5 , TiO_2 and MgO all decrease. The overall fractionation trend is from the coarse porphyritic foliated granite through the coarse porphyritic granite to the biotite-poor aphyric granite and aplites.

The silica contents extend from 68% in the Carna granite to 76% in the Murvey variety while alumina decreases from 15 to 13%. This is reflected in the general increase of quartz and potassium feldspar at the expense of biotite, hornblende and calcic plagioclase. Accompanying this trend is a decrease of total iron with increasing silica content resulting in a decrease of the oxidation ratios. This could indicate a relative diminution of water vapor pressure and partial pressure of oxygen in the more siliceous granites. The restriction of garnet to the Murvey granite tends to substantiate this view.

The decrease in MgO (from 1.42 to 0.18%) and CaO (from 2.42 to 0.35%) from the Carna to the Murvey granites could be correlated partly with the loss of hornblende and the decrease of biotite, and partly with the low anorthite contents of the Murvey granite plagioclase (which is albite) compared with that of the Carna granite (calcic oligoclase).

K_2O increases steadily from 4.08% in the Carna to a maximum of 4.64% in the Murvey granite. This is reflected petrographically by an increase of potash feldspar.

3.2.2 Trace Elements

The trace elements generally show consistent changes from the least siliceous granites (the Roundstone, Carna, and Omey granites) through the various intermediate types to the most siliceous granite (the Murvey granite). Thus Sr, Ba, and Zr increase at very high concentrations with increasing SiO_2 reaching a level of about 1,100 ppm, in the case of Ba, in the Roundstone granite and then decreases sharply to 200 ppm in the more siliceous rocks. Rb, U, and Th, however, show an increase with increasing SiO_2 throughout the different granite varieties.

Sr has a unique relationship with Ca according to Turekian and Kulp (1956). It has a positive slope plot in acid igneous rocks and a negative one for basic igneous rocks. A positive slope exists for the Galway granite examples but the correlation is no better than that of the Ba versus Sr. It appears that Sr increases with Ba, but shows a strong negative correlation with Rb (Fig. 3.17). Sr varies from 50 ppm in the Murvey granite to 750 ppm in the more granodioritic members of the Roundstone granite.

Ba generally substitutes for K. Therefore it is retained by either K-feldspar, which has a high distribution coefficient for Ba, or by biotite (Hanson, 1978). In the Galway granite, however, large variations in the Ba contents occur with small changes in K. Ba varies from about 20 ppm in the more acid rocks to over 100 ppm in some adamellites. The least acid rocks contain 600 - 1,200 ppm Ba.

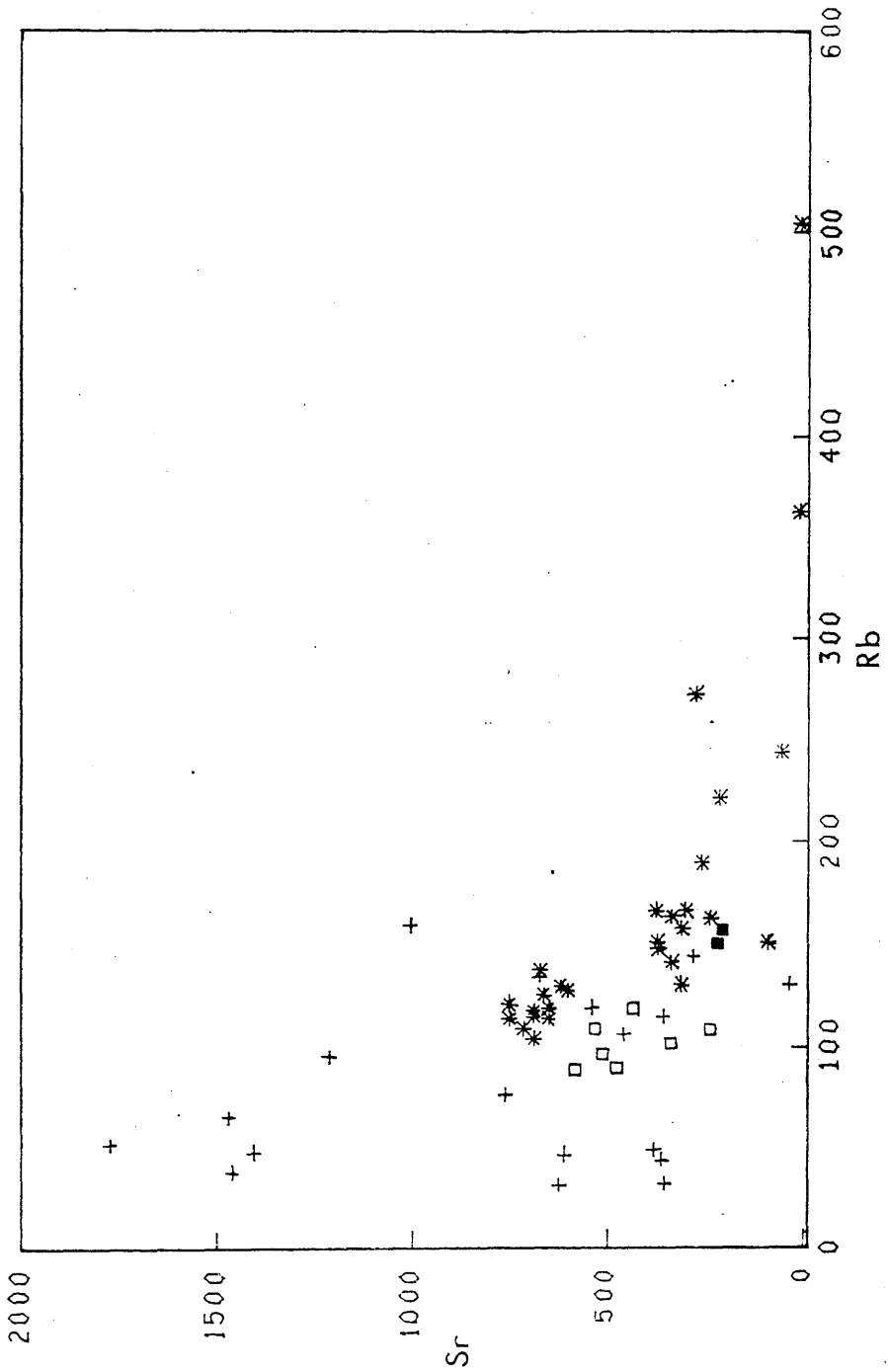


Fig. 3.17 Plot of Rb (ppm) versus Sr (ppm)

Zr has been detected in all granites showing a high concentration of about 120 - 170 ppm but it decreases to 60 ppm in the acid members of Inish and Murvey granites. This is also reflected petrographically in the decrease of zircon from the Carna granite towards the Murvey variety.

Rb tends to be concentrated in the latest differentiates because of its association with K. Therefore, K-feldspar contributes greatly to a reduction of the K/Rb ratio of the melt relative to the parent, as deduced by Hanson (1978). In the Galway batholith, Rb follows this pattern and is concentrated in more siliceous granites, where up to 500 ppm have been recorded (e.g. Murvey granite). In the porphyritic adamellite 150 - 250 ppm is present, while about 100 ppm has been recorded in the Roundstone granite.

Transition elements such as Cr, Co, Ni Zn and Pb are present in almost all samples. Cr varies between 1 and 36 ppm. Co and Ni have a maximum concentration of 6 and 10 ppm respectively, but they are not detected in all the specimens especially those with high silica contents. Zr was detected in all the samples and its concentration varies from 10 to 55 ppm, the more siliceous members have low concentrations of this element. Pb has the highest values of 30 - 35 ppm in the most acid rocks because of the affinity of Pb (i.r. - 1.20\AA) for K (i.r. - 1.33\AA).

3.3 GEOCHEMISTRY OF THE OUGHTERARD GRANITE

Chemically, the Oughterard granite as a whole has unremarkable major oxides; rather low CaO, TiO₂, Fe₂O₃ and MgO, with fairly high silica and variable alkali with slight predominance of mean soda over mean potash. It is most remarkable for the high content of both Ba and Sr, the average Ba being somewhat over 1,100 ppm while Sr averages 500 ppm. Almost equally remarkable is the deficiency in the rare earth elements Y, La, and Ce and the high K/Rb ratio of 320.

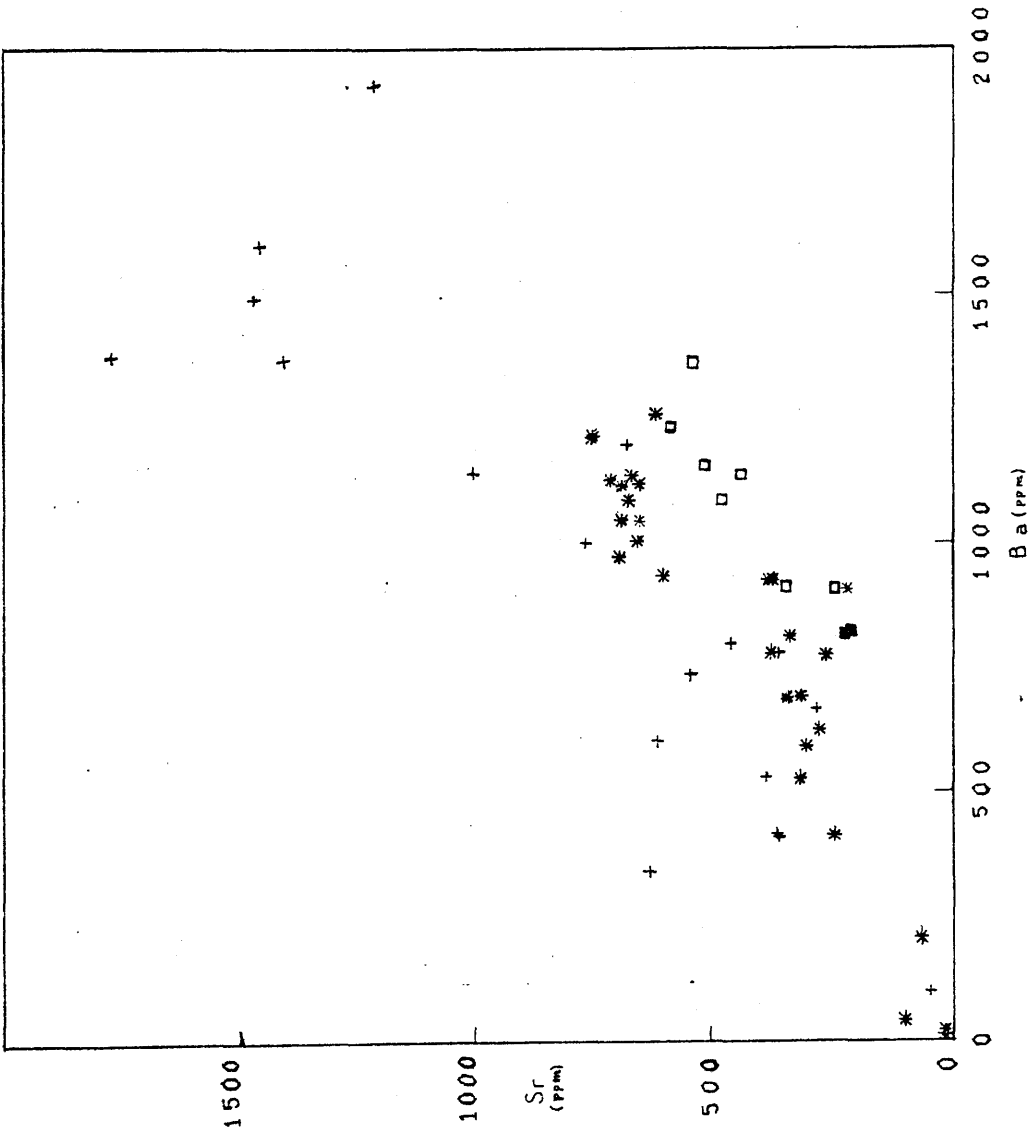
3.3.1 Major Elements

The major elements of the Oughterard granite generally show the usual trends commonly associated with magmatic differentiation. As SiO₂ increases Na₂O increases but there is a slight decrease of K₂O (Figs. 3.8 and 3.9) which is unusual for granites. MgO, Fe₂O₃, CaO, P₂O₅, and Ti show an overall, though rather erratic, decline with increasing silica contents. It is remarkable that the silica contents of the samples show a rather narrow range, between 73% and 76% except for the sample 3A which has 66.62% of SiO₂ and seems to be contaminated for its unique major oxides which are very different from those of the other samples. The ^{main} granite is also characterized by a low total iron, between 0.75% and 1.29%. This is reflected petrographically in the absence of magnetite in most of the samples. CaO and MgO also show low contents which average 0.67% and 0.34% respectively. This could be correlated with the loss of hornblende and the small amount of calcic plagioclase in the granite.

3.3.2 Trace Elements

The pattern of trace elements shows what would be predicted from major element geochemistry. The granite is, like other Caledonian granites of Scotland and Ireland, characterized by high Ba and Sr contents. However, it shows relatively low rare earth elements La, Ce, and Y compared with those of the Galway batholith.

Ba, having an average of 1,150 ppm, has a marked positive correlation with Sr (Fig. 3.18), and the Ba/Sr ratio is usually close to 3. The usual positive correlation of Sr and Ca occurs. The Sr is evidently largely, but not entirely, in the plagioclase as the latter has a high distribution coefficient for Sr and generally depletes the melts in this element (Hanson, 1978). Rb is generally low relative to K, and averages 100 ppm. This is almost certainly a consequence of the high Ba. Both Rb and Ba are largely contained in K-feldspars, when mica is low or absent, and they compete with K for the available sites. Taylor (1965), and Nockolds (1966) have demonstrated theoretically from the total single valence bonding energy, both K and Ba are preferred to Rb which is thus excluded when Ba is present in large amounts. The usual marked coherence of Rb and K occurs but it has a rather smooth slope (Fig. 3.19). Zr is present in all the specimens and tends to decrease with increasing silica contents. It varies from 140 ppm to 64 ppm but the sample 3A has a much higher content of 307 ppm for its low silica content of 66%.



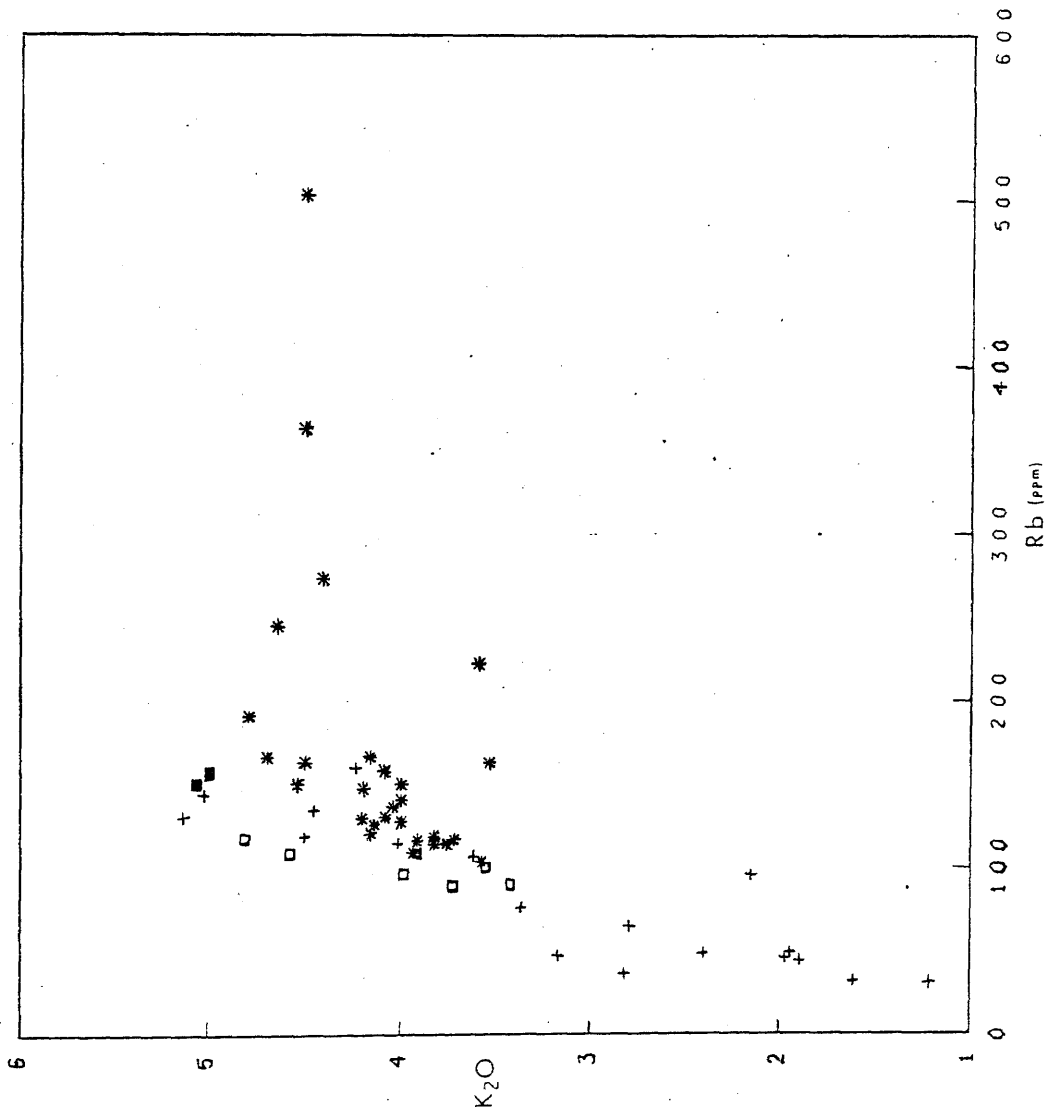


Fig. 319 Plot of Rb (ppm) versus K₂O (wt %)

Because Pb is known to occur in K-feldspars, it shows high concentrations of about 45 ppm. This is reflected by the large amount of K-feldspar in the granite. Zn, on the other hand, is very low and seems to occur in the most mafic rocks because it is probably mainly in the biotite, as noted by Tauson and Kravchenko (1956). Cu is not detectable in most samples.

Rare earth elements La, Ce, and Y are low in most of the samples. Y, varying from 9 to 12 ppm, increases irregularly as silica content increases so that the most acid rocks have the highest Y contents of all. Y shows a negative correlation with both Ca and Sr and a positive, rather erratic, correlation with K and Rb. It should be therefore concentrated in K minerals, probably K-feldspars. La and Ce, however, tend to decrease with increasing silica contents. Their concentrations in the granite vary from 26 to 11 ppm and 25 to 55 ppm respectively. According to Nockolds and Mitchell (1945), most of the La in granites is accommodated by sphene and apatite, in both of which it substitutes for Ca. Therefore, the low La and Ce contents of the Oughterard granite is reflected petrographically by the very little sphene and apatite present in the rocks in addition to the low CaO contents throughout the granite.

3.4 PRESENTATION OF GEOCHEMICAL DATA

Table 3.1: Major element data (in %) for some Caledonian granitoids of Main Britain (After Stephens and Halliday, 1984; Pankhurst and Sutherland, 1982).

Table 3.2: Trace element data (in ppm) for some Caledonian granitoids of Main Britian (After Stephens and Halliday, 1984; Pankhurst and Sutherland, 1982).

Table 3.3: Major element data (in %) for the Galway batholith.

Table 3.4: Trace element data (in ppm) for the Galway batholith.

Table 3.5: Major element data (in %) for the Oughterard granite and Cashel microgranite sill.

Table 3.6: Trace element data (in ppm) for the Oughterard granite and Cashel microgranite sill.

TABLE 3.1: Major and Trace Element Data for Some Caledonian Granite of Main Britain
(After Stephens and Halliday, 1984).

	ETIVE GRANITE			BALLACHULISH			
	Etv.47	Etv.48	Etv.49	Etv.50	Etv.51	Ba52 Ba53	
SiO ₂	57.60	64.20	67.60	73.50	77.11	58.30	67.19
TiO ₂	1.43	0.77	0.57	0.22	0.13	0.99	0.49
Al ₂ O ₃	18.27	15.85	15.94	14.05	12.88	17.44	16.34
Fe ₂ O ₃	2.51	4.32	2.93	1.32	0.10	6.02	3.57
FeO	3.97	NA	NA	NA	0.63	NA	NA
MnO	0.10	0.00	0.00	0.00	0.05	0.10	0.06
MgO	2.66	2.32	1.43	0.43	0.01	3.94	1.41
CaO	5.21	3.50	2.27	0.97	0.11	5.80	2.42
Na ₂ O	4.35	4.13	3.66	3.63	3.79	4.52	3.95
K ₂ O	2.15	3.36	4.50	5.03	5.14	2.80	4.23
P ₂ O ₅	0.44	0.33	0.15	0.04	0.01	0.37	0.27
Loss	1.20	0.86	0.68	0.44	0.26	0.00	0.40
Total(%)	100.31	99.88	99.92	99.76	100.28	100.90	100.63

NA = not analysed

TABLE 3.1 (Cont.)

	BALLACHULISH (ctd)		ARROCHAR		GLEN DOLL	
	Ba54	Ba55	Ar56	Ar57	Gd159	Gd160
SiO ₂	72.42	52.36	54.24	62.15	51.32	65.70
TiO ₂	0.21	1.24	1.03	0.70	2.63	0.77
Al ₂ O ₃	15.51	15.46	14.86	16.35	16.31	15.98
Fe ₂ O ₃	1.82	8.09	1.84	1.85	12.12	4.37
FeO	NA	NA	6.26	3.45	NA	NA
MnO	0.03	0.12	0.15	0.12	0.15	0.06
MgO	0.83	5.91	8.23	3.30	4.58	1.78
CaO	1.15	7.67	8.02	5.39	7.53	2.64
Na ₂ O	3.59	3.69	2.77	3.37	3.10	3.73
K ₂ O	4.46	1.94	1.61	2.40	1.21	3.61
P ₂ O ₅	0.11	0.00	0.28	0.22	0.18	0.22
Loss	0.00	2.20	0.00	0.80	1.40	1.60
Total (%)	100.47	99.08	99.48	100.25	100.70	100.66

NA = not analysed

TABLE 3.1 (Cont..)

	GLEN DOLL (ctd.)		KILMELFORD		STRONTIAN		SHAP Sh67
	Gd161	Gd162	Kd63	Kd64	Sr65	Sr66	
SiO ₂	58.82	68.45	62.35	59.09	62.95	76.26	67.89
TiO ₂	0.80	0.60	0.56	0.58	0.83	0.25	0.70
Al ₂ O ₃	12.04	15.87	16.96	17.27	16.31	14.67	14.62
Fe ₂ O ₃	6.41	3.41	1.74	0.00	1.33	0.49	1.16
FeO	NA	NA	2.38	4.38	2.57	0.92	1.68
MnO	0.14	0.06	0.06	0.08	0.08	0.03	0.03
MgO	8.31	1.33	3.26	3.69	2.79	0.66	1.59
CaO	7.32	2.03	4.63	4.93	4.26	1.34	2.56
Na ₂ O	2.14	4.29	4.04	4.63	5.25	4.71	3.36
K ₂ O	1.89	4.01	3.17	2.82	2.44	4.08	4.66
P ₂ O ₅	0.13	0.23	0.28	0.32	0.26	0.06	0.31
Loss	2.40	0.00	0.20	1.00	1.33	0.64	1.20
Total (%)	100.58	100.47	99.97	99.16	100.62	100.28	99.76

NA = not analysed

TABLE 3.1: Trace Element (p.p.m.)

	ETIVE GRANITE					BALLACHULISH				
	Etv.47	Etv.48	Etv.49	Etv.50	Etv.51	Ba52	Ba53	Ba54	Ba55	
Ba	1,921	1,000	735	667	100	1,488	1,137	1,196	1,371	
Rb	59	76	118	143	130	65	159	134	50	
Sr	1,213	766	543	282	36	1,469	1,003	678	1,771	
Th	6	7	13	11	21	0	37	20	1	
Zr	555	203	172	69	100	0	218	114	0	
Y	13	17	17	6	14	23	20	16	24	
La	60	41	41	33	47	44	56	45	40	
Ce	79	66	49	28	59	76	102	79	94	
Cr	22	46	26	0	0	79	21	3	105	
Ni	20	30	26	8	7	34	17	8	105	
Cu	15	9	10	5	4	30	17	433	24	
Zn	98	60	39	25	17	75	54	27	83	
Pb	5	15	14	33	30	19	29	22	19	

TABLE 3.2 (Cont.): Trace Element (p.p.m.)

	ARROCHAR		Ar58	Gd159	GLEN DOLL		KILMELFORD		
	Ar56	Ar57			Gd160	Gd161	Kd63	Kd64	
Ba	409	528	599	340	796	412	778	1,366	1,595
Rb	32	49	46	31	105	44	114	47	37
Sr	357	386	614	630	460	360	359	1,407	1,457
Th	7	7	0	3	13	9	12	5	0
Zr	122	99	110	121	269	139	284	126	83
Y	24	23	8	25	24	17	26	14	13
La	18	26	18	0	49	13	43	37	29
Ce	38	39	34	54	98	29	86	75	65
Cr	415	98	9	32	23	393	13	101	83
Ni	134	25	7	9	18	105	16	56	43
Cu	48	6	13	81	49	87	61	32	32
Zn	81	56	48	23	14	36	6	62	75
Pb	13	10	22	21	13	13	20	17	31

TABLE 3.3: Major and Trace Element Data for the Connemara Granites

	OMEY GRANITE			MURVEY GRANITE			
	R1	R2	R3	R4	R25	R26	R27
SiO ₂ (%)	69.34	71.32	68.82	69.54	75.95	78.65	74.13
TiO ₂ (%)	0.30	0.32	0.32	0.26	0.02	0.03	0.14
Al ₂ O ₃ (%)	14.52	14.22	14.60	14.51	12.77	12.01	13.22
Fe ₂ O ₃ (%)	1.09	1.19	1.26	1.09	0.17	0.02	0.26
FeO (%)	1.14	1.32	1.36	1.09	0.41	0.17	0.64
MnO (%)	0.06	0.06	0.07	0.07	0.11	0.03	0.03
MgO (%)	1.01	1.16	1.31	1.05	0.18	0.23	0.27
CaO (%)	2.26	2.26	2.39	1.99	0.35	0.23	0.54
Na ₂ O (%)	4.47	4.50	5.13	5.50	5.19	5.68	5.18
K ₂ O (%)	4.19	4.00	4.00	4.50	4.50	4.50	4.64
P ₂ O ₅ (%)	0.11	0.12	0.16	0.12	0.03	0.03	0.05
H ₂ O ⁺ (%)	0.90	0.85	1.11	1.02	0.41	0.30	0.45
CO ₂ (%)	0.31	0.17	0.16	0.21	0.06	0.07	0.08
Total (%)	99.71	101.49	100.69	101.93	100.15	101.95	99.63
A/CNK*	0.91	0.89	0.85	0.83	0.91	0.82	0.91

*A/CNK = mol Al₂O₃ / (CaO + Na₂O + K₂O)

TABLE 3.3 (ctd.)

	ERRISBEG TOWNLAND GRANITE				CARNA GRANITE			INISH GRANITE
	R21	R22	R24	R32	R33	R28	R29	
SiO ₂ (%)	70.70	68.66	71.27	68.46	69.18	68.94	76.40	
TiO ₂ (%)	0.34	0.29	0.29	0.36	0.36	0.32	0.06	
Al ₂ O ₃ (%)	13.67	16.14	13.78	14.92	14.76	14.89	13.25	
Fe ₂ O ₃ (%)	1.16	1.44	0.97	1.30	1.27	0.79	0.51	
FeO(%)	1.40	1.06	1.20	1.49	1.48	1.36	0.12	
Mn(%)	0.05	0.07	0.06	0.06	0.07	0.07	0.01	
MgO(%)	1.39	1.07	1.03	1.40	1.42	1.26	0.17	
CaO(%)	2.43	1.76	1.93	2.42	2.15	2.13	0.67	
Na ₂ O(%)	5.42	5.15	4.39	5.26	4.18	5.38	5.71	
K ₂ O(%)	3.53	3.59	4.41	4.16	4.08	4.79	4.54	
P ₂ O ₅ (%)	0.13	0.12	0.18	0.14	0.14	0.13	0.01	
H ₂ O ⁺ (%)	0.61	0.70	0.59	0.88	0.98	0.38	0.35	
CO ₂ (%)	0.12	0.16	0.11	0.16	0.22	0.06	0.08	
Total(%)	100.95	100.21	100.21	101.01	100.29	10.50	101.88	
A/CNK	0.79	0.86	0.88	0.85	0.97	0.83	0.85	

TABLE 3.3 (ctd.)

	INISH GRANITE (ctd)			ROUNDSTONE GRANITE				
	R30	R31	R5	R16	R17	R14	R11	R12
SiO ₂	70.11	71.39	65.72	65.91	66.06	66.42	66.54	66.55
TiO ₂	0.25	0.15	0.38	0.42	0.42	0.40	0.41	0.44
Al ₂ O ₃	13.93	14.57	16.38	15.84	15.86	16.07	15.84	15.48
Fe ₂ O ₃	0.76	0.51	1.28	1.34	1.06	1.08	1.23	1.32
FeO	1.16	0.90	1.72	1.70	1.81	1.73	1.79	1.88
MnO	0.05	0.04	0.05	0.06	0.05	0.07	0.06	0.08
MgO	0.73	0.69	1.54	1.60	1.62	1.65	1.83	1.61
CaO	1.55	1.34	2.73	2.77	2.75	2.65	2.74	1.87
Na ₂ O	5.31	6.22	4.86	5.30	5.63	5.09	5.26	4.84
K ₂ O	4.08	4.69	3.57	4.13	4.04	4.16	3.93	4.20
P ₂ O ₅	0.11	0.08	0.22	0.24	0.25	0.21	0.24	0.23
H ₂ O ⁺	0.41	0.39	0.89	0.79	0.84	0.80	0.67	0.84
CO ₂	0.10	0.07	0.22	0.18	0.17	0.19	0.20	0.24
Total	98.55	101.04	99.56	100.28	100.56	100.52	100.74	99.58
A/CNK	0.87	0.82	0.97	0.87	0.85	0.91	0.88	0.97

TABLE 3.3 (cont.)

	ROUNDSTONE GRANITE (ctd)							
	R8	R6	R15	R10	R7	R5	R18	
SiO ₂ (%)	66.66	66.75	66.76	66.77	67.62	67.91	67.97	
TiO ₂ (%)	0.42	0.40	0.42	0.40	0.38	0.39	0.37	
Al ₂ O ₃ (%)	15.80	15.87	15.81	16.21	15.68	15.36	15.63	
Fe ₂ O ₃ (%)	1.27	1.44	1.07	1.26	1.33	1.32	1.31	
FeO(%)	1.71	1.68	1.78	1.76	1.45	1.67	1.48	
MnO(%)	0.06	0.05	0.05	0.05	0.06	0.07	0.07	
MgO(%)	1.58	1.22	1.64	1.59	1.52	1.39	1.35	
CaO(%)	2.69	2.73	2.66	2.79	2.53	2.83	2.00	
Na ₂ O(%)	4.08	4.81	3.78	5.06	4.16	4.98	5.55	
K ₂ O(%)	3.91	3.81	3.75	3.81	3.82	3.71	4.00	
P ₂ O ₅ (%)	0.20	0.21	0.22	0.25	0.20	0.21	0.22	
H ₂ O ⁺ (%)	0.81	0.63	0.88	0.70	0.73	0.70	0.77	
CO ₂ (%)	0.18	0.16	0.23	0.17	0.20	0.13	0.20	
Total(%)	99.37	99.76	99.05	100.82	99.68	100.67	100.92	
A/CNK	0.99	0.93	1.04	0.92	1.00	0.88	0.91	

TABLE 3.4: Trace Element (p.p.m.)

	OMEY GRANITE				MURVEY GRANITE			ERRISEBEG TOWNLAND			
	R1	R2	R3	R4	R25	R26	R27	R21	R22	R24	
Ba	925	687	779	813	13	23	207	412	906	625	
Rb	147	140	150	163	504	363	244	162	221	272	
Sr	373	341	376	336	10	7	58	243	217	274	
Th	12	13	11	12	21	15	25	34	24	19	
U	4	4	3	5	10	7	4	5	6	6	
Zr	118	124	125	117	59	65	100	140	116	127	
Y	14	18	16	15	35	38	31	19	11	17	
La	17	23	23	18	14	11	19	31	9	24	
Ce	42	50	43	39	27	33	45	57	25	50	
Cr	10	12	17	11	1	-	10	23	16	24	
Co	2	5	2	2	-	-	-	3	0	3	
Ni	4	7	6	5	-	-	-	6	7	6	
Cu	-	4	-	-	-	-	-	-	1	1	
Zn	34	43	40	35	24	10	25	45	34	51	
Pb	26	26	28	28	51	26	39	29	42	26	
Ga	15	16	16	16	20	17	15	16	16	16	

TABLE 3.4 (cont.)

	<u>CARNA GRANITE</u>			<u>INISH GRANITE</u>			<u>ROUNDSTONE GRANITE</u>			
	R32	R33	R28	R29	R30	R31	R9	R16	R17	R14
Ba	927	691	776	41	523	591	1,114	1,135	1,084	1,218
Rb	166	157	190	150	130	166	103	125	137	120
Sr	378	314	261	94	313	299	692	667	674	751
Th	17	18	17	21	20	13	13	15	10	11
U	5	5	4	4	4	4	2	3	2	2
Zr	127	145	133	38	122	92	161	161	174	163
Y	15	17	18	5	11	7	10	9	11	10
La	30	29	25	5	21	17	35	38	37	41
Ce	57	57	42	7	38	28	59	61	68	62
Cr	27	30	33	2	11	7	24	21	24	21
Co	3	3	4	-	-	1	5	5	1	4
Ni	6	10	6	-	-	1	7	1	6	6
Cu	-	1	-	-	-	-	3	-	-	-
Zn	39	42	42	11	41	31	54	45	45	46
Pb	22	26	30	29	26	29	27	18	16	16
Ga	17	17	17	16	18	16	20	20	19	21

TABLE 3.4 (cont.)

	ROUNDSTONE GRANITE (Ctd.)												
	R11	R12	R8	R6	R15	R10	R7	R5	R18				
Ba	1,123	1,259	1,118	1,042	1,042	1,209	1,002	969	932				
Rb	108	129	116	114	113	113	118	117	127				
Sr	715	618	653	693	653	751	655	694	602				
Th	11	12	17	12	15	16	13	14	14				
U	1	3	3	4	2	4	2	3	3				
Zr	163	170	152	166	165	173	156	165	157				
Y	10	10	10	11	12	10	12	9	12				
La	36	31	39	42	38	45	39	28	35				
Ce	60	68	68	75	72	73	68	60	59				
Cr	32	21	20	20	21	21	36	20	18				
Co	4	3	3	4	4	5	6	5	4				
Ni	3	9	4	3	5	1	3	4					
Cu	-	0	1	-	-	-	-	-	-				
Zn	51	55	50	46	49	48	46	47	48				
Pb	21	15	22	18	23	24	24	18	24				
Ga	20	20	19	22	20	19	19	19	20				

TABLE 3.5

	OUGHTERARD GRANITE						CASHEL MICROGRANITE			
	3A	6A	7A	1A	4A	5A	2A	S21C	56	
SiO ₂ (%)	66.62	72.86	73.82	73.58	74.46	75.15	75.63	69.26	68.15	
TiO ₂ (%)	0.61	0.15	0.14	0.10	0.05	0.06	0.09	0.54	0.57	
Al ₂ O ₃ (%)	11.55	14.31	14.26	13.88	13.96	14.73	14.24	14.82	14.80	
Fe ₂ O ₃ (%)	0.96	0.38	0.37	0.20	0.38	0.32	0.53	0.58	0.28	
FeO(%)	3.20	0.76	0.38	0.49	0.82	0.44	0.56	2.04	2.36	
MnO(%)	0.07	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	
MgO(%)	4.72	0.45	0.27	0.42	0.331	0.19	0.45	1.25	1.42	
CaO(%)	3.53	0.41	0.79	0.47	0.87	0.89	0.59	1.33	2.29	
Na ₂ O(%)	2.90	4.34	5.44	4.00	5.18	4.65	4.94	3.32	2.96	
K ₂ O(%)	3.92	4.58	3.42	4.82	3.99	3.73	3.56	5.07	5.00	
P ₂ O ₅ (%)	0.15	0.04	0.04	0.05	0.04	0.06	0.07	0.26	0.24	
H ₂ O ⁺ (%)	0.55	0.61	0.81	0.35	0.67	0.44	0.41	1.06	1.11	
CO ₂ (%)	0.13	0.14	0.18	0.11	0.16	0.11	0.14	0.33	0.40	
Total(%)	98.91	99.05	99.94	98.49	100.91	100.79	101.23	99.89	99.61	
A/CNK*	0.75	1.11	1.01	1.09	0.97	1.11	1.09	1.11	1.02	

*A/CNK = mol Al₂O₃ / (CaO + Na₂O + K₂O)

TABLE 3.6: Trace Element (p.p.m.)

	OUGHTERARD GRANITE						CASHEL MICROGRANITE		
	3A	6A	7A	1A	4A	5A	2A	S21C	R56
Ba	912	1,362	1,085	1,138	1,157	1,236	913	820	825
Rb	109	108	90	118	96	89	101	150	157
Sr	243	539	481	439	515	587	343	223	209
Th	10	23	29	12	15	11	6	31	14
U	3	5	5	4	5	2	3	4	2
Zr	307	139	140	109	91	92	64	359	372
Y	26	9	10	11	11	10	12	22	12
La	22	26	24	19	21	11	14	87	57
Ce	55	53	51	41	41	29	25	177	135
Cr	49	3	3	5	6	2	6	19	26
Co	4	-	-	-	-	-	-	1	1
Ni	12	-	-	-	-	-	-	3	3
Ca	13	-	-	3	-	-	-	10	-
Zn	59	16	12	10	19	8	14	47	46
Pb	16	34	31	47	57	59	31	22	17
Ga	15	19	17	15	15	15	18	18	17

3.5 MINERALOGICAL AND GEOCHEMICAL DIFFERENCES BETWEEN AN I- AND S-TYPE GRANITE IN THE CONNEMARA PLUTONIC ROCKS

Previous geochemical and petrographic work carried out by Chappell and White (1974) on some granites of the Lachlan Fold Belt, southeastern Australia, has led them to recognize two different granite types. An I-type granite, derived from igneous source rocks, and an S-type granite derived from metasedimentary source rocks. Each of the two types is characterized by several distinct petrographic, chemical, and isotopic criteria. Some of the distinctive mineralogical, chemical, and isotopic properties of the two types are shown in Table 3.7.

3.5.1 Petrographic Differences

The differences in petrographic features usually reflect the differences in chemical composition of the granites. Hornblende is common in the more mafic I-types and is generally present in felsic varieties. The Galway granite is an example of that type with hornblende being present in most of the granite varieties of the batholith except the Murvey granite which is a later differentiate of the Errisbeg Townland Granite magma as pointed out by Leake (1978). Dark brown biotite is also common in most of the granite varieties. Magnetite and sphene are present throughout the granites except the Murvey variety, a feature supporting the I-type signature of the batholith. Coats and Wilson (1971) have shown that the fine-grained microdioritic xenoliths present within

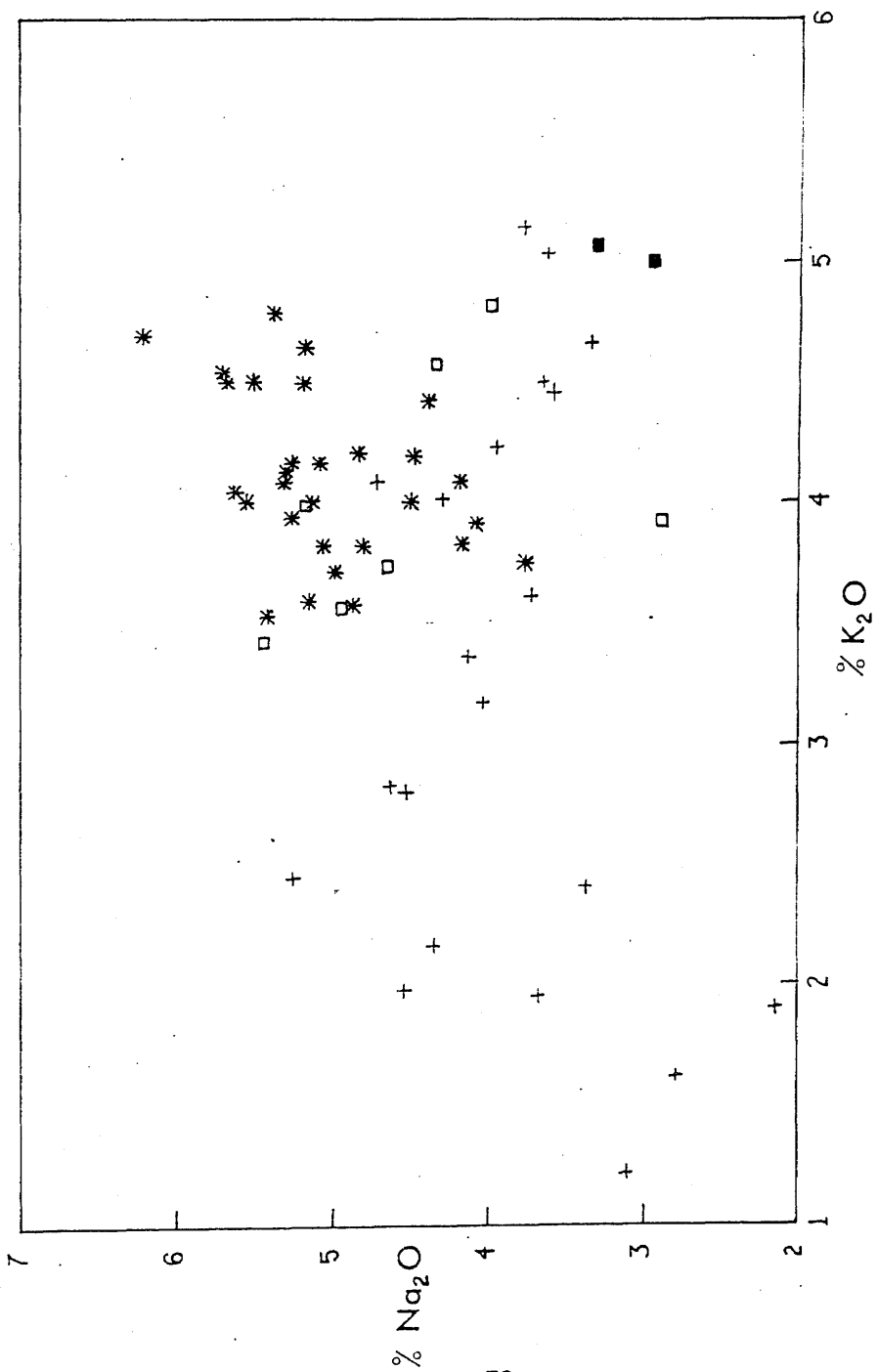
the Galway batholith are chemically more basic than any of the granite masses so far described in the batholith and they plot at the beginning of the differentiation trends of the various Galway Granite types; a criterion of an I-type granite.

The petrographic characteristics of the Oughterard granite and the Cashel microgranite sill, however, tend to give these granites an S-type signature. Hornblende is generally absent, partly chloritized biotite is present, and muscovite is a common secondary mineral although present in traces in some places. Magnetite and sphene are absent in the Cashel microgranite sill while they are irregularly present in the Oughterard granite. Xenoliths present in the Oughterard intrusion are usually of meta-sedimentary country rocks.

3.5.2 Chemical Differences

Hine et al., (1978) have pointed out that, chemically, S-type granitoids have a relatively restricted range of SiO_2 contents which are generally higher than those of the I-types. This is a consequence of S-type granitoids having been derived from a more SiO_2 -rich source. In the case of the Connemara granites, the Galway batholith can be separated from the Oughterard granite on this basis; the former having a wide range of SiO_2 , from 65% to 78% and the latter with a limited range, from 72% to 75%.

The $\text{Na}_2\text{O}-\text{K}_2\text{O}$ plot (Fig. 3.20) shows the most fundamental chemical difference between the I- and S-type granites of the Connemara granitic rocks. The more potassium-rich S-types are lower in sodium and the separation of the two groups is unambiguous. Differences of this type are a useful criterion in recognizing I- and S-type granitoids and were an important factor in deciding that the overall I- and S-type characteristics were inherited from fundamentally different sources (Chappell and White, 1974). The production of shales by chemical weathering processes enriched Al relative to Na and Ca, since Na is removed in solution and concentrated in sea-water and evaporites, and Ca is concentrated in shelf limestone. K, on the other hand, is absorbed by shales during sedimentation and diagenesis giving rise to increased K-contents relative to Na and Ca. The ultimate case is the production of pelitic sedimentary rocks that are strongly peraluminous in the sense of Shand (1950), i.e. $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$ values are greater than 1.1, and with high K/Na ratios. S-type granitoids derived from the ultrametamorphism of these pelitic rocks have these same chemical characteristics (White and Chappell, 1977). The Oughterard granite and the Cashel microgranite sill are examples of this type having high $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios (Fig. 3.20) and relatively low Ca contents (Fig. 3.7). These features are directly reflected in the higher $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$ values of these granites relative to those of the Galway batholith (Figs. 3.21, 3.22); the formers being peraluminous whereas the latter is metaluminous with low $\text{K}_2\text{O}/\text{Na}_2\text{O}$ and relatively high Ca contents.



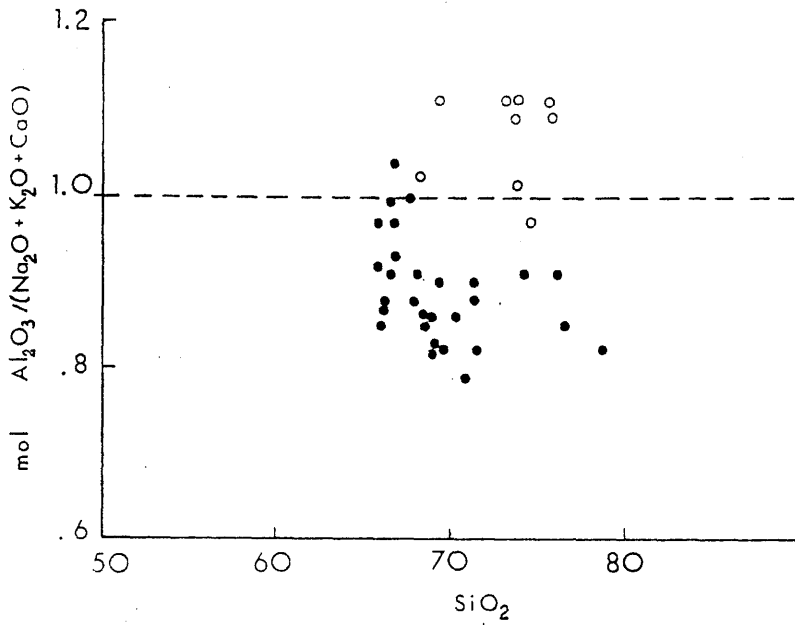


Fig. 3.21 Plot of SiO₂ versus Al₂O₃/(Na₂O+K₂O+CaO) ratio for the granites of Connemara; filled circles: Galway Granite, and open circles: Oughterard and Cashel granites.

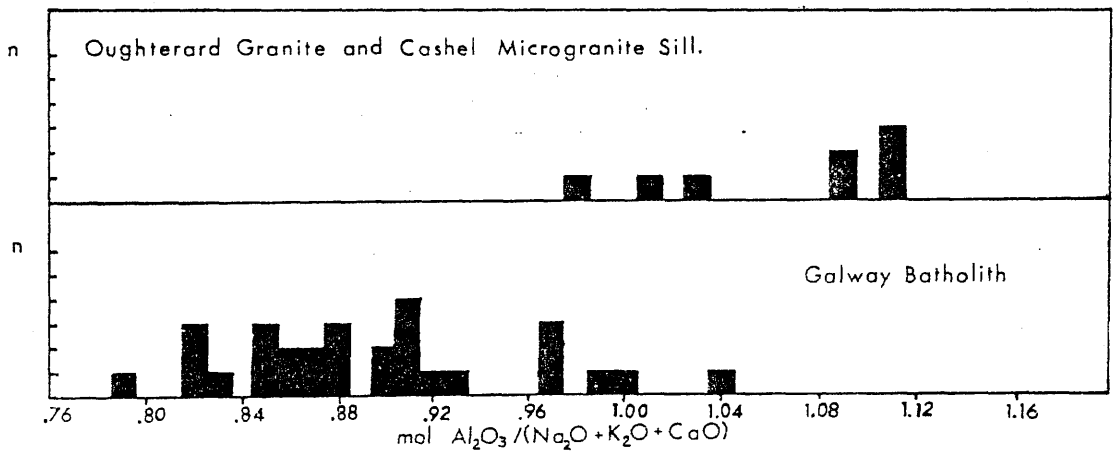


Fig.3.22 Histograms showing frequency of mol Al₂O₃/(Na₂O+K₂O+CaO) for the granites of Connemara.

Flood and Shaw (1975) have pointed out that S-type granitoids are generally much more reduced than I-types, arguing that the presence of carbon (Eugster, 1972) or sulphur in the sedimentary source rocks can cause the reduction of granite derived from such sources. The degradation of organic matter present in the sediments, produced CH_4 , graphite and CO , which can be oxidized. Granites and high-grade rocks usually contain very little graphite and it seems reasonable to assume that the organic matter originally present in the sediments was ultimately responsible for the reduction (Eugster, 1972). This is most noticeable for the Connemara granites. Low $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio of the Oughterard granite of 0.67 and the Cashel microgranite sill, 0.2, coupled with the high $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$ is reflected in the red-brown biotite and chloritized biotite, and the absence of magnetite. The Galway batholith, however, has a relatively high $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio (Fig. 3.23), of 0.89, and a low $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$ ratio.

Fig. 3.23 Plot of FeO (wt %) versus Fe_2O_3 (wt %) to show the higher oxidation state of the Galway Granite compared with the Oughterard and Cashel Granites.

Filled circles = Galway Granite
Open circles = Oughterard and Cashel Granites.

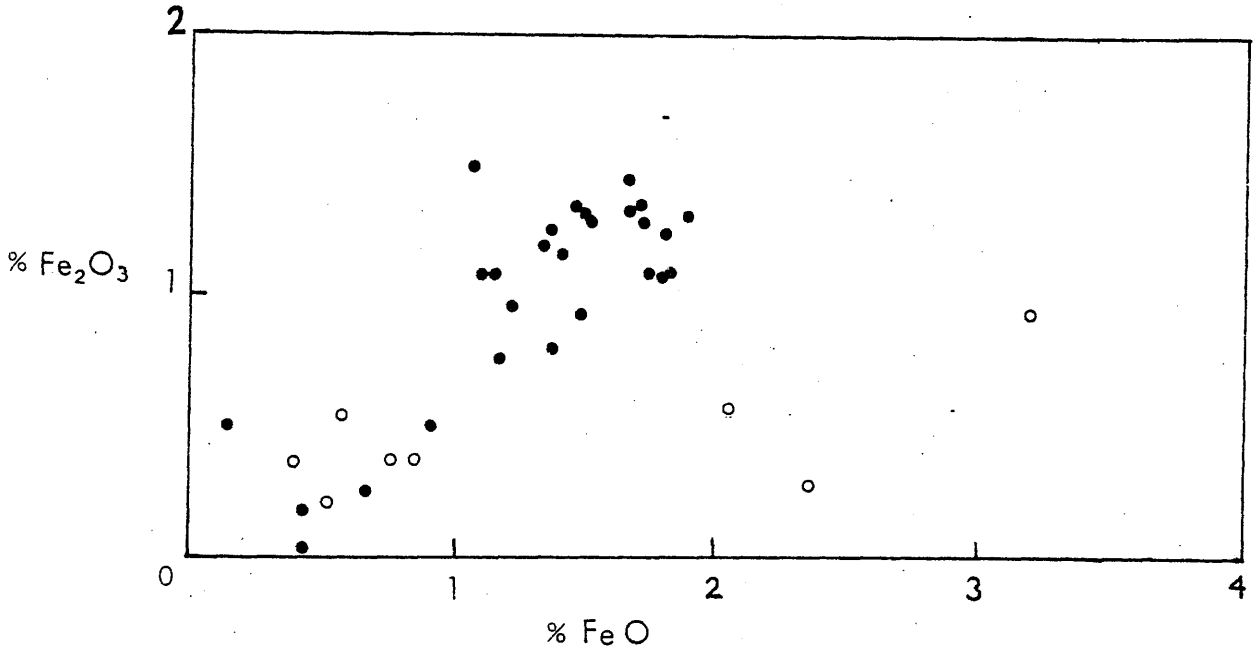


TABLE 3.7 Chemical, Mineralogical and Isotopic Differences Between S- and I-type Granitoids (Mostly after Chappell & White (1974), Hine et al (1978) except *McCulloch & Chappell (1982)).

Type Parameter	S-Type	I-Type
<u>Mineralogy</u>		
Ferromagnesian Mineral	Hornblende absent and Red biotite common	Hornblende and biotite common
Muscovite and Feldspar	Muscovite common and K-feldspar often as megacrysts	Muscovite rare and K-feldspar interstitial
Accessories	Ilmenite, Monazite, Garnet, cordierite	Magnetite, sphene
Xenolith Composition	Metasedimentary xenoliths predominant	Dioritic xenoliths
<u>Chemistry</u>		
SiO ₂	Within ranges 66 to 75%	Wide range 56 - 75%
K ₂ O/Na ₂ O	High	Low
Ca	Low	High
Molar Al ₂ O ₃ /(Na ₂ O+K ₂ O+CaO)	>1.1	<1.1
CIPW Norm components and alumina saturation of suite	>1% normative corundum. Nearly all S-types are peraluminous, some are metaluminous	Normative diopside or <1% normative corundum. Mostly metaluminous, some peraluminous
Fe ³⁺ /Fe ²⁺	Usually low	Usually high
<u>Isotopes</u>		
Initial ⁸⁷ Sr/ ⁸⁶ Sr	High, normally >0.708	Normally <0.709
εNd*	Low, all negative	Wide range, positive to negative
δ ¹⁸ O	High (>10‰)	Low (<10‰)

CHAPTER 4

ISOTOPE GEOLOGY

4.1 INTRODUCTION

Stable and radiogenic isotope analyses have proven powerful in understanding crust-mantle interaction and in fingerprinting the magma source regions. Various isotope reservoirs are characterized by different and distinctive isotope compositions. It is, therefore, important to understand the different processes resulting in enhanced sulphur-, oxygen-, and initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic values, in order to interpret any combined data. The variation in sulphur-isotopic composition is a consequence of equilibrium and kinetic fractionation (for details see Coleman, 1977; Nielsen, 1978; Rye and Ohmoto, 1974). In meteorites and basic igneous rocks, the sulphur-isotope values form a tight group around 0‰. By contrast, in sedimentary regimes, the fractionation of S-isotopes leads to a very much wider range in values ($-50\% \leq \delta^{34}\text{S} < +35\%$). Equilibrium fractionation between oxidized and reduced species give components enriched and depleted in ^{34}S , respectively (positive or negative $\delta^{34}\text{S}$). In addition, the magnitude of the fractionation is very small at high temperatures and increases greatly at lower ones. Following from this, it is possible to postulate various models for producing the sulphur-isotope compositions of granites and to test them on the data from different plutons.

Older continental rocks and sediments are enriched in ^{18}O because of the addition of materials such as clays, carbonates, and cherts which have high ^{18}O because they were formed from surface waters at low temperatures (Savin and Epstein, 1970). Consequently, high ^{18}O values can only be produced as a result of the action of surface or near-surface processes (i.e. during sedimentation, diagenesis, or hydrothermal alteration at relatively low temperatures), or in a magmatic environment, by the incorporation of such materials. Basic igneous rocks are characterized by low oxygen-isotope composition ($\delta^{18}\text{O}$ generally less than 7‰), whereas sedimentary rocks exhibit much higher values ($> 10\%$). The incorporation of sediments in a magmatic environment give intermediate $\delta^{18}\text{O}$ values (between 7 and 11‰).

Sediments are also enriched in ^{87}Sr because of the addition of radiogenic strontium produced by the decay of ^{87}Rb . The major 'reservoirs' are, therefore, older continental rocks and sediments derived therefrom. Furthermore, high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can be enhanced by assimilation at very high temperatures (Taylor, 1980) if Rb has been concentrated (e.g. by fluid/rock interaction). Present-day magmas derived from the mantle or a primitive (basic or ultrabasic) mantle-derived source have a characteristic isotopic composition of $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.703 \pm 0.001$ (Faure and Powell, 1972): The crust has developed a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio because of the time-dependent effect of its generally higher Rb/Sr ratios. As a result the crust

is enriched in ^{87}Sr relative to the mantle and thus produces high initial $^{87}\text{Sr}/^{86}\text{Sr}$.

4.2 SYSTEMATICS AND PRINCIPLES

4.2.1 Sulphur Isotope Systematics

Sulphur has four naturally occurring stable isotopes with the mass numbers 32, 33, 34 and 36. ^{35}S is radioactive with a half life of 88 days and is frequently used in tracer studies. The abundances, as percentages of individual stable isotopes in terrestrial materials are as follows:

$$^{32}\text{S} \approx 95\%$$

$$^{33}\text{S} \approx 0.77\%$$

$$^{34}\text{S} \approx 4.2\%$$

$$^{36}\text{S} \approx 0.017\%$$

It is generally convenient to measure the ratio between the two most abundant isotopes; i.e. $R = ^{34}\text{S}/^{32}\text{S}$. The two other ratios $^{33}\text{S}/^{32}\text{S}$ and $^{36}\text{S}/^{32}\text{S}$ have been of interest only for extra-terrestrial materials where excessive amounts of these rarest isotopes can be produced by nuclear reaction with high energy radiation.

Sulphur isotope data are given in the δ -notation, where

$$\delta^{34}\text{S}(\%) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000$$

i.e. as permil deviation in $^{34}\text{S}/^{32}\text{S}$ ratio (=R) of the unknown sample from a standard. Primary standard is troilite sulphur from the Cañon Diablo meteorite. Its $^{34}\text{S}/^{32}\text{S}$ is taken as 0.0450045 (or $^{32}\text{S}/^{34}\text{S} = 22.220$) by convention (Ault and Jensen, 1962).

Figure 4.1 gives a synopsis of the S-isotope distribution in a variety of typical natural sulphur compounds. The whole $\delta^{34}\text{S}$ range of natural samples reported until early 1977 extends from about - 65‰ to + 95‰, but 98% of all samples investigated at the Göttingen Laboratory are within -40‰ and + 40‰ (Nielsen, 1978). The variation in S-isotopic composition is a result of equilibrium and kinetic fractionation processes.

The sulphur isotopic fractionations between coexisting sulphide minerals could be used to estimate the temperatures of formation of ore mineral assemblages. The successful application of any sulphur isotope geothermometer to any particular deposit depends upon the suitability of the samples; i.e. to analyse contemporaneous samples that crystallized in equilibrium with each other. The success of this method of geothermometry rests on the assumption that isotopic equilibrium has been attained and maintained throughout the formation of a given mineral pair, and that subsequently these minerals were not subject to isotopic exchange.

Besides their use as a geothermometer, sulphur isotope ratios have been useful as indicators of the origin of metasomatic and hydrothermal fluids (e.g. Jensen, 1967; Rye and Ohmoto,

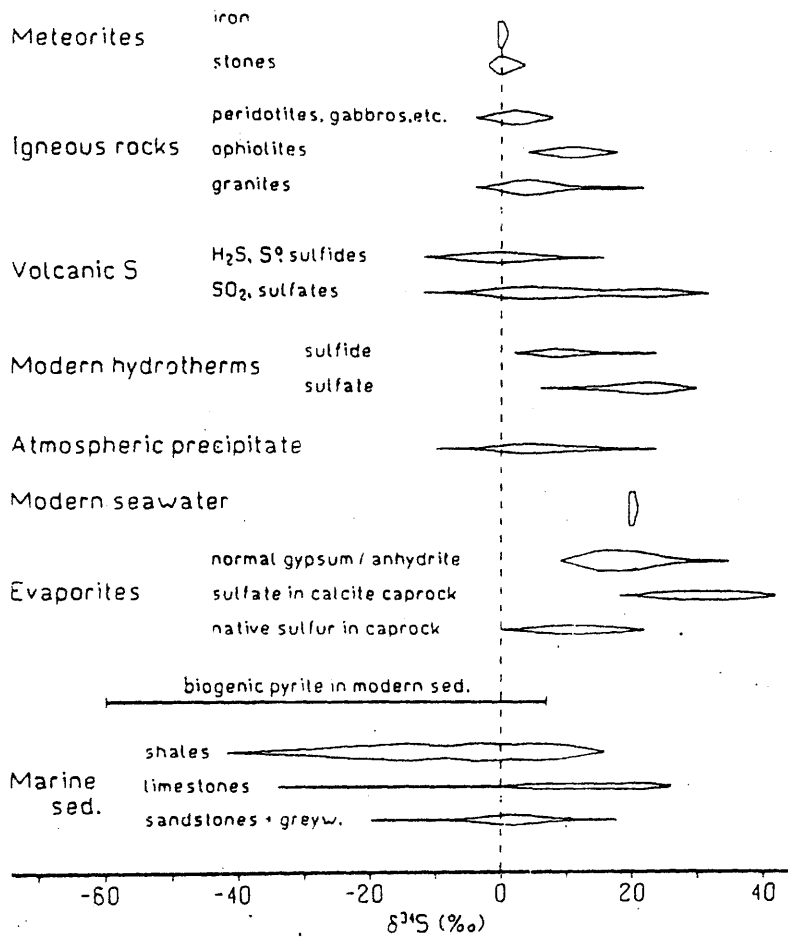


Fig.4.1. Synopsis of $\delta^{34}\text{S}$ distribution patterns of some natural material of geochemical relevance (After Nielsen, 1979).

1974) as well as the origin of igneous rocks of granitic composition (Coleman, 1977, 1979, Sasaki and Ishihara, 1980).

4.2.2. Oxygen Isotope Systematics

Oxygen is the most abundant element on Earth, occurring in gaseous, liquid and solid compounds, that are thermally stable over a wide range of temperatures. There are three stable isotopes of oxygen with the following abundances (Garlick, 1966):

$$^{16}\text{O} = 99.763\%$$

$$^{17}\text{O} = 0.037\%$$

$$^{18}\text{O} = 0.199\%$$

As the proportion of ^{17}O is extremely small and there is a greater mass difference between the other two isotopes, the $^{18}\text{O}/^{16}\text{O}$ is normally determined. In order to compare changes and variations in stable isotope ratios, it is necessary to eliminate any instrumentation or laboratory bias that has been introduced during analysis. Hence, as with S-isotopes, results are determined relative to an internally agreed standard (SMOW = Standard Mean Ocean Water) and any fractionations are expressed in parts per mil (‰) as shown below:

$$\delta^{18}\text{O} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{standard}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} \right] \times 1000$$

Like sulphur isotopes, oxygen isotopic composition of oxygen-containing minerals are temperature dependent and follow a linear relationship if isotopic equilibrium was established at time of precipitation. This leads to the first main use of oxygen isotopes in igneous petrology - as a geothermometer. Thus, if two minerals are forming at the same time, with the same access to a given source of oxygen the distribution of the light and heavy isotopes between them should be an indication of the temperature of equilibration.

Oxygen isotope ratios have also been used as indicator of the origin of hydrothermal and metasomatic fluids (Taylor, 1968; Faure, 1977). As the average $\delta^{18}\text{O}$ of crustal sedimentary rocks is higher than that of mantle-derived igneous rocks, the assimilation of country rocks by a magma could affect the oxygen isotopic composition of that magma. Additionally, because high ^{18}O values are only produced as a result of surface- or near-surface processes, they may serve as indicators of hydrothermal alteration at relatively low temperatures. Figure 4.2 shows the $\delta^{18}\text{O}$ values, relative to SMOW, and the approximate $^{18}\text{O}/^{16}\text{O}$ ratios of a wide variety of natural substances.

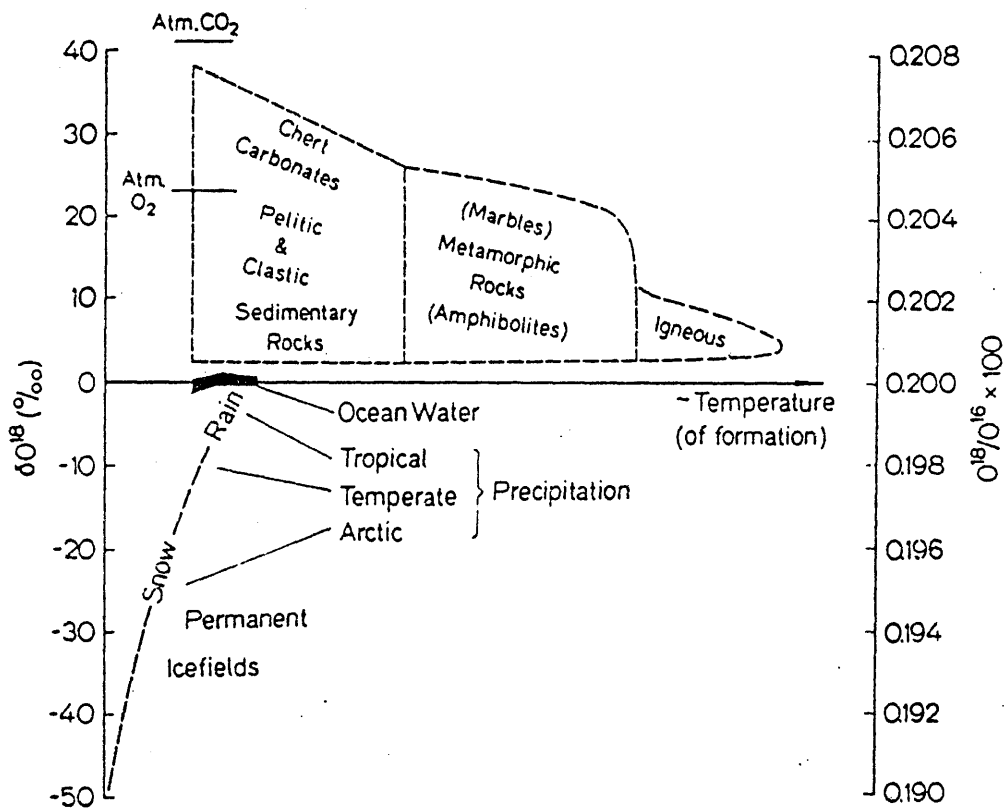


Fig. 4.2 . Oxygen isotope variation in nature (relative to Snow)
 (After Garlick, 1978).

4.2.3 Strontium Isotope Systematics

Strontium has four naturally occurring isotopes ^{84}Sr , ^{86}Sr , ^{87}Sr , and ^{88}Sr (Nier, 1938) of which the isotopic abundances of ^{84}Sr , ^{86}Sr and ^{88}Sr are constant in nature because they are neither radioactive, nor the decay product of any naturally occurring radioactive isotopes. There are, however, variations in the abundance of ^{87}Sr , due to the proportions produced by the radioactive decay of ^{87}Rb . The decay of ^{87}Rb to ^{87}Sr (with a half-life of 4.89×10^{10} yr) is expressed by equation: (1)

$$(^{87}\text{Sr})_p = (^{87}\text{Sr})_i + (^{87}\text{Rb})_p (e^{\lambda t} - 1) \dots\dots(1)$$

where 'p' denotes present day,

'i' denotes initial (i.e. time of formation and closure of the system),

't' is the time since the closure of the system to Rb-Sr equilibration,

' λ ' constant.

The non-radiogenic isotope of ^{86}Sr is used to monitor changes in the isotopic composition of ^{87}Sr and hence, such changes are expressed in terms of the ratio $^{87}\text{Sr}/^{86}\text{Sr}$, thus:

$$(^{87}\text{Sr}/^{86}\text{Sr})_p = (^{87}\text{Sr}/^{86}\text{Sr})_i + (^{87}\text{Rb}/^{86}\text{Sr})_p (e^{\lambda t} - 1) \dots\dots(2).$$

This equation, of the form $y = mx + c$, is that of a straight line, where the intercept on the y-axis represent the initial

$[(^{87}\text{Sr}/^{86}\text{Sr})_i]$ ratio and the age is given by the gradient of the line (Fig. 4.3).

The Sr-isotopic method could be used to determine whether particular igneous rocks were derived purely from the mantle, or by interaction with pre-existing crustal rocks (see subsection 4.1).

4.3 PREVIOUS ISOTOPE STUDIES

Over the past fifteen years or so, there has been a growing interest in using radiogenic and stable isotope systems to study Caledonian magmatism. At present there is an extensive amount of Sr-isotopic data and lesser amounts of O-, Pb- and Nd-isotopic data for representative populations of granitoids from the different British Caledonian provinces.

Long (1964), Bell (1968), Pankhurst (1974), Busrewil et al. (1976), and Pankhurst and Pidgeon (1976) recognized that both the pre-tectonic Older granites of the Scottish highlands and the syn- and post-tectonic Newer granites of Aberdeenshire in the eastern Grampian Highlands had a large range of Sr-isotopic composition with high $(^{87}\text{Sr}/^{86}\text{Sr})_i$ ratios, generally well in excess of 0.710. This, together with their S-type nature, has led to the generally accepted view that these granites were derived by partial melting of local Upper Proterozoic country rock. Subsequent work by Halliday et al., (1980), and Clayburn

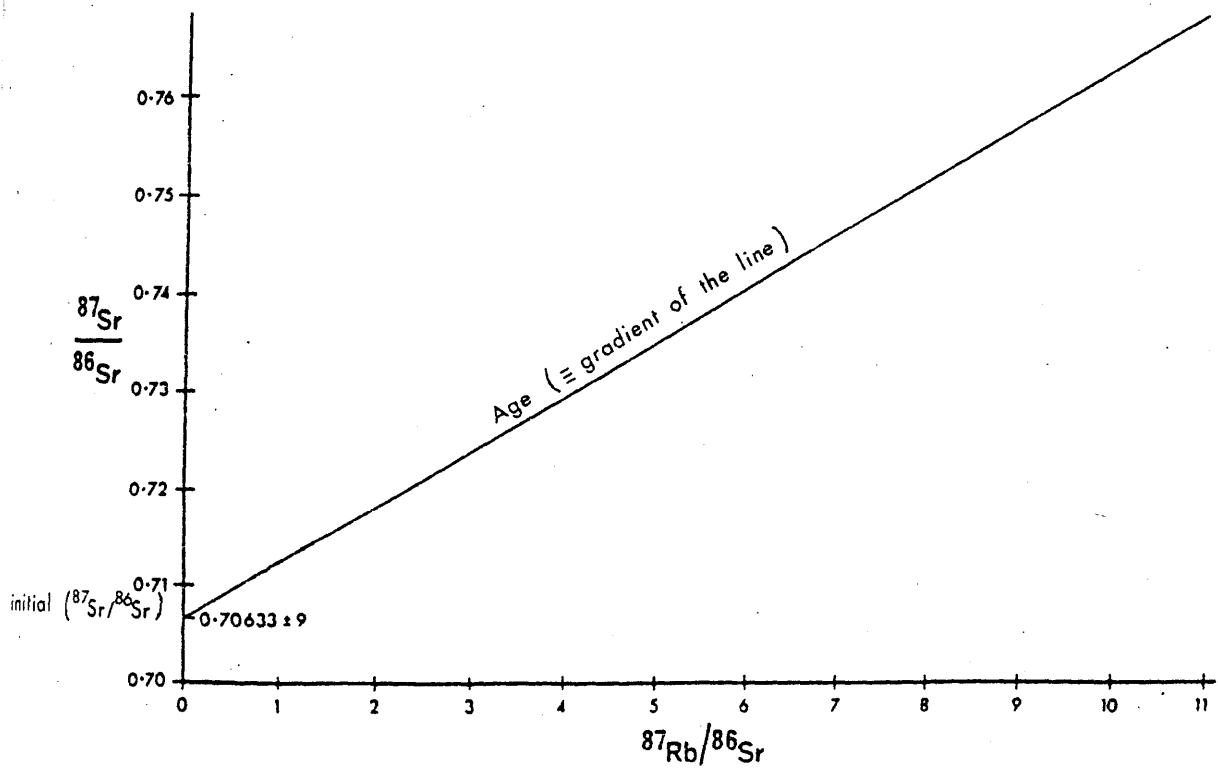


Fig. 4.3 Schematic plot of $^{87}\text{Rb}/^{86}\text{Sr}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ to show the age and initial Sr-isotope determination.

(1981) on the post-tectonic Newer granitoids documented a range of O-isotopic composition similar to that of the Older granites, but with initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios generally below 0.710 (Fig. 4.4). Considering the tectonic style of emplacement, the Newer Last granitoids have ($^{87}\text{Sr}/^{86}\text{Sr}$)_i values that fall in a narrow range, from 0.704 to 0.707, which together with their I-type character has led to the opinion that they were derived from a mantle or lower crustal source. The Newer Forceful granites exhibit a great diversity in terms of their petrographic and chemical character and tend to fall in an intermediate position in terms of their initial Sr-isotopic composition (0.704 - 0.718), although more biased toward the Newer Last granitoids than the Older granites. This is consistent with their geophysical and aeromagnetic character, as noted by Brown and Locke (1979), and suggests a highly complex origin for these granitoids.

A small amount of O-isotope data has been considered in conjunction with Sr-isotopic variation to place more precise limits on the role of continental crust in the origin of the Caledonian granitoids (Table 4.1 and Fig. 4.5). The overall, positive correlation between $^{18}\text{O}/^{16}\text{O}$ and ($^{87}\text{Sr}/^{86}\text{Sr}$)_i ratios for the Newer Caledonian granitoids documented by Harmon and Halliday (1980) is similar to that observed at modern and ancient destructive plate margins (Taylor and Silver, 1978; Harmon and Halliday, 1980; Masi et al., 1981). Those granitoids with low

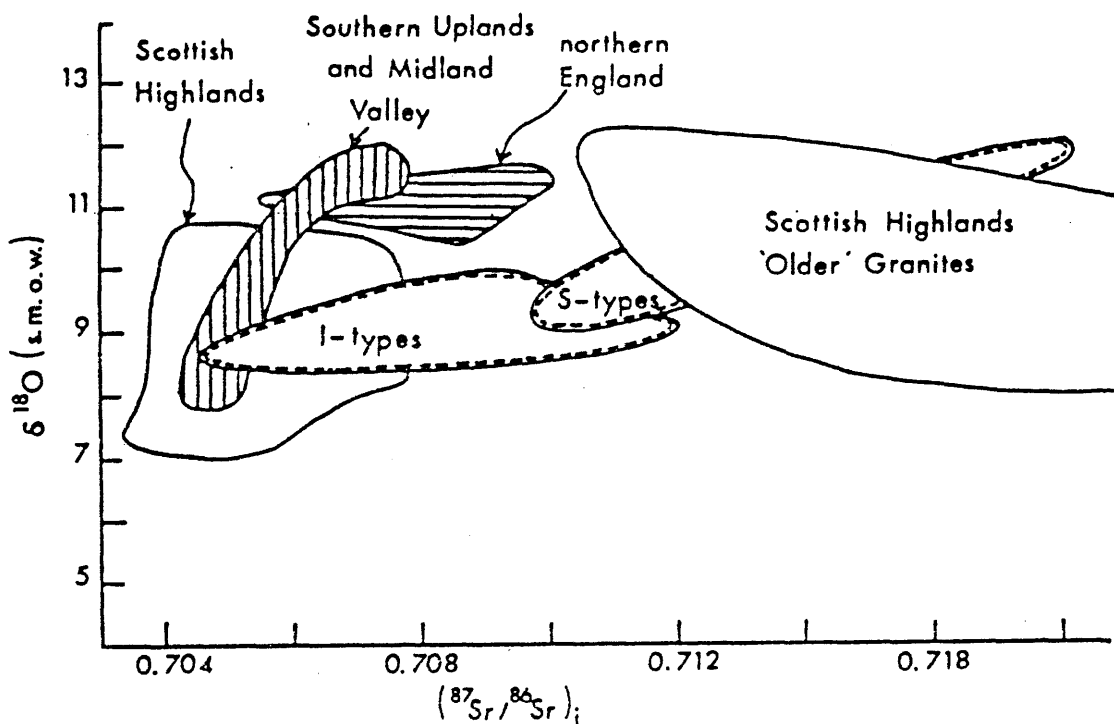


Fig 4.4 Plot of $\delta^{18}\text{O}$ against $(^{87}\text{Sr}/^{86}\text{Sr})_i$ for the British Caledonian granitoids subdivided according to the different geographic provinces. Also shown, for comparison, are the $\delta^{18}\text{O} - (^{87}\text{Sr}/^{86}\text{Sr})_i$ fields for the Lower Palaeozoic Berridale and Kosciuszko Batholiths of the Lachlan Fold Belt of Southeastern Australia (O'Neil and Chappell, 1977; McCulloch and Chappell, 1982). (Mostly after Harmon *et al.*, 1984).

○ Lachlan Fold Belt, SE Australia.

TABLE 4.1: Geochronological, Compositional and Isotopic Characteristics of some British Caledonian Granitoids

Pluton	Rock Type	Age (Ma)	$(^{87}\text{Sr}/^{86}\text{Sr})_t$	$\delta^{18}\text{O}_{\text{SMOW}}$ (‰)	Reference
Shap	gr.	392 \pm 2	0.7075	10.6	(1)
Strontian	gd.	435 \pm 10	0.7052	7.1	(1)
	bt.gr.		0.7070	8.5	
Ratagain	gd	415 \pm 5	0.7052	10.3	(1)
Kilmelford	gd	410	0.7044	9.4	(1)
	d		0.7038	7.5	
Etive	gd.	400 \pm 5	0.705	8.8	(2)
	d		0.704	7.2	
	gr		0.705	9.4	
Ballachulish	gd	401	0.7042	7.8	(1)
			0.7043	8.0	
Ross of Mull	g	414 \pm 3	0.7061	8.9	(3)
Cairnsmore of Fleet	g	392 \pm 2	0.7062	11.2	(1)
Aberdeen	g	485*	0.712	10.3	(1)
Kemnay	2mgr	411 \pm 7	-	10.0	
Oughterard	gr	469 \pm 7	0.710	-	(4)
Galway	gr	407 \pm 12	0.7048	9.5***	(4)
Roundstone	gr	418	0.705	8.2***	(4)
Inish	gr	427 \pm 8	0.704	-	(4)
Cashel micro-granite sill	gr	487 \pm 3	0.7208	-	(5)
Upper Findhorn	d	413 \pm 5**	0.706**	8.0 ⁽¹⁾	

References: (1) Harmon and Halliday (1980); (2) Hamilton et al (1980); (3) Harmon et al (1984); (4) Leake (1978); (5) Jagger (1980) unpublished thesis.

*Sutherland (1982)

**Van Breeman and Piasecki (1983)

***Jenkin (pers. comm.)

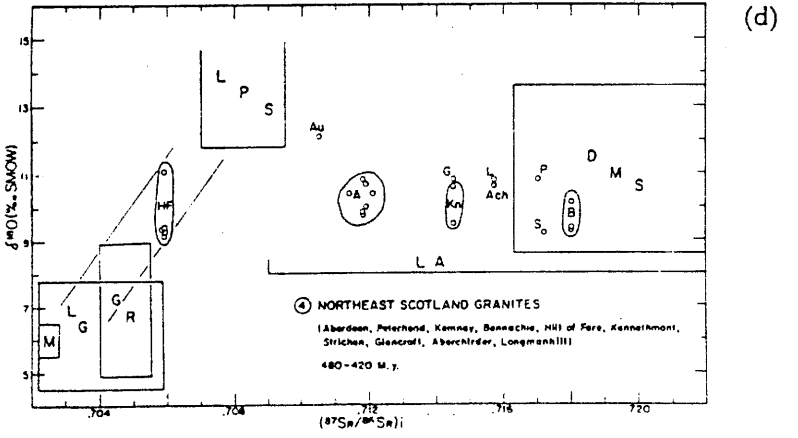
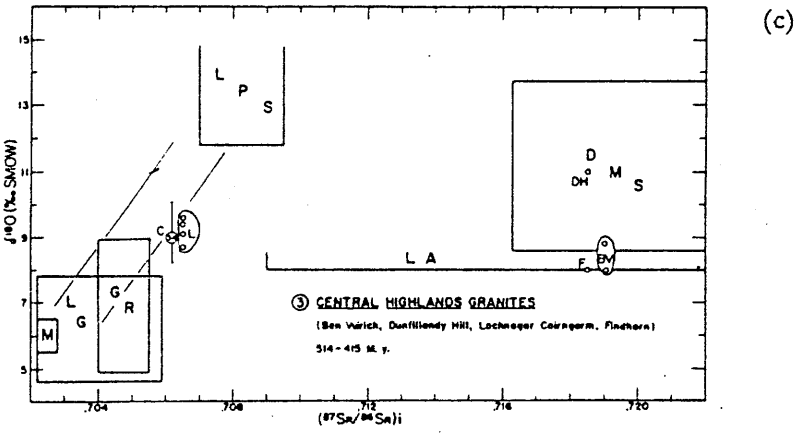
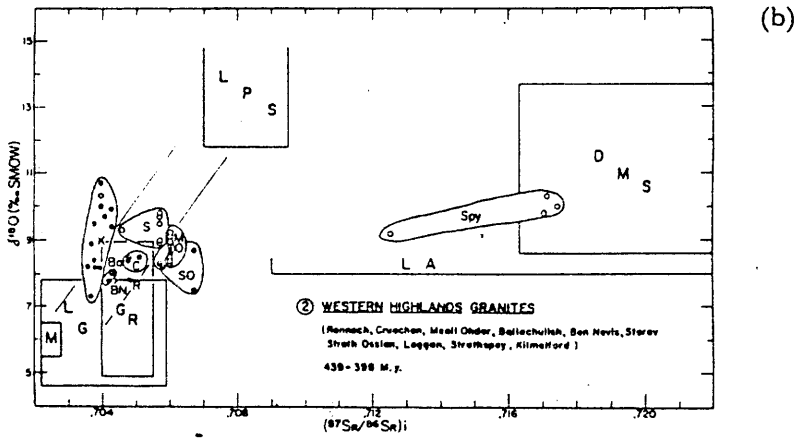
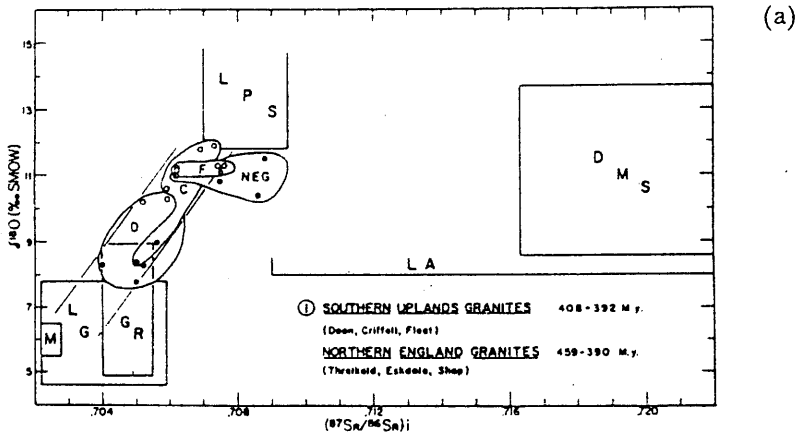


Fig. 4.5: See overleaf

Fig. 4.5 Diagrams of $\delta^{18}\text{O}$ versus $(^{87}\text{Sr}/^{86}\text{Sr})_i$ in British Caledonian granites from restricted geographic areas: (a) northern England and the Southern Uplands; (b) the Western Highlands; (c) the Central Highlands; (d) Northeast Scotland. Symbols for the source regions are: M = Mantle; L.G. = Lewisian granulites; G.R. = Grenville Paragneisses, Migmatites, and Granites; L.P.S. = Lower Palaeozoic Sediments; L.A. = Lewisian Amphibolites; and D.M.S. = Dalradian Metasediments.

(After Harmon, 1983).

$\delta^{18}\text{O}$ and ($^{87}\text{Sr}/^{86}\text{Sr}$)_i values are considered, in general, to be derived largely from a primitive mantle or lower crustal source, whereas those substantially enriched in ^{18}O and ^{87}Sr are thought to contain a crustal component derived from assimilation or magma mixing.

4.4 SULPHUR ISOTOPE DATA

4.4.1 Introduction

The theory and practice of sulphur isotope studies have been reviewed extensively in the last decade by Rye and Ohmoto (1974); Faure (1977); Coleman (1977); Nielsen (1978); and Ohmoto and Rye (1979). The application of the sulphur isotope technique to the study of mineral genesis of sulphide and sulphate deposits of economic importance has attracted most attention and has been successful. Recently, sulphur isotope studies on primary sulphides associated with granites have proved useful in understanding the petrogenesis of the granites; that is in terms of granites derived either from igneous or metasedimentary protoliths. Based on a systematic survey on the whole rock sulphur isotopic composition of Japanese granitoids, Sasaki and Ishihara (1980) succeeded in discriminating between two groups of granitoids that correlate, respectively, to the two genetic series (magnetite-series and ilmenite-series granitic rocks) previously established

by Ishihara (1977). Similar work has been carried out on S- and I-type granitoids of the New England batholith of eastern Australia and proved to be successful in differentiating between the two granite types (Coleman, 1979).

Although there has been extensive work on isotope geochemistry, there has been no sulphur-isotope data relating to the British Caledonian granites and their origin. In an attempt to throw the light on the petrogenesis of these granites, several plutons from Scotland, northern England and Ireland have been subjected to the study of their sulphur isotopic composition.

4.4.2 Sample Preparation

About 200 samples from different granite plutons of Scotland were provided by Dr. W.E. Stephens, St. Andrews University; 38 samples were collected from granites of Connemara, Ireland; and 5 samples from Shap granite intrusion in northern England for sulphur isotope analyses. From a total of about 50 intrusions, conventional separation techniques have yielded sulphide separates from only 19. Since sulphides associated with these granites are in trace amounts, all the samples were crushed to a fine-grained (60 - 100 and 100 to 120 mesh) powder after removing weathered surfaces. The crushed samples were sieved and washed. The techniques used for separation were magnetic separation, heavy liquid separation (both carried out at the Department of

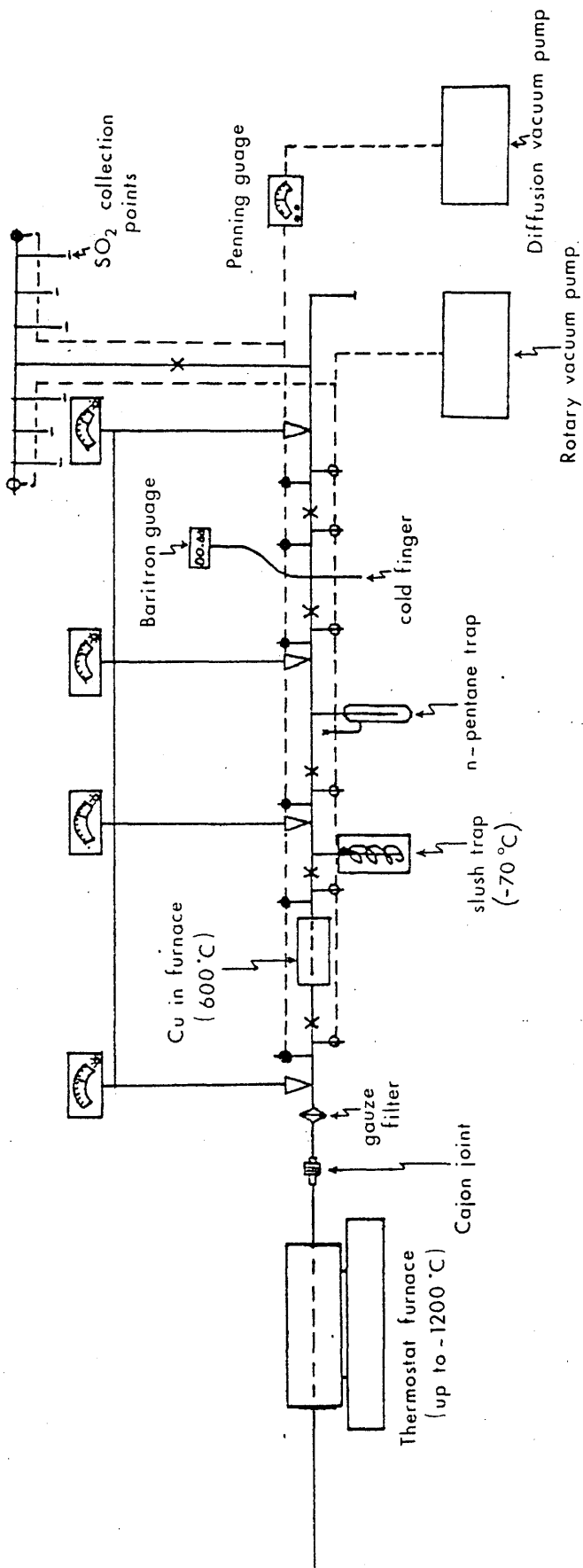
Applied Geology, University of Strathclyde) and hand picking techniques under a binocular microscope. Samples obtained were checked for purity by means of X-Ray Diffraction analyses in the Geology Department, University of Glasgow. It was found that in almost every case, small amounts of the host silicate contaminated the sulphide, but that samples contained only one sulphur-bearing phase. The technique of conversion to SO_2 (see below) is such that silicate contamination presents little problem to the determination of $\delta^{34}\text{S}$ ratios. Consequently, samples were analysed as they were originally prepared.

4.4.3 Sulphide Mineralogy

The sulphide-phases are mainly pyrite, pyrrhotite and rarely chalcopyrite. Pyrite is present generally as a fine-grained mineral either disseminated or as cubic granules or skeletal cubes within the granites. The grain size is from less than a millimeter to a few mm. Pyrrhotite often constitutes thin layers (1-2mm) or granules (1-3mm in diameter) and is usually associated with magnetite. Unlike pyrite which is ubiquitous in all granite compositions, pyrrhotite is almost restricted to diorites or granodiorites. Chalcopyrite is found only in massive sulphides associated with the granite. It is present in porphyroblasts (1mm - 1cm in diameter) and is usually associated with pyrite.

4.4.4 Analytical Techniques

In order to analyse samples to determine the isotopic ratios, the sulphur is most commonly converted to sulphur dioxide. The extraction of the gas SO_2 and sulphur isotope determination were carried out in the Scottish Universities Research and Reactor Centre at East Kilbride. The method used for SO_2 extraction is that described by Robinson and Kusakabe (1975). 5-6mg of pyrite, 8-10mg of pyrrhotite or chalcopyrite are mixed with an excess of cuprous oxide ($\text{Cu}_2\text{O} \approx 250\text{mg}$) and ground and homogenized automatically to a fine grain size in an agate Micromill. The mixture is then combusted within the SO_2 extraction line, which is evacuated by means of a vacuum system (Fig. 4.6), at 1070°C for about 25 to 30 minutes to obtain a complete yield of SO_2 . A few percent of CO_2 gas is often present in the SO_2 . It originates as carbon impurities in the sample. The sample - Cu_2O mixture can be safely outgassed above 100°C without loss of SO_2 . Any CO_2 produced with the SO_2 is most effectively extracted by fractional sublimation in a n-pentane-liquid nitrogen trap (Fig. 4.6). This method usually failed to produce a 100% yield of SO_2 of most samples because of the host rock contamination. However, the analytical procedure was accepted because of routinely consistent 100% yields from identical combustion of the internal laboratory standard which is run every 3 to 4 sample runs.



- ⊕ rough valves
- ↑ diff. valves
- vacuum line
- main line
- ⤵ vacuum guages
- × main line seal off valves

Fig. 4.6. SO₂ EXTRACTION LINE
(a schematic diagram)

The prepared gas was analysed for sulphur isotopic composition on a new 12cm model double collector mass spectrometer (Isospec 64) manufactured by Spectamass Limited, Congleton, UK. The ion beams monitored are m/z 66 and 64, with standard correction factors applied to raw $\delta^{66}\text{S}$ ratios (e.g. Craig, 1957). The entire instrument is operated at 110°C to avoid fractionation of SO_2 on cool metal inlet pipes. Within run, precision of $\delta^{66}\text{S}$ ratios is typically $\pm 0.05\%$ (2σ) or better, with a long term reproducibility (including sample preparation) of $\pm 0.3\%$ (1σ).

Standards analysed during this study were: CP-1 (a British Geological Survey standard chalcopyrite, supplied by M.L. Coleman), which has an isotopic value of -4.56% and was used as a routine internal standard; SL-277-5 and SL-277-4 (two McMaster standard silver sulphides, McMaster University (Rees, 1978)) giving $+7.76\%$ and 17.25% respectively.

4.4.5 Presentation of Data

In this study sulphur isotopic data are available for 19 British Caledonian granites. These plutons are distributed through all the geographic provinces (see Fig. 1.1), and span the total age from 485 to 390 Ma. They cover the complete compositional spectrum of the Caledonian granites from diorites through to peraluminous granites. The $\delta^{34}\text{S}$ values group in two ranges: -4.5

to +4.4‰ and +5.6 to +16.0‰ (Fig. 4.7). Included in the first range are the results of two samples (RAT 10/A and RAT 10/B) from a syenitic hybrid, and an appinite sample (RAT 13/1), all from Ratagain intrusion.

Variation of $\delta^{34}\text{S}$ values within a single, non-zoned intrusion (e.g. Shap, Ratagain, Arrochar), or a member of zoned pluton (e.g. Strontian), is not very large; thus, a single analysis from some plutons is considered representative of the whole intrusion (e.g. Corran, Ross of Mull, Aberdeen, Mullach nan Coirean).

It is clear from Fig. 4.8 that all 'Newer' Caledonian granites fall within a restricted range of $\delta^{34}\text{S}$ (-4.5 to +4.4‰) except the zoned Strontian intrusion in which the biotite granite shows an average value of +7.0‰ and the granodioritic member with $\delta^{34}\text{S}$ of -1.7‰. The 'Older' Caledonian granites tend to exhibit a range of values from +6.2 to 16.0‰. Some of the intrusions have negative $\delta^{34}\text{S}$ values (e.g. Ratagain, Kemnay, Strontian granodiorite, Cairnsmore of Fleet), but many plutons show positive values regardless of age or geographic distribution. This is due to the redox conditions of the magma and/or the nature of the magma source rock (see below). All Connemara granites have positive $\delta^{34}\text{S}$ values; the Galway batholith shows a restricted range of 0.0 to +4.2‰ whereas the Oughterard granite has a wide range of +6.2 to

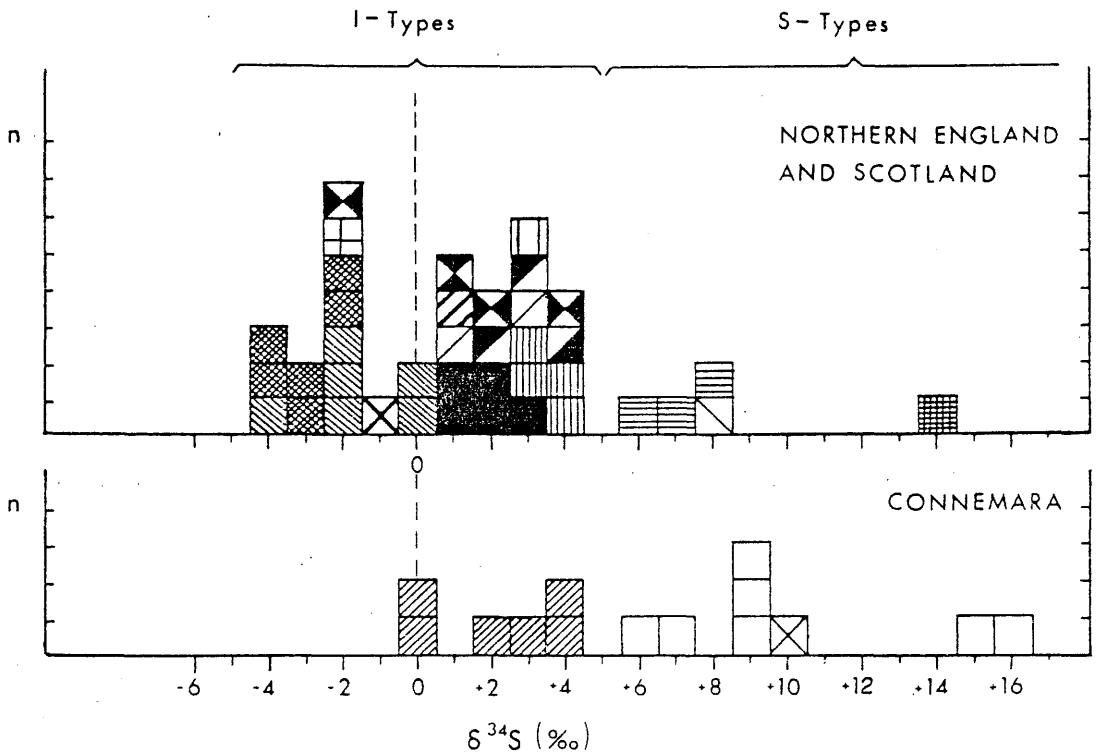





















Fig. 4. 7. Histograms showing the distribution and frequency of $\delta^{34}\text{S}$ values for some British Caledonian granites. Symbols are:

Northern England and Scotland

- | | | | | | |
|---|------------------|---|---------------------|---|--------------------------|
|  | Shap |  | Kilmelford |  | Corran |
|  | Strontian (gd) |  | Ross of Mull |  | Aberdeen |
|  | Strontian (btgr) |  | Glen Doll | <u>Connemara</u> | |
|  | Arrochar |  | Mullach nan Coirean |  | Galway |
|  | Ratagain |  | Upper Findhorn |  | Oughterard |
|  | Etive |  | Kemnay |  | Cashel Microgranite sill |
|  | Ballachulish |  | Fleet | | |

1. Fleet
2. Shap
3. Etive
4. Ballachulish
5. Galway
6. Kemnay
7. Upper Findhorn
8. Ratagain
9. Ross of Mull
10. Kilmelford

11. Roundstone
12. Inish
13. Strontian (granodiorite)
13. " (biotite granite)
14. Oughterard
15. Aberdeen
16. Cashel microgranite sill

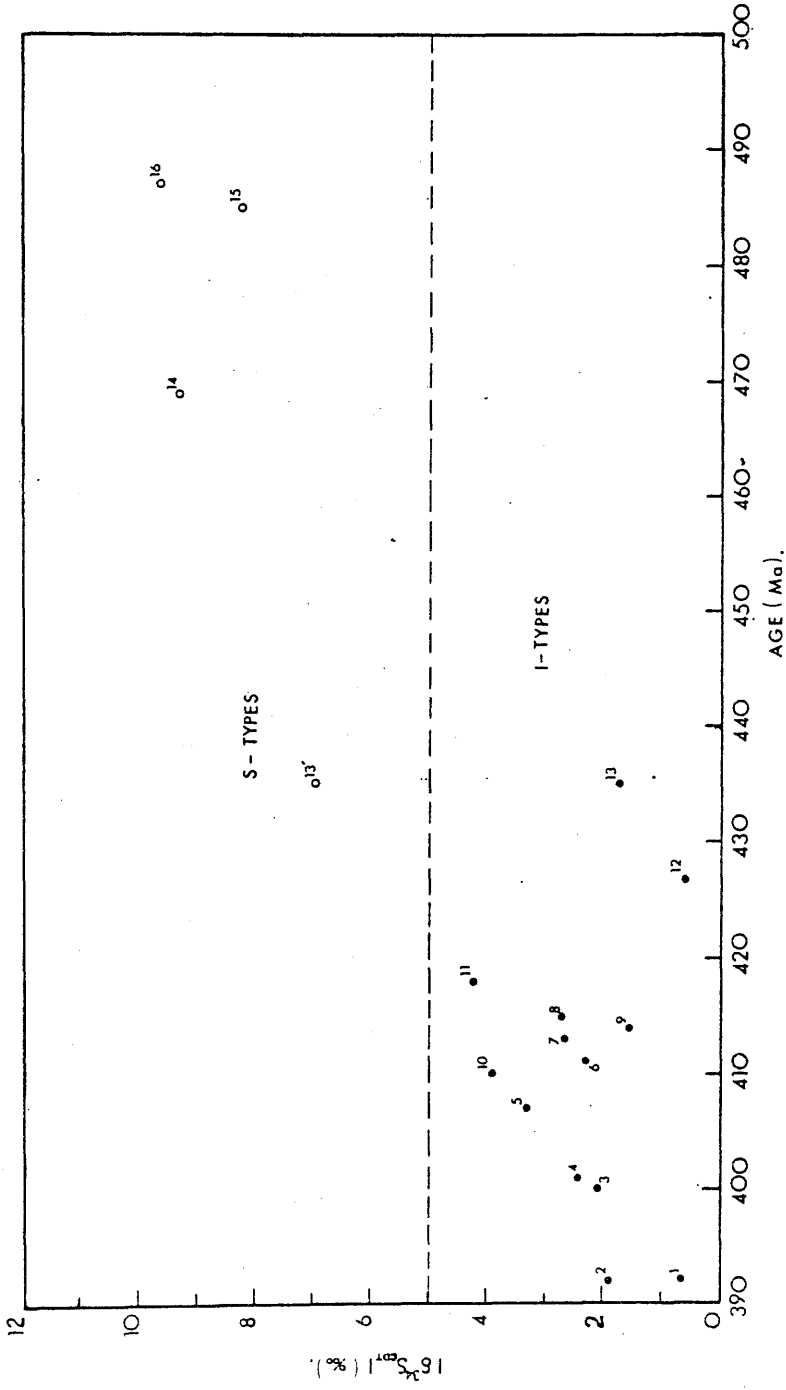


Fig. 4.8. Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus Rb-Sr age for Caledonian granites separated into older and younger, S- and I-type groups respectively. Open circles are S-types and filled circles are I-types.

+16.0‰. A single $\delta^{34}\text{S}$ analysis from the Cashel microgranite sill gives +9.6‰.

4.4.6 Interpretation

In order to interpret the data sensibly, pertinent natural ranges of $\delta^{34}\text{S}$ could be useful (see Fig. 4.1). Sulphide from nine meteorite samples analysed by Jensen (1967) gave a result relative to Canon Diablo of +0.18‰ ± 0.17 (1σ). Many igneous rocks (especially those considered to be more directly derived from the mantle) give a similar value. Shima et al., (1963) analysed sulphides separated from various basic sills, and excluding massive sulphides or samples of chilled margins, the data gave a mean of +0.95‰ with a range of -1.95 to +3.85. Similarly, Smitheringale and Jensen (1963) found that sulphides in basic intrusives gave an average of +0.1‰ (range -3.6 to +3.3). It can be seen from Fig. 4.1 that present day seawater sulphate also has a very narrow spread; Thode et al (1961) published a value of +20.1‰ ± 0.3 from 16 samples taken from the Atlantic, Pacific and Antarctic oceans. The fractionation of sulphur isotopes in sedimentary regimes, however, leads to a very much wider range in values (-50 to +50‰) but sulphates in evaporites are generally enriched in ^{34}S ($\delta^{34}\text{S}$ higher than +30‰). Ancient sediments also exhibit a wide range of $\delta^{34}\text{S}$ (-40 to \sim +40‰) (Coleman, 1977).

TABLE 4.2: $\delta^{34}\text{S}$ Results

Pluton	Lab.No.	Sample No.	Mineral	% Yield	% $\delta^{34}\text{S}_{\text{CDT}}$	$\bar{X} \delta^{34}\text{S}$
Shap	S0335	R1SH	Pyrite	99%	+2.99	+1.90
	S0336	R2SH	"	87%	+1.98	
	S0444	R3SH	"	96%	+2.40	
	S0338	R4SH	"	98%	+1.31	
	S0340	R5SH	"	97%	+0.83	
Strontian	S0360	SG83/25	Pyrrhotite	57%	-4.54	-1.77
	S0361	SG83/25	Pyrite	89%	-1.79	
	S0362	SG83/3	"	88%	-0.35	
	S0363	SG83/35	Pyrrhotite	60%	-2.09	
	S0367	SG83/25	"	112%	-1.70	
	S0471	83SR21	"	119%	-0.14	
	S0472	SR108	"	90%	+6.92	
	S0474	SR108C	"	95%	+8.36	
	S0460	R81053	Pyrite	89%	+5.63	
Ratagain	S0451	RAT 10/A	Pyrrhotite	106%	-4.34	-2.97
	S0452	RAT 10/B	"	111%	-2.84	
	S0453	RAT 12/1	"	102%	-2.31	
	S0454	RAT 13/1	"	116%	-3.63	
	S0456	RAT 13/1	Pyrite	100%	-2.24	
	S0457	RAT 14/1	Pyrrhotite	105%	-2.47	
Arrochar	S0377	82 AO 77	Pyrite	90%	+2.92	+3.44
	S0379	82 AO 94	"	88%	+3.26	
	S0270	82 AO 96	"	71%	+3.94	
	S0378	82 AO 99	"	95%	+3.63	
Kilmelford	S0387	R82KD89	Pyrrhotite	82%	+3.98	+3.98
Glen Doll	S0365	GD 39	Pyrite	89%	-1.93	+1.40
	S0366	GD 47	"	99%	+4.42	
	S0355	GD 45	Pyrrhotite	92%	+1.71	
Etive	S0368	RB 43	Pyrite	97%	+3.03	+2.09
	S0375	RB109	"	74%	+1.15	
Ballachulish	S0380	R JC1	Pyrrhotite	119%	+1.86	+2.37
	S0381	R JC1	Pyrite	84%	+2.89	
Ross of Mull	S0268	R81148	Pyrite	101%	+1.54	+1.54
Corran	S0457	R81051	Pyrite	86%	+14.17	+14.17
Mullach nan Coirean	S0458	82MC126	Pyrite	99%	+0.96	+0.96

Pluton	Lab.No.	Sample No.	Mineral	% Yield	$\delta^{34}\text{S}_{\text{CDT}}$	$\bar{\delta}^{34}\text{S}$
Cairnsmore of Fleet	S0459	R77014	Chalcopyrite	83%	-0.63	-0.63
Kemnay	S0470	82KY39	"	104%	-2.27	-2.27
Aberdeen	S0269	R82AB24	Pyrite	79%	+8.26	+8.26
Upper Findhorn	S0446	R82MY55	Pyrrhotite	25%	+2.67	+2.67

CONNEMARA GRANITES

Pluton	Lab.No.	Sample No.	Mineral	% Yield	$\delta^{34}\text{S}_{\text{CDT}}$	$\bar{\delta}^{34}\text{S}$
Oughterard	S0267	R Sulf Od.G	Pyrrhotite	94%	+6.21	
	S0271	"	Pyrite	94%	+6.81	
	S0341	R2A Od.G.	"	90%	+8.57	
	S0342	R3A Od.G.	Chalcopy.	99%	+15.10	+10.10
	S0277	R7A Od.G.	Pyrite	89%	+9.18	
	S0278	R7A Od.G.	Pyrite	90%	+8.78	
	S0276	R3A Od.G.	Pyrite	81%	+16.04	
Galway <u>Batholith</u>						
Roundstone(1)	S0280	R15-16 RG	Pyrite	62%	+4.24	+4.24
Galway(2)	S0281	R24ETG	"	90%	+2.94	+3.35
	S0287A	R27-28MG	"	39%	+3.77	
Inish(3)	S0283	R29IG	"	91%	+0.23	
	S0284	R30IG	"	58%	+1.73	+0.65
	S0289	R31IG	"	91%	-0.01	
Cashel MG* Sill	S0287B	RS21C	Pyrite	48%	+9.61	+9.61

*MG = microgranite

Equilibrium fractionation during petrogenesis will only produce relatively small effects, because of the high temperatures involved (Ohmoto and Rye, 1979). However, the chemical environment may cause loss of vapour phase constituents. Under reducing conditions, expulsion of isotopically light hydrogen sulphide (H_2S) will leave the residual sulphur relatively heavy. Conversely, in an oxidizing environment loss of sulphur dioxide (SO_2) will leave the resulting rock isotopically light. With even more oxidation, sulphur dioxide may not be lost but could be fixed as sulphate, producing a value nearer to that of the original composition as complete oxidation is approached (Schneider, 1970). Furthermore, because of the existence of significantly large isotopic fractionation factors between SO_2 and the reduced sulphur species, even at magmatic temperatures, the $\delta^{34}S$ value of magmatic fluids can be quite different from that of silicate magmas, and that the extent of the deviation in $\delta^{34}S$ values is dependent on the SO_2/H_2S ratio in the fluid, temperature, and the relative masses of fluid and magma at the time of fluid separation (Ohmoto and Rye, 1979).

The fractionation of sulphur isotopes between coexisting sulphide-phases may be used to estimate the temperature of formation of high-temperature mineral assemblages (Sakai, 1957), like those suspected in the granitic environment.

4.4.6.1 Newer Caledonian Granites

From Fig. 4.7 and Table 4.2, it can be seen that the Newer Caledonian granites of Britain and Ireland, examined in this study, fall within a narrow range of $\delta^{34}\text{S}$ (-4.5 to +4.4‰). These values are more characteristic of sulphides associated with basic igneous rocks. Therefore, the S-isotope data of the Newer Caledonian granites are consistent with derivation from an igneous protolith; i.e., lower-crust or upper-mantle materials. The Ratagain intrusion shows relatively high negative $\delta^{34}\text{S}$ values (-2.2 to -4.5‰) and high SO_2 yield (up to 116%) extracted from pyrrhotite phase. This intrusion is also unusual in exhibiting extremely high concentrations of some trace elements, alkali-enrichment, syenites, and apinites intimately associated with pluton emplacement (Halliday *et al.*, 1984). Halliday *et al.* (1984) suggested that a vapour phase transfer is likely to have been important in some components of the intrusion during emplacement. If the magma was sufficiently oxidized and SO_2 released was among the fugitive gases, the residual $\text{SO}_2/\text{H}_2\text{S}$ ratios will decrease. Therefore, the residual total sulphur will be depleted in ^{34}S giving negative $\delta^{34}\text{S}$ (down to -4.5‰). The high SO_2 yield extracted from pyrrhotite (e.g. Ratagain, Strontian, Balachulish) could be related to a deficiency of iron below that required for the stoichiometric formula FeS (used in yield calculation for pyrrhotite), thus reducing the theoretical weight of pyrrhotite required for analysis to give a 100% yield SO_2 .

The excess contribution of sulphur will therefore give a high SO₂ yield. Another possibility may be the presence of minute sulphide (e.g. pyrite) or sulphur inclusions in the pyrrhotite which could produce a high SO₂ yield.

4.4.6.2 Older Caledonian Granites

The Old Caledonian granites examined in this study are those of Aberdeen in Scotland, and Oughterard and Cashel microgranite sill in Connemara, Ireland. In contrast to the Newer granites, these intrusions show a wide isotopic range (+6.2 to +16.0‰) dominated by positive $\delta^{34}\text{S}$ values. This is consistent with their supposed crustal origin suggested by many authors (e.g. Harmon et al., 1984). O'Nions et al., (1983) suggested that the older granitoids were produced by upper crustal anatexis and the most likely source, supported by isotopic evidence, being the Late Proterozoic (Dalradian) metasediments which had a substantial crustal residence time before melting. Iron sulphides from representative lithologies from the Lower Dalradian Ballachulish slates, Scotland, analysed by Hall et al., (1986) gave $\delta^{34}\text{S}$ values ranging from +12.8 to +16.6‰. This is compatible with the sulphur isotope data of the older Caledonian granites supposed to be derived from these metasediments; Corran granite having $\delta^{34}\text{S}$ of +14.2‰, and Aberdeen intrusion with an isotopic composition of +8.3‰. In Ireland, the Oughterard and Cashel microgranite intrusions, with $\delta^{34}\text{S}$ ranging from +6.2 to

+9.6%, could have been derived from the Dalradian metasediments inheriting their sulphur isotopic composition with a slight depletion in ^{34}S produced during petrogenesis.

In the northwestern part of the Oughterard granite, and next to a small sulphide deposit, is a fine-grained member of the intrusion, severely altered and sheared. Sample 3A Od.G. collected from this granite exhibit an enrichment of ^{34}S ($\delta^{34}\text{S} \approx +16\%$) compared with the overall range of $\delta^{34}\text{S}$ of both the intrusion and the deposit (+6.2 to +9.2%). Petrographically and chemically, this fine-grained granite tends to be more basic than the whole intrusion, and more reduced ($\text{Fe}_2\text{O}_3/\text{FeO} = 0.3$) compared with the oxidation state of the main granite ($\text{Fe}_2\text{O}_3/\text{FeO} = 0.67$) (see Section 3.4.2). Two explanations can be offered to the source of the sulphur of the fine-grained granite:

1. the sulphur could be inherited from a metasedimentary component enriched in ^{34}S twice as much as that from which the main granite has been derived, or
2. the enrichment of ^{34}S could be related to the oxidation state of the magma. It was sufficiently reduced to have lost substantial proportions of isotopically light hydrogen sulphide, thereby leaving the residual sulphur relatively heavy. In this case the inherited composition has been modified (at least 7% more) by fractionation of sulphur during petrogenesis. This

is unlikely, because to obtain a fractionation of 7‰ higher than the original $\delta^{34}\text{S}$, most of the SO_2 needs to be converted to H_2S to give such value.

4.4.7 Temperature Significance of $\delta^{34}\text{S}$ Variations Among Coexisting Sulphide Minerals

Sulphur isotope geothermometry is based on the equilibrium sulphur isotope fractionation between coexisting sulphur-bearing compounds (Fig. 4.9). The larger the separation of the curves for any two minerals, the more sensitive will the mineral pair be an isotope thermometer; i.e., the order of sensitivity of sulphur isotope fractionations to temperature among mineral pairs is: pyrite (py) - galena (ga) > sphalerite (sp) (or pyrrhotite (po)) - galena > pyrite - chalcopyrite (cp) > pyrite-pyrrhotite (or sphalerite) > pyrrhotite (or sphalerite) - chalcopyrite. (Rye and Ohmoto, 1974).

To be able to determine the temperature of formation of two sulphur-bearing phases, three conditions must be satisfied:

1. Both phases must be shown to have crystallized together from the same source, or to have recrystallized together during post-emplacement metamorphism, at isotopic equilibrium;
2. The phases must be essentially pure: for example, ZnS-FeS solid solution will fractionate S-isotopes differently than pure ZnS;

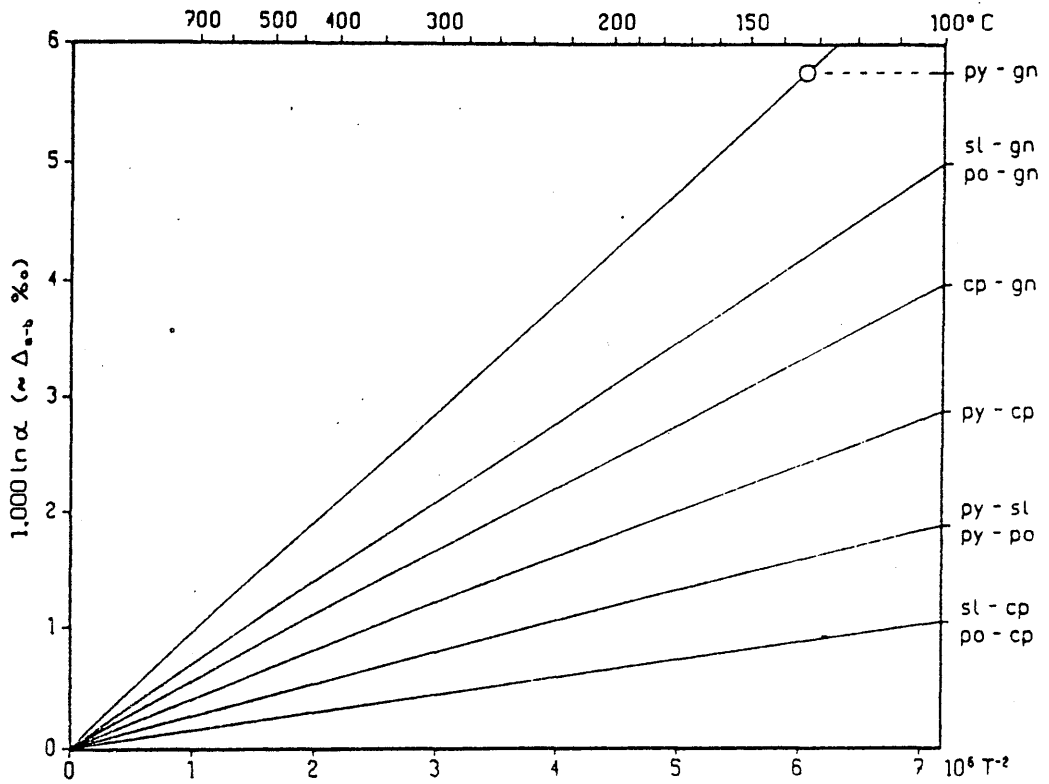


Fig. 4.9:

Calibration curves for the "sulfide pair thermometers". The sulfides are each assumed to be in isotopic exchange equilibrium with the dissolved sulfide in a common fluid. Data from calculations and laboratory experiments.

(After Nielsen, 1979).

3. There must be no evidence of a sequential paragenetic relationship between the phases (e.g. veining, encrustation, etc.) (Grootenboer and Schwarcz, 1969).

For py-po and py-cp pairs formed in equilibrium, we must have $\delta^{34}\text{Spy} > \delta^{34}\text{Spo}$ and $\delta^{34}\text{Spy} > \delta^{34}\text{Scp}$. The absolute temperature can be determined using the following equation:

$$T \text{ (in } ^\circ\text{Kelvin)} = A/\Delta^{1/2}$$

where A is a constant the value of which for py-cp pair is $(0.67 \pm 0.04) \times 10^3$ with ± 35 to ± 40 uncertainty and for py-po pair, A is $(0.55 \pm 0.04) \times 10^3$ with ± 40 to ± 55 uncertainty (Ohmoto and Rye, 1979). $\Delta = \delta^{34}\text{Sa} - \delta^{34}\text{Sb}$.

The $\delta^{34}\text{S}$ values reported on coexisting pairs of py-po and py-cp for the Caledonian granites are listed in Table 4.3 with their calculated temperatures.

The isotope temperatures for the 'Newer' Caledonian granites of Ratagain and Ballachulish are too low to be in agreement with the formation of mineral assemblages ($T > 270^\circ \text{C}$). It seems, therefore, that the two mineral phases are not in equilibrium to estimate the temperature of their formation. Sulphur isotopic composition of pyrite in the Strontian granodiorite is lower than that of pyrrhotite; thus the pair is not in equilibrium and an isotopic temperature cannot be calculated.

TABLE 4.3: Application of Sulphur-Isotope Geothermometer

Pluton	Sample No.	$\delta^{34}\text{S}$ (‰)			Isotope Temperature (°C)	
		py	po	cp	py-po	py-cp
Strontian	SG83/25'	-1.79	-1.70	-	-	-
Ratagain	RAT 13/1	-2.24	-3.63	-	193	
Ballachulish	JC 1	+2.89	+1.86	-	260	-
Oughterard	R Sulf Od G	+6.81	+6.21	-	441	-
"	R 3A Od G	+16.03	-	+15.10	-	418

Isotope temperatures are calculated assuming the relationship:

$T = A / \Delta^{1/2}$ ($\Delta = \delta^{34}\text{S}_a - \delta^{34}\text{S}_b$). The A values for py-po, py-cp pairs are taken as $(0.55 \pm 0.04) \times 10^3$ and $(0.67 \pm 0.04) \times 10^3$, respectively.

py = pyrite; po = pyrrhotite; and cp = chalcopyrite.

Temperatures estimated for the 'Old' Caldonian granite of Ougherard in Ireland (418°C for the granite and 441°C for the ore deposit) seem to be fairly reasonable for the formation of mineral assemblages. The best criterion for the attainment of equilibrium is that $\Delta\delta^{34}\text{S}$ values for different pairs of sulphides give similar temperatures.

CHAPTER 5

S-, O-, AND Sr- ISOTOPES AND THE GENESIS OF THE BRITISH CALEDONIAN GRANITOIDS

Consideration of combined S-, O-, and Sr-isotopic variations in a suite of related igneous rocks provides a means of identifying the magma source region as well as assessing the importance of contamination prior to magma emplacement and crystallization. This is possible because variations in $^{34}\text{S}/^{32}\text{S}$, $^{18}\text{O}/^{16}\text{O}$ and $(^{87}\text{Sr}/^{86}\text{Sr})_i$ ratios result from three geologically independent processes.

Sediments and their metamorphic counterparts are enriched or depleted in ^{34}S caused by the fractionation processes of sulphur on the Earth's surface during the sedimentary cycle. Additionally, sediments are enriched in ^{18}O because they contain a substantial proportion of minerals formed at the Earth's surface at low temperatures. Finally, the Earth's crust is enriched in large-ion-lithophile elements relative to the mantle and, as a result, old continental crust is also enriched in ^{87}Sr which has been produced from the radioactive decay of ^{87}Rb . It is, therefore, possible to delineate the source region of an altered granitic rock based upon its $^{34}\text{S}/^{32}\text{S}$, $^{18}\text{O}/^{16}\text{O}$, and $(^{87}\text{Sr}/^{86}\text{Sr})_i$ ratios because the mantle and various crustal provinces can be discriminated on the basis of their S-, O-, and

Sr-isotopic composition. It is also possible, in many instances, to use mixing models to ascertain the extent to which S-, O-, and Sr-isotopic variations observed within a suite of genetically related granites have resulted from contamination during transit within the crust (Taylor, 1980; James, 1981; Coleman, 1979).

Combined O- and Sr-isotope data of previous isotopic work, together with interpretation of these data for the genesis of the British Caledonian granites are summarized in subsection 4.3. The O- and Sr-isotope data listed in Table 4.1 are used in combination with the present results of S-isotopic composition of the different intrusions to shed more light on possible magma source regions and magma-crust interaction for the Caledonian granites of Britain and Ireland.

$\delta^{34}\text{S}$ values are plotted against $(^{87}\text{Sr}/^{86}\text{Sr})_i$ (Fig. 5.1) and $\delta^{18}\text{O}$ (Fig. 5.2) for 15 British Caledonian granitoids. Although the correlation between O- and S-isotopes is rather erratic, it is, however, clear that an overall correlation between Sr- and S-isotopic composition exists. The Newer Caledonian granitoids fall within the field of I-type granites (with: $\delta^{18}\text{O} < 10.5\%$; $(^{87}\text{Sr}/^{86}\text{Sr})_i < 0.708$; and $+5\% > \delta^{34}\text{S} > -5\%$) whereas the older granites have high $\delta^{18}\text{O}$, high $(^{87}\text{Sr}/^{86}\text{Sr})_i$, and exhibit a spread of

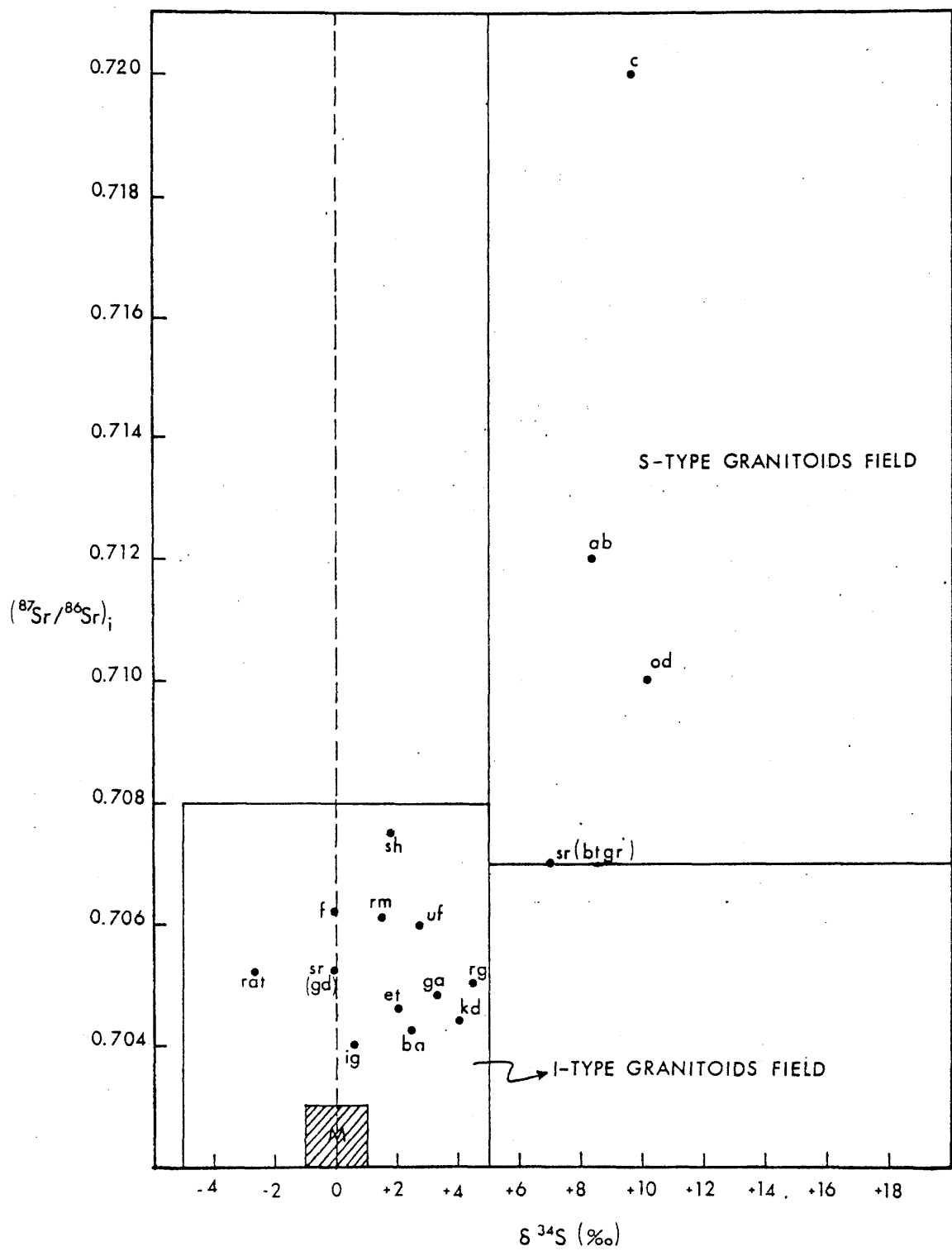


Fig. 5.1: (see overleaf)

Fig. 5.1: Diagram of mean $\delta^{34}\text{S}$ versus $(^{87}\text{Sr}/^{86}\text{Sr})_i$ for some British Caledonian granitoids showing the isotopic composition for various possible source regions.

Symbols are:

Main Britain - rat = Ratagain; sr(gd) = Strontian granodiorite; f = Cairnsmore of Fleet; ab = Aberdeen; Sr(btgr) = Strontian biotite granite; et = Etive; rm = Ross of Mull; ba = Ballachulish; kd = Kilmelford; sh = Shap; uf = Upper Findhorn.

Ireland - ga = Galway; ig = Inish; rg = Roundstone; od = Oughterard; c = Cashel microgranite sill.

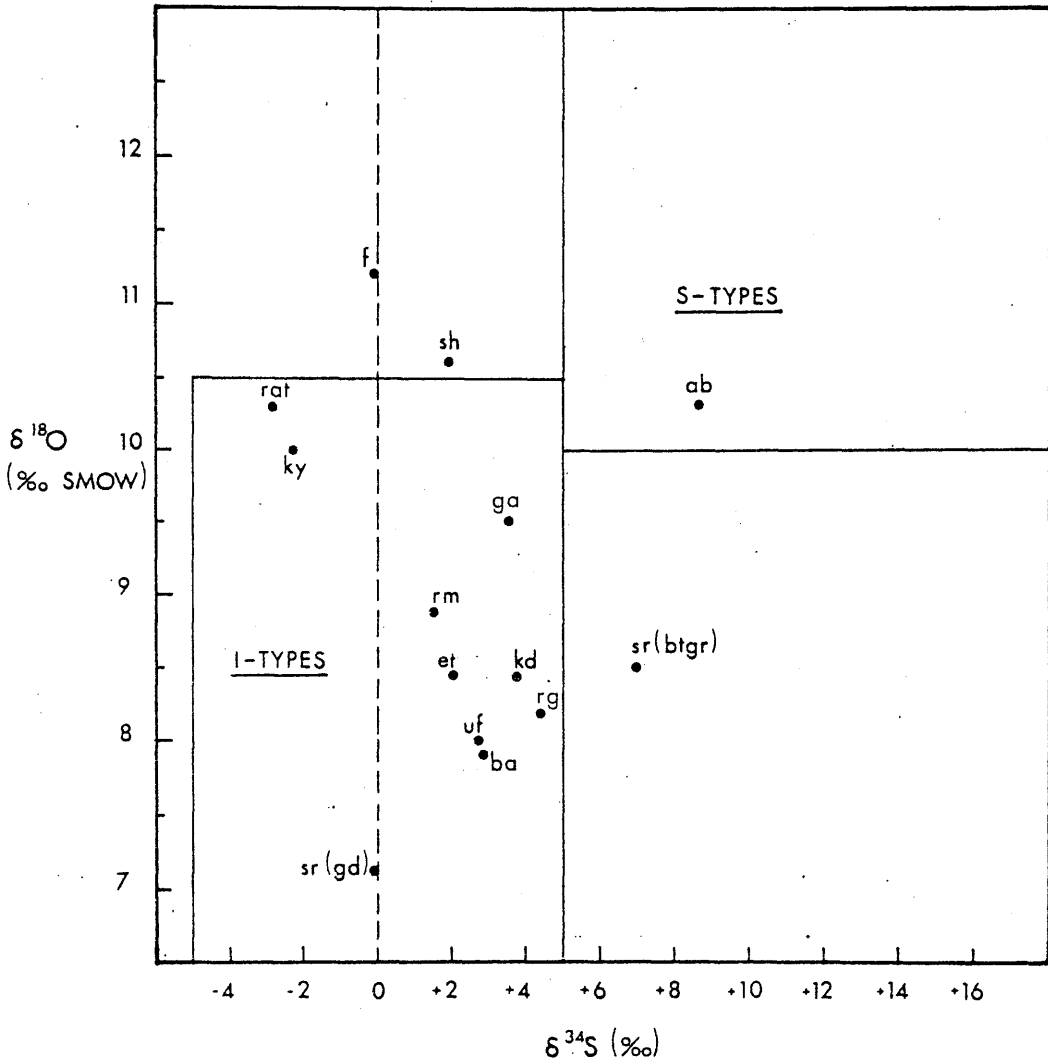


Fig. 5.2: Diagram of mean $\delta^{34}\text{S}$ versus $\delta^{18}\text{O}$ (SMOW) for some British Caledonian granitoids showing the isotopic composition for various possible source regions.

Symbols are as for Fig. 5.1 except ky = Kemnay.

positive $\delta^{34}\text{S}$ values and plot in the S-type granitoids field ($\delta^{18}\text{O} > 10\%$; $(^{87}\text{Sr}/^{86}\text{Sr})_i > 0.707$; and $\delta^{34}\text{S} > + 5.0\%$).

However, separate consideration of some intrusions reveals some important trends in the S-, Sr- and O-isotopic data.

5.1 SOUTHERN UPLANDS AND NORTHERN ENGLAND

In Northern England, the Eskdale, Skiddaw, and Shap intrusions were examined in this study, but only samples from Shap granite yielded sulphides for $\delta^{34}\text{S}$ analyses. The sulphur isotopic composition of the granite ranges from +0.8 to +2.9%. This, together with the I-type mineralogy, low initial Sr-isotopic composition (0.707) and the geophysical evidence postulating an upper mantle origin for the granite (Locke and Brown, 1978), suggests an igneous source of the magma, probably from upper mantle materials. The high O-isotopic composition (10.6%) observed in this intrusion implies a mantle derived magma which had been contaminated by melts of sedimentary upper crust. The Cairnsmore of Fleet biotite-granite, in the Southern Uplands of Scotland, with $\delta^{34}\text{S}$ of -0.6%, low $(^{87}\text{Sr}/^{86}\text{Sr})_i$ of 0.706, and high $\delta^{18}\text{O}$ of 11.2% suggests a similar primitive source mixed with an upper crustal component which seems responsible for the ^{18}O enrichment. In conclusion, the Southern Uplands and Northern England granitoids were generated, as envisaged by Halliday et al., (1980), largely by the bulk mixing of crustal melts produced within the relatively non-radiogenic, immature geosynclinal-type sediments with a primary mafic magma derived from a

mantle source region. It is noteworthy that, although $\delta^{18}\text{O}$ data show upper crustal involvement, $\delta^{34}\text{S}$ data retain the primary signature (with the proviso that this is a reconnaissance survey).

5.2 GRAMPIAN HIGHLANDS

In the Western Highlands, the plutons of Etive, Ballachulish, and Kilmelford have respective $\delta^{34}\text{S}$, $(^{87}\text{Sr}/^{86}\text{Sr})_i$, and $\delta^{18}\text{O}$ values which fall within a limited range, from +1.1 to +3.9‰, 0.704 to 0.705, and 7.2 to 9.4‰. A mantle or lower crustal origin is inferred for these magmas. Many other intrusions in the Western Highlands were examined (e.g. Moor of Rannoch, Ben Nevis, Foyers) but these did not yield any sulphides for $\delta^{34}\text{S}$ analyses. However, they were examined previously in terms of their O- and Sr-isotopic composition (see Harmon, 1983) the interpretation of which give a mantle-derived product subsequently modified by upper crustal assimilation and fractional crystallization (see Fig. 4.3). The only isotopic data available for the Arrochar and Mullach nan Coirean granites are the S-isotopic composition presented in this study. The $\delta^{34}\text{S}$ range from +2.9 to +3.9‰ for the former intrusion, and a single result of +0.9‰ for the latter predicting a mantle source for both magmas, and $(^{87}\text{Sr}/^{86}\text{Sr})_i$ and $\delta^{18}\text{O}$ are expected to be low.

The Upper Findhorn diorite of 413 Ma, in Central Highlands, is characterized by moderate $\delta^{18}\text{O}$ values ($\sim 8.0\%$), low

$(^{87}\text{Sr}/^{86}\text{Sr})_i$ of 0.706 and $\delta^{34}\text{S}$ of +2.7‰ indicating a substantially primitive source of the magma; thus a mantle source is postulated. There are no O- and Sr- isotope data for the Glen Doll intrusion, but a mantle source region is also suggested for this granite because the range of $\delta^{34}\text{S}$ values from -1.9 to +4.4‰ is similar to those of basic igneous materials.

In Northeast Scotland, the Kemnay granite has $\delta^{34}\text{S}$ value of -2.3‰ and moderate to high $\delta^{18}\text{O}$ (10.0‰) suggesting primary derivation from a deep (lower crustal) source. However, the high $\delta^{34}\text{S}$ value of +8.3‰ of Aberdeen old granite, together with the high $(^{87}\text{Sr}/^{86}\text{Sr})_i$ of 0.712, and high $\delta^{18}\text{O}$ (10.3‰) require a predominant derivation from the upper crust. This is consistent with the S-type mineralogy and chemistry of the intrusion.

5.3 NORTHWEST HIGHLANDS

The S-, Sr-, and O-isotopic relationships for the Newer Caledonian granites north of the Great Glen Fault are similar to those observed in the Grampian Highlands. The Ratagain and Ross of Mull intrusions have $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $(^{87}\text{Sr}/^{86}\text{Sr})_i$ values of -4.3 to +1.5‰, 8.9 to 10.3‰, and 0.705 to 0.706 which fall within the range of other post-tectonic granitoids north of the Highland Border Fracture Zone. By analogy, a primitive deep-seated source is inferred for these granitoids, with some late modification of the magma by contamination during transit to produce the observed range in $\delta^{18}\text{O}$ values, and the unusual extreme high concentrations of

some trace elements and alkali-enrichment of the Ratagain intrusion (Halliday et al., 1984) (see Section 4.4.6.1). The Strontian complex is distinct in terms of its lower ^{18}O content and the correlation observed between sulphur-strontium and sulphur-oxygen isotopic composition. The granodiorite $\delta^{34}\text{S}$ and ($^{87}\text{Sr}/^{86}\text{Sr}$)_i values are -4.5 to -0.1‰ and 0.705, respectively, as compared with values of +5.6 to +8.4‰ and 0.707 for the biotite granite. Similarly, the granodioritic member of the complex has low $\delta^{18}\text{O}$ values of 7.1‰ whereas the biotite-granite exhibit a higher value (8.5‰). Nd- and Sr-isotope relationships record the presence of an older crustal component in the Strontian magmas which is manifest to a greater degree in the biotite-granite than in the granodiorite phases of the intrusion (Hamilton et al., 1980). This is compatible with the S-, O-, and Sr-isotope data which suggest a mantle-like source for the early tonalite and granodiorite, followed by crustal assimilation and fractional crystallization to produce the spread $\delta^{34}\text{S}$ values, and the ^{18}O and ^{87}Sr enriched biotite-granite. The Corran granite emplaced in the northern side of the Great Glen Fault, has a $\delta^{34}\text{S}$ value of +14.2‰ indicating a crustal source of the magma, probably produced by partial-melting of Lower Dalradian metasediments, which gave similar $\delta^{34}\text{S}$ values (Hall et al., 1986) (see Section 4.4.6.2), and segregation of the melt during tectonic movements along the fault. At present, no Sr- and O-isotope data are available for this intrusion, but are predicted to give high isotopic values.

5.4 THE GRANITES OF CONNEMARA, IRELAND

The only isotope data previously published for the Connemara granites were those of the initial strontium (Leake, 1978). A good correlation between S- and Sr-isotopic composition of those intrusions existis (Fig. 5.1). The Newer Caledonian plutons of Inish, Galway, and Roundstone have $\delta^{34}\text{S}$ and $(^{87}\text{Sr}/^{86}\text{Sr})_i$ values which fall respectively within a limited range from +0.6 to +4.2‰ and 0.704 to 0.705. Two samples from Roundstone and Galway granites were analysed for their O-isotopic composition (G. Jenkin, pers. comm.). A whole-rock fresh, non-altered sample (G.J.001) from Roundstone granite gave $\delta^{18}\text{O}$ value of +8.2‰ and a slightly altered sample (G.J. 015) from the Galway granite (Murvey phase, near contact) gave $\delta^{18}\text{O}$ value of +9.5‰. These results are compatible with S- and Sr-isotopic composition of the Galway batholith and suggest an igneous source material for these intrusions. However, the 'Old' Oughterard granite has a greater spread of $\delta^{34}\text{S}$ (from +6.2 to +16.0‰) and high $(^{87}\text{Sr}/^{86}\text{Sr})_i$ value of 0.710. A crustal assimilation and fractional crystallization is postulated for this granite; thus falling within the S-type granitoids field (see Fig. 5.1). This is compatible with its S-type mineralogy and chemistry as discussed in Chapter 4. Leake (1970) suggested that the Cashel microgranite sill was formed by partial melting of the semi-pelites within the hornfelsed zone of the Cashel-Lough-Weelaun intrusion and that this melt segregated

during tectonic movements to form a small sill-like body within the metasediments. This proposition is compatible with the S- and Sr-isotopic composition of the microgranite sill showing high positive $\delta^{34}\text{S}$ value of +9.6‰ and extremely high $(^{87}\text{Sr}/^{86}\text{Sr})_i$ value of 0.720. Since variations in $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{34}\text{S}/^{32}\text{S}$ ratios result from two geologically independent processes, they can be used to identify the magma source region but they may not be necessarily in good correlation with each other. This is observed in the case of the Cashel microgranite sill where both S- and Sr-isotopes indicate a crustal origin for the granite but the extremely high $(^{87}\text{Sr}/^{86}\text{Sr})_i$ is not reflected in a very high $\delta^{34}\text{S}$.

Similar to the Galway batholith and the 'Newer' Caledonian granites of Main Britain, the other 'Newer' intrusions of Ireland seem to have an I-type character regarding their petrogenesis. The Donegal granite suite, implaced into orthotectonic Caledonian (Dalradian) rocks between 418 and 407 Ma, has initial Sr-isotope ratios of 0.705 to 0.706. O'Connor et al., (1982) suggested that this suite was derived by the melting of upper mantle and/or juvenile lower crust followed by varying degrees of contamination with upper crustal materials (e.g. Lewisian). The same source region is attributed to the origin of the c.a. 404 ± 24 Ma Leinster granite and the Newry igneous complex (399 ± 21 Ma) which have initial Sr-isotope ratios of 0.708 (O'Connor and Brück, 1978) and 0.706 (O'Connor, 1975) respectively.

On the basis of S-, O- and Sr-isotopic systematics, a mantle-derived component was observed in virtually all post-tectonic Caledonian granites examined in this study. However, some of these magmas were substantially modified by interaction, exchange or assimilation of Dalradian upper crust prior to emplacement, although, in terms of S-isotopic composition, this can only be observed in the Strontian complex. On the other hand, a crustal component is attributed to the genesis of the pre-tectonic 'Old' Caledonian granites of Main Britain and Ireland.

CHAPTER 6

CONCLUSIONS

Petrographical, chemical and sulphur-isotopic composition of the Caledonian granites of Britain and Ireland, together with previous published and unpublished oxygen and strontium isotope data, document clearly the participation of two main isotopically distinct reservoirs in their petrogenesis. North of the Highland Boundary Fracture Zone in the Scottish Highlands, the major component of the 'Newer' granitoids was subcontinental mantle ($\delta^{34}\text{S} \approx -4.5$ to $+4.4\%$; $(^{87}\text{Sr}/^{86}\text{Sr})_i \approx 0.7035 - 0.7070$; $\delta^{18}\text{O} \approx 6$ to 10%). In the Southern Uplands and Northern England, the 'Newer' granitoids were largely derived from the upper mantle or subducted oceanic lithosphere with subsequent contamination or mixing with an upper crustal component. Whereas $\delta^{34}\text{S}$ and $(^{87}\text{Sr}/^{86}\text{Sr})_i$ still reflect the primary material for the genesis of these granites ($\delta^{34}\text{S} \approx -0.6$ to $+2.9\%$; $(^{87}\text{Sr}/^{86}\text{Sr})_i \approx 0.705 - 0.707$), $\delta^{18}\text{O}$ data ($\delta^{18}\text{O} \approx 11$ to 11.2%) are of importance in recognition of crustal contamination. The 'Older' granites of the Scottish Highlands, however, were derived from metasedimentary upper crust ($\delta^{34}\text{S} \approx +8.3\%$; $(^{87}\text{Sr}/^{86}\text{Sr})_i \approx 0.712$; $\delta^{18}\text{O} \approx 10.3\%$).

The Etive complex, north of the Highland Boundary Fracture Zone, is characterized by a predominant pre-emplacement history involved bulk contamination of a mantle derived magma by bulk melting of Middle Proterozoic (Grenvillian) lower crust. It is likely, therefore, that the other intrusions of the Southwestern Grampian Highlands, similarly characterized by low initial Sr-isotope ratios, low to intermediate $\delta^{18}\text{O}$, and $\delta^{34}\text{S}$ values around 0‰ (e.g. Ballachulish, Rannoch of Moor, Ben Nevis, Mullach nan Coirean), have a similar origin. The Strontian complex in Northwest Highlands also originated from a mantle source region. However, the higher $\delta^{18}\text{O}$, ($^{87}\text{Sr}/^{86}\text{Sr}$)_i, and spread of positive $\delta^{34}\text{S}$ values of its more felsic members are likely the result of contamination by Moinian metasedimentary upper crust through a process of low pressure fractional crystallization-assimilation.

South of the Highland Boundary Fracture Zone where Precambrian metasedimentary upper crust is absent, the 'Newer' granitoids define an I-type to S-type trend which is attributed to mixing in variable proportions between basalts or basaltic andesite magmas and siliceous partial melts produced within the sedimentary accretionary prism by the hot mafic magmas.

By contrast to the 'Newer' Caledonian granites, the 'Older' granitoids (e.g. Ben Vuirich, Strichen, Aberdeen) are S-type intrusions which have a chemical, mineralogical and isotopic character comparable with that of the Dalradian metasedimentary upper

crust of the Grampian Highlands; thus, an origin by local anatexis melting of this isotopically heterogeneous crust is implied.

In Ireland, the mineralogical, chemical and sulphur isotopic compositions of the Connemara granites have revealed two granite types. The Galway batholith, characterized by $\delta^{34}\text{S}$ values ranging from +4.2 to 0.0‰, low initial Sr-isotope ratios (0.704 - 0.705), and low $\delta^{18}\text{O}$ values (8.2 - 9.5‰), and mineralogical and chemical compositions characteristic of an I-type granite, as defined by Chappell and White (1974), is considered to be derived from upper mantle materials. The 'Old' Oughterard granite and Cashel micro-granite sill, however, show sulphur isotopic composition ranging from +6.2 to +9.6‰, high initial Sr-isotope ratios (0.710 and 0.720) respectively) and S-type mineralogy and chemistry, characteristic of granites derived by partial melting of metasedimentary protoliths (probably Dalradian metasedimentary rocks). The fine-grained granitic member of the Oughterard granite show very low oxidation state ($\text{Fe}_2\text{O}_3/\text{FeO} = 0.3$) compared with that of the whole granite ($\text{Fe}_2\text{O}_3/\text{FeO} = 0.67$). It seems that, this fine-grained member was either sufficiently reduced to have lost light H_2S and leave the residual sulphur isotopically heavy giving values of $\delta^{34}\text{S} \approx +16\%$, or the sulphur has been inherited from a different source from which the main granite has been derived.

In terms of Sr-isotopic composition, the other 'Newer' Caledonian intrusions of Ireland (e.g. Donegal granite suite, Leinster, Newry) seem to have an I-type character regarding their petrogenesis:

($^{87}\text{Sr}/^{86}\text{Sr}$) ranging from 0.705 to 0.708); thus an upper mantle origin is attributed to these granitoids.

The sulphur isotope studies on primary sulphides associated with the Caledonian granites of Britain and Ireland have proved valuable in understanding their petrogenesis; that is in terms of granites derived either from igneous or metasedimentary protoliths. The $\delta^{34}\text{S}$ analyses also prove most informative when compared with the following: mol $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$, K/Na, $\text{Fe}_2\text{O}_3/\text{FeO}$ ratios, initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$, and coupled with these parameters, the sulphur isotope analyses could be a very useful tool in understanding the granite genesis, and hence distinguishing between the Caledonian intrusions in terms of precursor protolith.

Sulphur isotope analyses of coexisting sulphide minerals are also useful as a geothermometer. If two sulphur-bearing phases are in equilibrium, the temperature of formation of sulphide minerals during cooling stages of the magma could be determined.

The temperature of formation of two coexisting mineral pairs from the Oughterard granites has been calculated; 418°C from a pyrite-pyrrhotite pair and 441°C from a pyrite-chalcopyrite pair, indicating the temperature of formation of these minerals.

The understanding of the origin of the British Caledonian granites is by no means complete, and much more detailed work

using sulphur and other isotopes needs to be done on a pluton by pluton basis to more precisely characterize the source(s) and evolutionary history of the Caledonian granites. The results presented in this piece of work are just a first attempt to use sulphur isotope studies for the genesis of the Caledonian granites of Britain and Ireland and document the 'Newer' Caledonian granites being derived from upper mantle materials while the 'Older' granites have a metasedimentary origin.

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