THE GEOCHEMISTRY AND PETROGENESIS OF THE LOWER PALEOZOIC GRANITOIDS OF NORTH WALES

By

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A thesis submitted for the degree of Doctor of Philosophy
under the special regulations of the University of Birmingham

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University of Birmingham
March 1980

Synopsis

The Lower Paleozoic rocks of North Wales are penetrated by numerous bodies of dolerite and intermediate-acid material which are closely associated with pillow basalts, acid and basic tuffs and ignimbrites. Igneous activity occurred throughout the Ordovician although in Snowdonia and Lleyn it reached a climax during the Caradoc stage. The present study has considered the granitoids of Snowdonia and Lleyn which are intruded as stocks, laccoliths and high level plugs (< 5 km^2) into clastic and volcaniclastic sediments.

A substantial body of new chemical data has been obtained for over thirty intrusions. Twenty-four major and trace elements were determined on each sample by X-ray fluorescence techniques and the rare earth abundances of forty-five selected samples were measured using a radiochemical neutron activation procedure.

Three distinctly different types of granitic material are recognised and their possible evolutionary mechanisms are discussed in detail. On the basis of the geochemistries of the various sampled intrusions it is concluded that they were all ultimately derived from the mantle by partial melting. One group originated from the remobilisation of calc-alkaline plutons formed by hydrous melting of the mantle wedge above a destructive plate margin. The other two groups, it is argued, evolved from tholeiitic basaltic magma by low-pressure fractional crystallisation. The geochemical affinity between some Caradocian andesitic material from Lleyn and the tonalitic-granitic intrusions of the same area has provided good evidence against a view that the latter were emplaced late in the Caledonian cycle (Silurian-Devonian).

A paleo-tectonic reconstruction of the North Wales region is presented and it is claimed that the area evolved as a volcano-tectonic rift zone, a precursor of a back-arc basin.

Acknowledgements

I wish to express my thanks to my Supervisor, Mr. E.D. Lacy, for his help, advice and criticism throughout my stay in Birmingham. Dr. Graham Hendry has also provided friendly advice and criticism and his expertise with the X-ray Fluorescence Analysis has been invaluable. The Birmingham Radiation Centre generously allowed many of their facilities to be used and particular thanks go to Dr. Keith Randle for his good-natured technical assistance with neutron activation procedures.

The research students and fellows within the department have provided many fruitful discussions which have helped to shape the ideas expressed in this thesis. My gratitude goes especially to Mr. Nigel Donnellan, Mr. N.G. Marsh, Mr. S. Paritsis and Mr. B. Weaver. I am also grateful to Mr. S. Corbin, Mr. S. Longshaw and Mr. D.P. Mattey for their help and advice on many occasions.

Mr. P. Garner was responsible for the efficient operation of the laboratories and Mrs. Lena Williams provided much assistance with photography.

Part of this work was funded by a N.E.R.C. research studentship.

Mrs. I. Browne has typed the original manuscript in an attractive and accurate way and I am thankful to her.

My wife, Wendy, has tolerated my years of research, helped with diagrams and provided essential moral and financial support.

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A GLOSSARY OF SOME WELSH WORDS

Aber, a river mouth.
Ach, water.
Aderyn, a bird.
Ael, a brow or edge.
Afon, a river.
Allt, a wooded slope.
Aran, a high place.
Arddu, a black crag.

Bach, little.
Bala, a lake outlet.
Ban, peak, crest, beacon.
Bedd, a grave.
Ber, a hilltop.
Bera } beak, top, point.
Bere }
Betws, a chapel.
Beudy, a byre or cowhouse.
Blaen, the head of a valley.
Boch, a cheek.
Bod, a home or abode.
Bont, a bridge.
Braich, an arm or branch.
Bran, a crow.
Bras, thick or fat.
Brith, speckled.
Bron, the slope of a hill.
Brwynog, marshy.
Bryn, an eminence.
Bwlch, a pass.
Bychan, small.

Cadair, a chair or throne
Cae, an enclosed field.
Caer, a camp or fortress.
Cafn, a trough.
Canol, middle.
Capel, a chapel.
Carn, a cairn or heap of stones.
Carnedd, a cairn.
Carreg, stone.
Caseg, a mare.
Castell, a castle or fortress.
Cau, a hollow.
Cefn, a ridge.
Celyn, holly.
Cidwm, a wolf.
Clogwyn, a cliff or precipice.
Clwyd, a gate.
Clyd, a shelter.
Cnicht, a knight.
Coch, red.
Coed, a wood.
Congl, a corner.
Cors, a bog or swamp.
Craig, a rock or crag.
Crib, a ridge or jagged edge.
Cribin, the small crest of a hill.
Croes, a cross.
Crug, a mound.
Cwm, a hollow or coombe.
Cwn, dogs.
Cymer, a confluence.

Dau, two.
Dinas, a natural fortress
Dol, a dale or meadow.
Drosgl, a rough hill.
Drum, a ridge.
Drws, a door.
Du or *ddu*, black.
Dwr, water.
Dyffryn, a wide valley.
Dysgl, a dish or plate.

Eglwys, a church.
Eigiau, a shoal of fish.
Eira, snow.
Erw, an acre.
Eryri, a highland.
Esgair, a shank or limb.

Fach, small.
Faes, a field or meadow.
Fan, peak, crest, beacon.
Fawr, large.
Felin, a mill.
Ffordd, a road.
Ffynnon, a well or fountain.
Foel, a bare or bald hill.
Fyny, upwards.

Gaer, a camp.
Gafr, a goat.
Gallt, a slope.
Ganol, middle.
Gardd, a garden.
Garn, an eminence.
Garth, an enclosure.
Gawr, a torrent.
Glas, blue-green.
Gludair, a heap.
Glyn, a deep valley.
Goch, red.
Golau, a light or beacon.
Golwg, a view.
Gors, a swamp.
Grach, scabby.
Groes, a cross.
Grug, heather.
Gwastad, a plain.
Gwern, an alder coppice.
Gwyn, white.
Gwynt, wind.

Hafod, a summer dwelling.
Hebog, a hawk.
Helgi, a hunting dog.
Helyg, willows.
Hen, old.
Heulog, sunny.
Hir, long.
Hydd, a stag.

Isaf, lower.

Las, blue-green.
Llan, a church.
Llech, a flat stone.
Llefn, smooth.
Llithrig, slippery.
Lloer, moon.
Llwyd, grey.
Llwyn, a grove.
Llyn, a lake.
Llys, a hall.
Lon, a lane.

Maen, a block of stone.
Maes, a field or meadow.
Man, a place.
Mawr, large.
Meirch, horses.
Melin, a mill.
Melyn, yellow.
Mign, a bog.
Min, lip or edge.
Mir, fair.
Moch, pigs.
Moel, a bare or bald hill.
Mor, sea.
Morfa, flat seashore—sea fen.
Mur, a wall.
Mynach, a monk.
Mynydd, a mountain.

Nant, a brook.
Newydd, new.

Oer, cold.
Og, harrow.
Ogof, a cave.
Oleu, light.
Onn, an ash tree.

Pair, a cauldron.
Pant, a hollow.
Parc, an enclosure.
Pen, a peak or top.
Penrhyn, a promontory.
Pentre, a village.
Perfedd, centre.
Perth, a hedgerow bush.
Pistyll, the spout of a waterfall.
Plas, a mansion.
Poeth, hot.
Pont, a bridge.
Porth, a port, gateway.
Pwll, a pool.

Rhaeadr, a waterfall.
Rhiw, hill or slope.
Rhyd, a passage or ford.
Rhyn, a cape.

Saeth, an arrow.
Sarn, a causeway.
Silin, spawn.
Sych, dry.

Tal, end.
Tan, under.
Tir, soil.
Tomen, a mound.
Traeth, sandy shore.
Tref, a town.
Tri, three.
Trum, a ridge.
Twll, a cavern.
Twr, a tower.
Ty, a house.
Tyddyn, a small farmstead.

Uchaf, upper or higher
Un, one.

Waun, moorland.
Wen, white.
Wern, an alder swamp.
Wrach, a witch.
Wrth, near.

Y—Yr, the.
Yn, in.
Ynys, an island.
Ysfa, a sheep walk.
Ysgol, a ladder.
Ysgubor, a barn.
Ystrad, a street or dale.
Ystum, a curve or bend.
Ystwyth, winding.

Chapter 1

INTRODUCTION

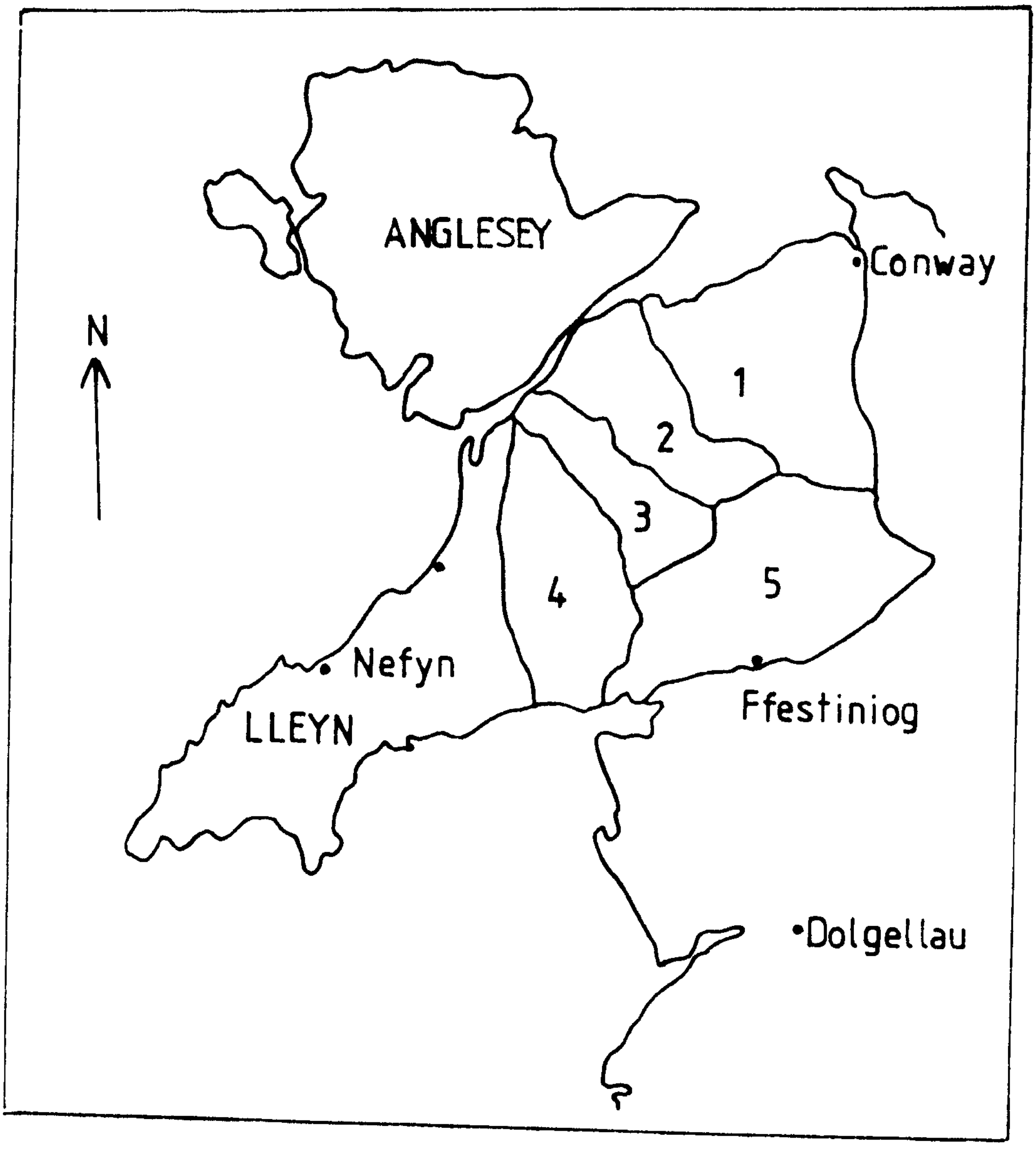
A. The Regional Setting and Topography

The rocks studied consist of over thirty intrusions of Lower Paleozoic age which outcrop in the North Welsh areas of Snowdonia and Lleyn (see fig. 2, page 3). They vary in composition from tonalite to granite and form stock-like bodies, sheets and laccoliths with an areal extent of up to 5km^2.

The Snowdonian intrusions may be split into five mountain groups, namely the Carneddau (area 1, fig. 1), Glyderau (area 2), Snowdon (area 3), Hebog (area 4) and Manod-Moelwyns (area 5). These ranges are bounded by glacial river valley, such as Nant Francon, Nant Gwynant, and Nant Gwyryd, by the Conway valley and the sea. The intrusions of Penmaenmawr, Drosgl, Foel Fras and some smaller intrusions lie on the high ground, up to 1052 m, of the northern Carneddau and they are generally poorly exposed owing to a cover of boulder clay and vegetation. The Penmaenmawr stock is an exception to this owing to extensive quarrying operations.

The intrusions of Bwlch-y-Cywion and Mynydd Perfedd lie above 805 m on the northern edge of the Glyderau above the Nant Francon pass. Exposure varies from poor to fair and the igneous material is often weathered deeply which is assisted by the jointing and cleavage. The Snowdon range rises steeply from valleys at 50 m to over 1076 m and the area comprises a number of small rhyolite plugs which are well exposed near Crib Goch but less well on the lower land where scree, boulder clay and vegetation obscure the solid geology. The Hebog group contains the intrusions of Mynydd Mawr, Y Garn, Mynydd Tal-y-Mignedd, some microgranophyric sheets and two rhyolite plugs. The exposure associated with these bodies is fair to good. The Manod-Moelwyn group contains the intrusions of Tan-y-Grisiau, Manod Bach and a set of composite minor sills.

Figure 1



A general map of North Wales showing the main regions.

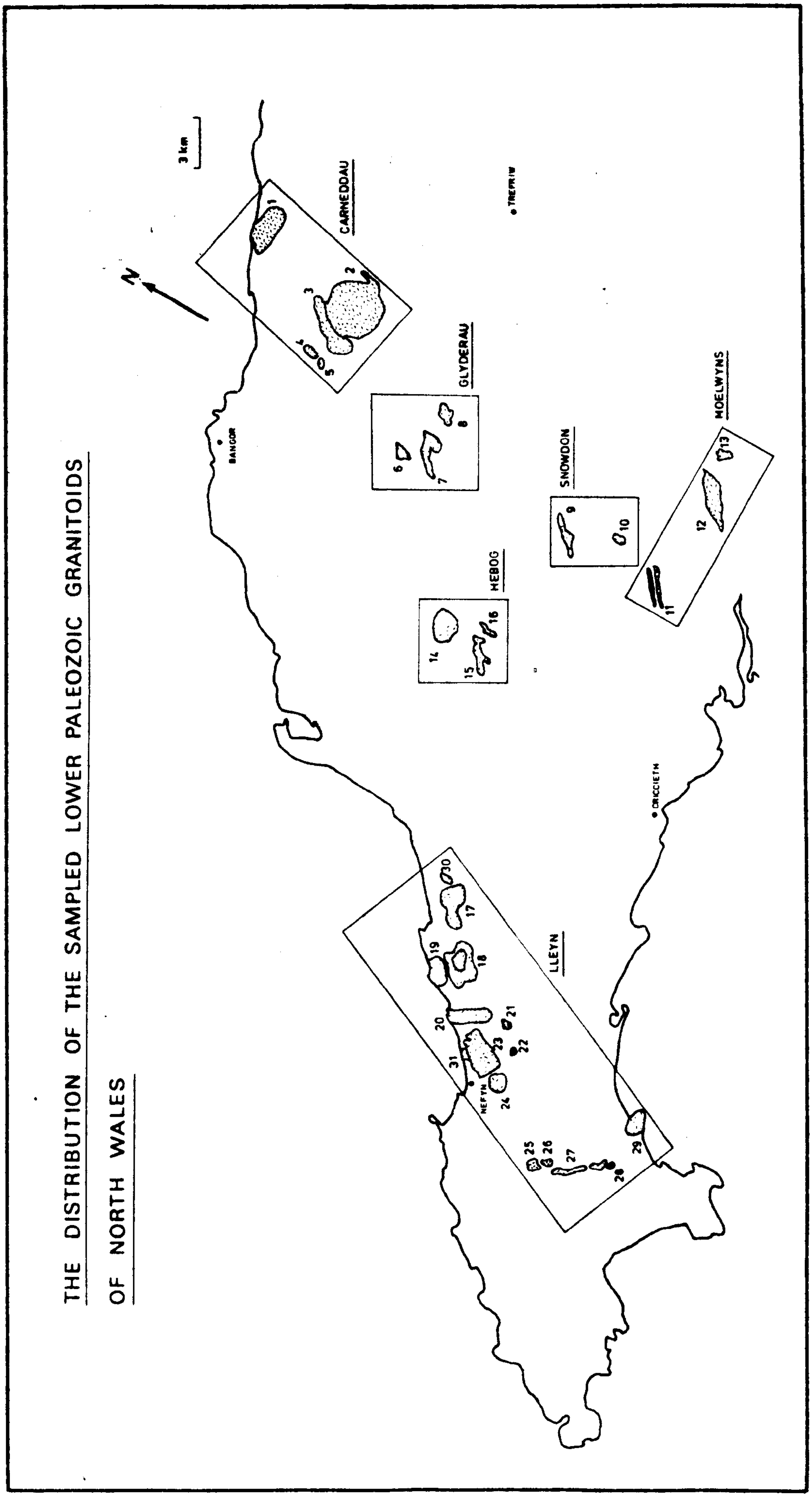
1. Carneddau
2. Glyderau
3. Snowdon
4. Hebog
5. Manod-Moelwyns

1. Penmaenmawr .... μτ
2. Foel Fras .... Qλ
3. Aber-Drosgl ..... μγδ
4. Moel Wnion ...... μγδ
5. Gyrn .... μγδ
6. Mynydd Perfedd .... μγδ
7. Bwlch-y-Cywion .... μγ
8. Ogwen .... μγ
9. Nant Gwynant ...... ρ
10. Castell .... ρ
11. Composite minor sills ... μγ
12. Tan-y-Grisiau ..... μγ
13. Manod Bach ...... Qλ
14. Mynydd Mawr ...... πμγ
15. Tal-y-Mignedd ... μγδ
16. Y Garn .... μγδ
17. Gurn-Odu, Moel Pentlechog .... μτ
18. Yr Eifl .... μγ, φ
19. Garnfor .... μτ–μγδ
20. Carreg-y-Llam ..... μγδ
21. Penprys .... φ
22. Moel-y-Penmaen .... α
23. Mynydd Nefyn ...... μτ
24. Carn Bodfean ...... μτ
25. Carn Fadryn .... μτ
26. Carn Bach .... μγδ
27. Nant Bodlas .... πγφ
28. Foel Gron .... πγφ
29. Llanbedrog .... γφ
30. Gurn Goch .... γφ
31. Penrhyn Bodeilas ..... μτ

<u>KEY</u>

γφ	Granophyre
μγ	Microgranite
μγδ	Microgranodiorite
Qλ	Quartz-latite
ρ	Rhyolite
φ	Felsite
πμγ	Peralkaline microgranite
μτ	Microtonalite
α	Andesite
πγφ	Peralkaline granophyre

Figure 2



THE DISTRIBUTION OF THE SAMPLED LOWER PALEOZOIC GRANITOIDS OF NORTH WALES

The north coast of the Lleyn peninsula between Clynogg Fawr and Nefyn contains over ten closely spaced intrusions of intermediate to acid composition. Looking from the top of Yr Eifl (650 m) one gets an impressive panoramic view and it is a simple matter to recognise the sites of the intrusions as they form prominent rounded hills. South of Nefyn another line of intrusions are seen although their trend is NW-SE. Quarrying operations have been carried on in most of the intrusions which outcrop along the coast and exposure for these is very good. Elsewhere the crests of the rounded hills are well exposed while the flanks are not owing to a cover by glacial drift.

B. Previous Research in North Wales

A great amount of attention has been paid to the Precambrian and Lower Paleozoic rocks of North Wales over the last 150 years. Notable geologists who visited and contributed to an understanding of the area include Sedgwick, Murchison, Lapworth, Ramsay, Harker, Greenly, Fearnsides, Jones, Matley, Heard, D. Williams, H. Williams, Dakyns, Shackleton, and Rast.

The Precambrian rocks of the area form the Anglesey Mona Complex, a strip of land on the north-western edge of the Lleyn Peninsula and two elongate tracts of land called the Bangor and Padarn Ridges (fig. 3 , page 5). These rocks consist of ortho- and paragneisses, a bedded succession, formed of more or less metamorphosed sedimentary and igneous material, and some ultrabasic, basic and granitic intrusions. The Bangor and Padarn ridges consist of rhyolitic volcanics, particularly ignimbrites, and smaller volumes of ash-fall tuffs, acid breccias and granites. Cambrian rocks form the Harlech Dome, the Welsh Slate Belt of Central Snowdonia and a number of small inliers. They consist of purple and green slates, acid and basic tuffs and a great thickness of greywackes. The Ordovician series is represented by acid and basic tuffs, ignimbrites, pillow lavas, acid breccias, grits and slates which rest with marked unconformity on the Precambrian or Cambrian over a considerable area of North Wales and Anglesey.

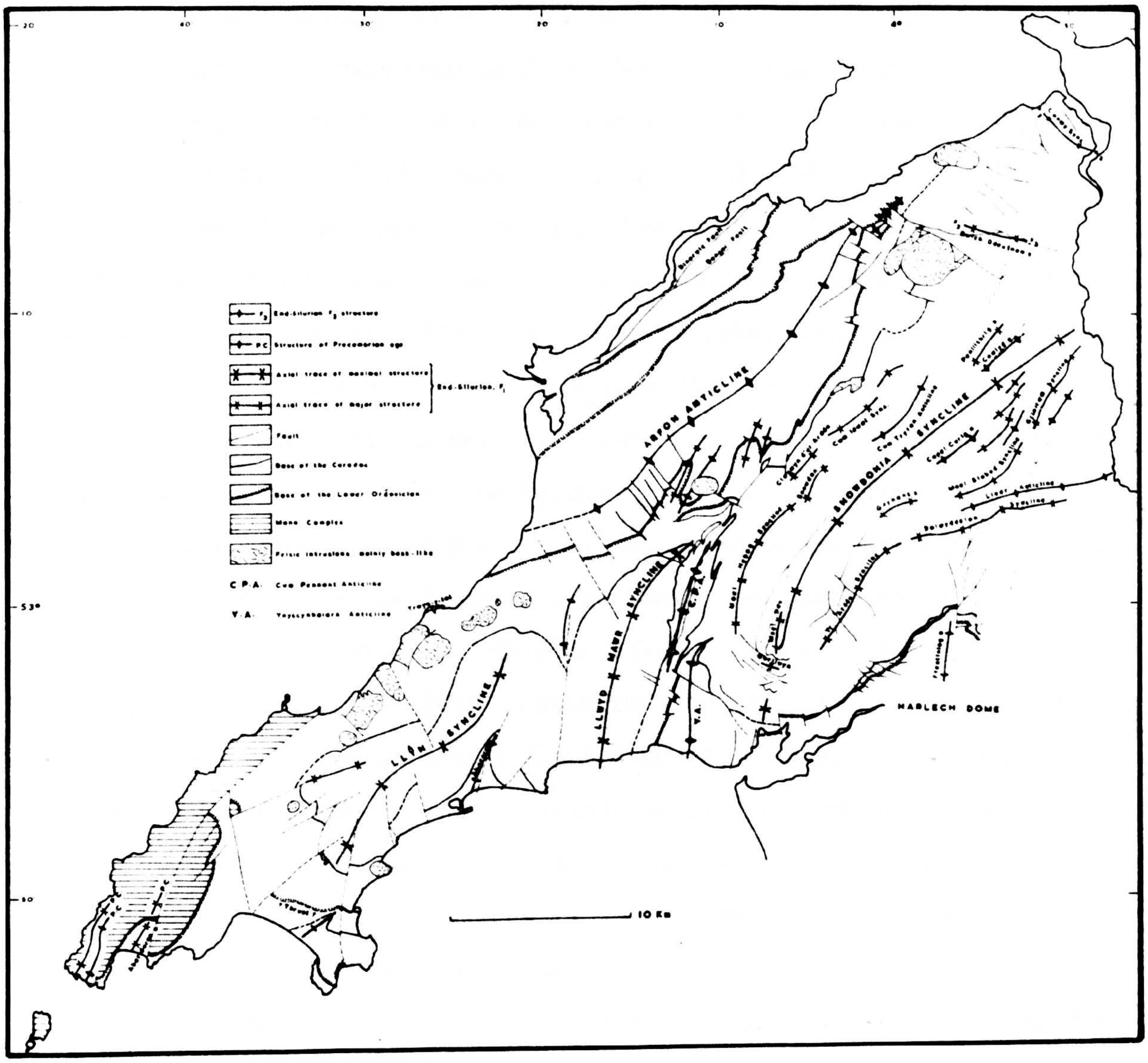
Figure 3

Geological map showing the distribution of the Precambrian and Lower Paleozoic formations in North Wales and Anglesey.

The structured geology of the area is complex and it has been described by Shackleton (1953) and an historical account was made by Basset (1969). Early ideas held that two main periods of deformation occurred, the first caused the widespread deformation observed in the Mona Complex while the second, Caledonian deformation, occurred some time during the Silurian-Devonian. The situation is now known to be more complex than this and polyphase deformation within the Lower Paleozoic has been recognised by Helm et al. (1963). Three main episodes of deformation are thought to have occurred although smaller scale events may also have taken place. The evidence for these consists of i) the oldest radiometric dates obtained from Precambrian rocks are ca. 600 m.y. ii) a major angular unconformity is found at the base of the Ordovician iii) Ordovician and Lower Silurian rocks are deformed. The three events took place during the Late-Precambrian, end-Tremadoc and end-Silurian - early-Devonian (Roberts, 1979). The main structural features of North Wales are shown in fig. 4 (page 7) where it may be seen that the rocks of Snowdonia and Lleyn are disposed in a series of anticlines and synclines trending approximately NE - SW.

The systematic study of the geology of North Wales and Anglesey began with the work of Sedgwick in 1831 and within a short time he had described the salient features of the structures and lithologies of the area. In 1835 he had classified the rocks as upper, middle and lower "Cambrian", the Precambrian rocks of the Bangor and Padarn Ridges were considered to be intrusive and the eruptive nature of some Snowdonian rocks was realised. The Geological Survey commenced its studies in 1849 under Sir Andrew Ramsay and co-workers and by 1852 the whole of North Wales, including Anglesey, had been mapped on the 1-inch scale and by 1866 the large memoir was published. Ramsay used the stratigraphic column devised by Murchison (1839) which consisted of the "Cambrian" and "Silurian" series where the Precambrian, Cambrian, Ordovician and Silurian are now used. The oldest rocks of the area were classed as "unfossiliferous Cambrian" and they were claimed to represent the metamorphosed equivalent of "Cambrian" rocks such as those found around the Harlech Dome. The volcanic rocks of

Figure 4



Structural map of North Wales showing main folds and faults of the area (from Roberts, 1979).

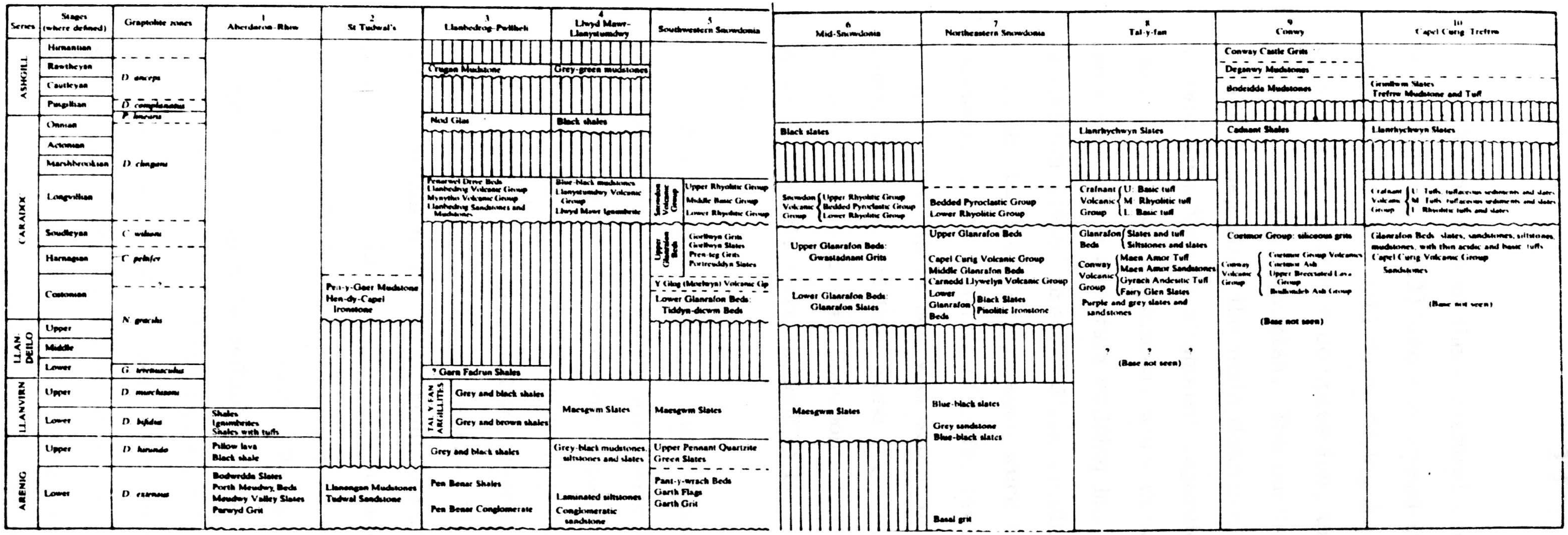
the Bangor and Padarn Ridges were thought to be formed by a process akin to granitisation; thus, "and below these are other thinner bands of slate,grit and conglomerate, the lowest of which by Llyn Padarn and elsewhere, passes by insensible gradations into the great mass of quartz-porphyry..." (Ramsay, 1881; p. 173). Ramsay showed that the Snowdon "lavas" were not equivalent to the older volcanic rocks of the Arans, Arenig and Cader Idris, as supposed by Sedgwick, since he found the latter were 6000' below the Snowdon sequence. The Snowdon syncline was found to be more complex than envisaged by Sedgwick since it "contains within itself several smaller undulations". The Snowdon Volcanic Series, as it is now termed, was found to consist of three main units which correspond in all but name to the units recognised now and they were considered to be water-laid tuffs and subaqueous lavas. The intrusive, boss-like and felsic nature of Mynydd Mawr, Penmaenmawr and the Lleyn granitoids was realised and the sheet-like intrusions of Foel Fras and Y Garn were described. Y Garn, a feldspar-porphyritic granodiorite, was described as a hornblendic greenstone, a term which was normally applied to altered basic material. The abundant augite-dolerites of Snowdonia were classified as greenstones and along with the felsic intrusions they were thought to have been emplaced in "Lower Silurian" times (i.e. Ordovician). The intrusions of the Lleyn Peninsula were claimed to represent the deep-seated roots, exposed through considerable denudation, of the Snowdonian volcanoes.

In 1889 Harker produced his essay entitled "The Bala Volcanic Series of Caernarvonshire and associated rocks." Rhyolite lavas, acid intrusions, andesite lavas, diabase sills and hornblendic basic intrusions were distinguished and the large areas of acid volcanics in Snowdonia were stated to be "true interbedded lava flows". The intrusive nature of the various granitic bodies was noted and owing to their petrological and chemical similarity to the extrusive rocks they were thought to be consanguineous. The intrusions of Foel Fras, Bwlch-y-Cywion Mynydd Mawr and Carn Bodfean were claimed to be the sites of volcanoes which had supplied the acid material. A Bala age (Caradoc) was proposed for the acid and basic volcanic and intrusive rocks of Snowdonia and Lleyn although those exposed along the Bangor and Padarn Ridges were known to be pre-Bala since they occurred as conglomeratic pebbles in the basal Cambrian conglomerate.

A significant advance in the understanding of the nature of the acid material was made when Dakyns (1900) and Dakyns and Greenly (1905) stated that some of the Snowdonian volcanics were of pyroclastic origin and that an intrusive rhyolite, formerly thought to be a lava flow, existed near Llechog, a ridge lying south-west of Snowdon. The lack of bedding in the volcanic rocks suggested that they may have been erupted as a submarine, Pelean-type pyroclastic flow. Although it was known that the eruptions of Pelee were sub-aerial Dakyns and Greenly were swayed by the current consensus of a submarine origin for the Welsh acid volcanics. The views expressed by Dakyns and Greenly were not widely accepted and further studies in the area (e.g. Fearnsides, 1910) restated the submarine lava flow hypothesis.

Detailed studies of the areas around Snowdon, Ogwen and Dolwyddelan were made by H. Williams (1927), D. Williams (1930) and H. Williams and Bulman (1931). Although the acid volcanics around Snowdon were interpreted as lava flows, the succession established by H. Williams is almost identical to that accepted today (fig. 5 , page 10). The Snowdon Volcanic Series was thought to rest on rocks of Lower Llandeilo age on the basis of graptolite fauna although the current view is that the Llandeilo Series is missing in North Wales. Williams found a close chemical similarity between the Upper Rhyolite Series, the Lower Rhyolite Series and the intrusive rhyolites of Crib Goch, Tal-y-Llyn and Crib-y-Ddysgl and he also considered that these were consanguineous with the intrusions of Mynydd Perfedd, Mynydd Mawr and Bwlch-y-Cywion. Williams and Bulman (1931) showed that in the Dolwyddelan area, the Snowdon Volcanic Series is underlain by a considerable thickness of fossiliferous sediments whereas around Snowdon the Series is separated from similar sediments by 200 feet of slates and the Pitt's Head Flow.

Figure 5



Series	Stages (where defined)	Graptolite zones	1 Aberdaron-Rhiw	2 St Tudwal's	3 Llanbedrog-Pwllheli	4 Llwyd Mawr-Llanystumdwy	5 Southwestern Snowdonia	6 Mid-Snowdonia	7 Northeastern Snowdonia	8 Tal-y-fan	9 Conwy	10 Capel Curig-Trefriw
ASHGILL	Hirnantian										Conway Castle Grits	
	Rawtheyan	D. anceps			Crugan Mudstone	Grey-green mudstones					Deganwy Mudstones	
	Cautleyan										Bodeidda Mudstones	Grinllwm Slates Trefriw Mudstone and Tuff
	Pusgillian	D. complanatus										
CARADOC	Onnian	P. linearis D. clingani			Nod Glas	Black shales		Black slates		Llanrhychwyn Slates	Cadnant Shales	Llanrhychwyn Slates
	Actonian											
	Marshbrookian											
	Longvillian				Penarwel Drive Beds Llanbedrog Volcanic Group Mynytho Volcanic Group Llanbedrog Sandstones and Mudstones	Blue-black mudstones Llanystumdwy Volcanic Group Llwyd Mawr Ignimbrite	Snowdon Volcanic Group: Upper Rhyolitic Group Middle Basic Group Lower Rhyolitic Group	Snowdon Volcanic Group: Upper Rhyolitic Group Bedded Pyroclastic Group Lower Rhyolitic Group	Bedded Pyroclastic Group Lower Rhyolitic Group	Crafnant Volcanic Group: U: Basic tuff M: Rhyolitic tuff L: Basic tuff		Crafnant Volcanic Group: U: Tuffs, tuffaceous sediments and slates M: Tuffs, tuffaceous sediments and slates L: Rhyolitic tuffs and slates
	Soudleyan	C. wilsoni					Upper Glanrafon Beds: Gorllwyn Grits Gwllwyn Slates Pren-teg Grits Portreuddyn Slates	Upper Glanrafon Beds: Gwastadnant Grits	Upper Glanrafon Beds	Glanrafon Beds: Slates and tuff Siltstones and slates	Coetmor Group: siliceous grits	Glanrafon Beds: slates, sandstones, siltstones, mudstones, with thin acidic and basic tuffs Capel Curig Volcanic Group Sandstones
	Harnagian	C. peltifer							Capel Curig Volcanic Group Middle Glanrafon Beds Carnedd Llywelyn Volcanic Group	Conway Volcanic Group: Maen Amor Tuff Maen Amor Sandstones Gyrach Andesitic Tuff Fairy Glen Slates	Conway Volcanic Group: Coetmor Group Volcanics Coetmor Ash Upper Brecciated Lava Group Bodlondeb Ash Group	
	Costonian	? N. gracilis		Pen-y-Gaer Mudstone Hen-dy-Capel Ironstone			Y Glog (Moelwyn) Volcanic Gp Lower Glanrafon Beds: Tiddyn-dicwm Beds	Lower Glanrafon Beds: Glanrafon Slates	Lower Glanrafon Beds: Black Slates Pisolitic Ironstone	Purple and grey slates and sandstones	(Base not seen)	(Base not seen)
LLANDEILO	Upper											
	Middle											
	Lower	G. teretiusculus			? Garn Fadrun Shales					? ? ? (Base not seen)		
LLANVIRN	Upper	D. murchisoni			TAL Y FAN ARGILLITES: Grey and black shales	Maesgwm Slates	Maesgwm Slates	Maesgwm Slates	Blue-black slates			
	Lower	D. bifidus	Shales Ignimbrites Shales with tuffs		TAL Y FAN ARGILLITES: Grey and brown shales				Grey sandstone Blue-black slates			
ARENIG	Upper	D. hirundo	Pillow lava Black shale		Grey and black shales	Grey-black mudstones, siltstones and slates	Upper Pennant Quartzite Green Slates					
	Lower	D. extensus	Bodwrdda Slates Porth Meudwy Beds Meudwy Valley Slates Parwyd Grit	Llanengan Mudstones Tudwal Sandstone	Pen Benar Shales Pen Benar Conglomerate	Laminated siltstones Conglomeratic sandstone	Pant-y-wrach Beds Garth Flags Garth Grit		Basal grit			

Correlation table for Snowdonia and Lleyn (from Roberts, 1979)

A synthesis of the structural evolution of North Wales was made by Shackleton (1953) who considered that the Lower Paleozoic rocks of North Wales were laid down during a prolonged geosynclinal phase followed by a shorter phase of compression, the latter occurring during the late-Silurian to early-Devonian. The augite-dolerites were thought to have been intruded after the main deformation since they were claimed to have a consistent NW-SE alignment regardless of fold trends. Granitic rocks, described as inconspicuous, were thought to have formed at the roots of the crust where mountain building had thickened the crust. A little later Shackleton (1959) presented the results of his studies around Moel Hebog. Volcanic rocks of various ages were found beginning with the Y Glog formation which consists of tuffs, lavas and agglomerates of andesitic composition. Their age was shown to be Llanvirinian on the basis of faunal evidence and they were correlated with the Moelwyn Volcanic Series of south-eastern Snowdonia. The Pitt's Head Flow and the Llwyd Mawr ignimbrite were thought to be rhyolite flows and laterally equivalent in age.

A contribution to the understanding of the geology of North Wales of considerable importance was made by Oliver (1954) and later by Rast, Beavon and Fitch in a number of papers. Oliver recognised that many of the Borrowdale Volcanic Series rhyolites were ignimbrites and an examination of Harker's thin-sections revealed that they also occurred in the Capel Curig area of North Wales. Fitch (1967) claims to have identified similar rocks in the Lleyn Peninsula in 1953 while Rast noted their occurrence in Snowdonia in 1954. A number of publications resulted describing the nomenclature and petrography of the Welsh ignimbrites (Rast, Beavon and Fitch, 1958; Rast, 1958; Beavon, Fitch and Rast, 1961). Ignimbrites were originally defined by Marshall (1935) although the term was redefined by Beavon, Fitch and Rast (1961) to include, "all the strictly primary fragmental volcanic rocks in which the great majority of constituent fragments are thought to have been deposited from nuees ardentes." Two types of ignimbrite are recognised which may grade into each other. The first is a welded tuff and the second is a non-welded or sillar variety; both consist of varying proportions of vitric, lithic and crystal fragments.

Welded tuffs are characterised by a wide areal extent, textural uniformity, absence of brecciation and flow folding and a near parallelism of crystal and lithic fragments. The textures of ignimbrites reflect their cooling history and superincumbent load and the glass shards, representing the broken walls of pumice which surrounded gas bubbles, may either be flattened, agglutinated and distorted (eutaxitic texture) or partially remobilised and extremely drawn out (parataxitic texture). The Ordovician ignimbrites of North Wales show complete devitrification of the glass shards and both welded and non-welded zones have been identified within flows (Beavon, Fitch and Rast, 1961; Olver, 1979).

Prior to the 1950s the consensus view was that the Lower Paleozoic rocks of North Wales were deposited in a long, narrow trough of the type envisaged by Jones (1938) and that the volcanic material was erupted into a marine environment. The discoveries by Oliver, Rast, Fitch and Beavon, however, completely changed this notion and it has become accepted by most geologists that throughout the Ordovician there were periods of elevation and subsidence where subaerial and subaqueous volcanism occurred. The close association between the two depositional environments are seen in parts of Snowdonia where some basic lavas have pillow structures and are mixed with muddy sediments at their base but have an upper ropy surface suggesting that the latter part was subaerial. In a number of areas Rast (1961) has identified volcanic mudflows or lahars which consist of a disordered mass of volcanic and sedimentary clasts set in an ashy matrix. Such rocks are formed by a water or ice-ignimbrite interaction and the Llyn Dinas Breccias around Pen-y-Pass are of this type.

On the basis of geological evidence found in the Gwynant-Glaslyn valley, Rast (1961) proposed that mid-Ordovician tectonism had occurred which could explain the absence of certain lithological units in that area. The Pitt's Head and Flinty Flows are missing from the Snowdon Volcanic Series (Williams, 1927) in this locality, a Lahar Series is developed and a pre-cleavage fault system (Beddgelert Fault) exists. These facts, along with the observation near Moel Hebog that the Pitt's Head Flow is separated into two units by shallow-water sediments, suggested to Rast that intra-

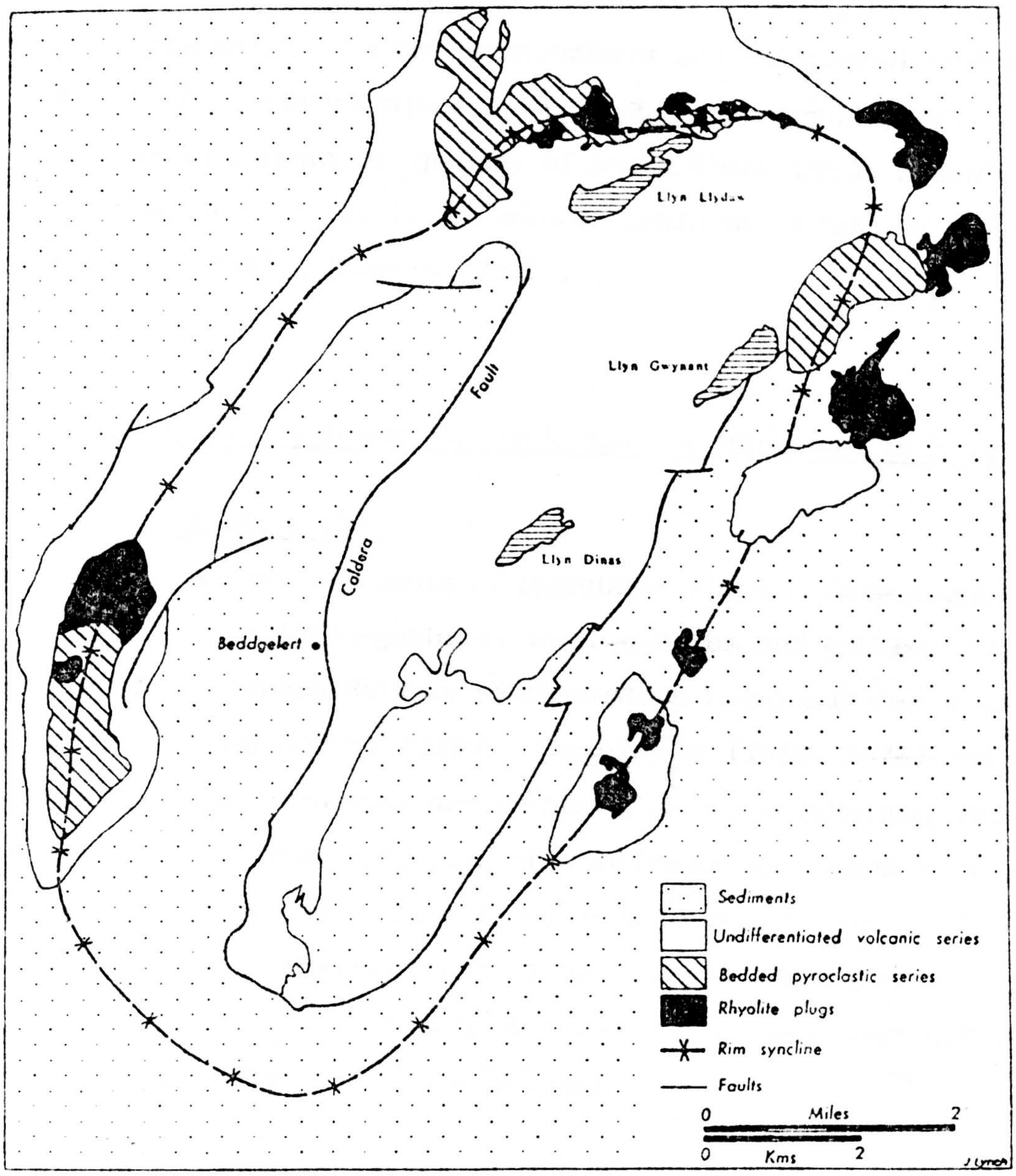
Caradocian tectonic movements had occurred in Central Snowdonia. It was postulated that these movements resulted from the formation of magma blisters which periodically ruptured giving rise to ignimbrite volcanism.

Further work in Snowdonia by Rast (1969) and Bromley (1969) independently led them to reach similar conclusions concerning the evolution of the area. They proposed that the magmatism and structures resulted from volcano-tectonic movements, an idea briefly considered by Shackleton (in discussion of Beavon, 1963). The synclines of Yr Arddu, Moel Hebog, Crib Goch and Snowdon were stated to form an oval structure which rimmed a fault-zone (Beddgelert, Nanmor, etc.) and some of the rhyolite plugs around Snowdonia occupied the core of the rim-syncline. The whole structure was claimed to result from magmatic doming and the fault-zone was thought to represent the rim of a caldera. It was also suggested that the sheet-like intrusions of dolerite, quartz-latite and micrograncphyre, which outcrop on the western limb of the Moel Hebog syncline and the eastern and south-western limbs of the Yr Arddu syncline, were cone-sheets (fig. 6 , page 14). The occurrence of gravity highs over Snowdonia and other Welsh areas, such as the Harlech and Berwyn Domes, have been interpreted as deep seated plugs of basic material underlying substantial bodies of granite (Bromley, 1969; Rast, 1969; Griffiths and Gibb, 1965).

Olver (1979) has examined the geochemistry and field relationship of volcanic and sub-volcanic rhyolites in eastern Snowdonia and the Conway area. His results show:

1) The Lower and Middle Lapilli Tuffs of Yr Arddu are not equivalent to the Pitt's Head Flow as suggested by Beavon (1963).
2) The Llyn Dinas Breccias are post-Lower Lapilli Tuffs but pre-Middle Lapilli Tuffs.
3) The Upper Lapilli Tuff is probably equivalent to the Lower Rhyolitic Series of Snowdon.
4) A marginal source vent exists near Yr Arddu for the Lower and Middle Lapilli Tuffs.
5) Two periods of intrusion are recognised.

Figure 6



Rim-syncline and caldera fault in Snowdonia
Beddgelert Fault—west of Llyn Dinas
Nanmor Fault—east of Llyn Dinas

Model after Rast (1969)

The literature clearly reflects the changing views concerning the interpretation of the volcanic and intrusive rocks, their mode and age of emplacement, the paleoenvironment and the overall evolution of the area. The interpretations made by Rast and Bromley have been a bold attempt to explain the geology of North Wales within a unified framework although their model is not without criticism (Fitch, in discussion of Bromley, 1969; Roberts, 1979).

C. Varieties of Lower Paleozoic Igneous Intrusions in North Wales

1) Ultrabasic rocks

These rocks consist of cumulates which include hornblende picrites, hornblende-gabbros, leuco-gabbros and gabbros rich in ores. They occur around Rhiw in south-western Lleyn and they have received attention from Harker (1889), Cattermole (1969, 1976) and Hawkins (1970). The intrusions are emplaced as three sill-like, rhythmically banded bodies into sediments of Llanvirnian age although Harker (1889), from fossil evidence, considered them to rest on sediments of Upper Arenig age. Cattermole (1976) has outlined their geochemistry and mineralogy and he considers it probable that they were derived from a water- and alkali-rich basic magma.

2) Augite-Dolerites

Dolerites consisting of augite, iron ore and calcic plagioclase (labradorite) when fresh, are present throughout North Wales although they are most abundant in Snowdonia. The dolerites generally form sills in the Upper Ordovician rocks and E-W running dykes in the Upper Cambrian and Lower Ordovician rocks; their mineralogy has often been altered by the low grade regional metamorphism. The age of emplacement of these basic rocks has been a point of controversy for nearly a century and it is likely that they were intruded at a number of times. Harker (1889) considered them to be of Bala age (Mid-Ordovician) owing to their absence in Silurian rocks and Williams (1927) and Williams (1930) were of the opinion that they were pre-cleavage in age. Williams and

Bulman (1931) considered both a pre- and post-cleavage age while Shackleton (1959) and Fitch et al. (1963) favoured a post-cleavage age. Dolerites occur throughout Snowdonia cutting, being cut and as xenoliths in the acid intrusions of Ordovician age (Bromley, 1969). The bulk of the present evidence favours an Ordovician age for the doleritic rocks although detailed studies are clearly required to resolve the uncertainties.

3) Quartz-Latites

Quartz-latites plugs and sills have been described by Bromley (1965), Evans (1968) and Lynas (1973) in the Blaenau Ffestiniog, Aber Falls and Migneint areas of North Wales respectively. The rocks show flow-folding, autobrecciation, and devitrification textures are observable in some samples (Roberts, 1979). Bromley (1965) has shown that the quartz-latites around Blaenau Ffestiniog have a probable Middle Llandeilo-Lower Caradoc age and Lynas (1973) has correlated those of the Migneint area with these. Evans (1968) considers that the Foel Fras quartz-latite was emplaced during the mid-Caradoc based on its structural relationship with volcanic and intrusive rocks.

4) Microgranophyric Sills

These bodies occur primarily in two localities; west of Moel yr Ogof dipping steeply eastwards and east of Yr Arddu where they dip westwards (Shackleton 1959, Olver 1979). Their age relationships are not clear for they are cut by and they cut basic intrusions. Olver (1979) considers that they are chemically distinct from the rhyolite plugs and ignimbritic rocks.

5) Rhyolite Plugs

Over thirty rhyolite plugs have been identified in Snowdonia and they are occasionally associated with overlying breccia-pipes. They appear to have an annular distribution and this feature coupled with other observations led Rast (1969) and Bromley (1969) to conclude that they marked the site of a volcano-tectonic rim-syncline. Their age can be shown to be post-Lower Rhyolitic Tuff and some are seen to intrude the Middle Basic Series and the Upper Rhyolitic Tuff (Shackleton, 1959;

Olver, 1979). The current view concerning these intrusions is that they are sub-volcanic structures which may have acted as feeders for the copious ignimbrites. Bromley (1969) and Olver (1979) have presented the view that they represent the degassed equivalent of deeper seated acidic material produced via crustal melting.

6) Composite Minor Intrusions

Sills consisting of a thick microgranite or quartz-latite and a thin envelope of dolerite have been described by Beavon (1963) and Bromley (1968, 1969). These intrusions, confined to the south-eastern limb of the Arddu syncline, were thought to be contemporaneous with the Snowdon Volcanic Group by Beavon (1963), although Bromley (1969) considered the acid portion to be formed by remobilisation of the older Moelwyn quartz-latites.

7) Microgranites, Microgranodiorites and Microtonalites

These intrusions form stocks, and laccoliths up to 3 km^2 in area and they are found throughout Snowdonia and Lleyn. The timing of emplacement of these intrusions was thought to be Ordovician by Harker (1889), Williams (1930), Bromley (1969) and Rast (1969) while Jennings et al. (1891), Fearnsides et al. (1944), Shackleton (1953) and Tremlett (1972) believed them to be post-deformational (i.e. Silurian-Devonian). Strong evidence has been obtained for a number of the intrusions which shows them to be of an Ordovician age although information is not presently available which may permit a detailed correlation of the various intrusions of North Wales (see section on timing, page 20).

D. Petrographic, Geochemical and Structural Aspects of the Intrusions

The close petrographic and chemical similarity between the extrusive and intrusive acidic rocks of Snowdonia has been noted by Harker (1889), Ramsay (1866), Williams (1930) and Olver (1979) although high precision data for these rocks were not obtained until recently. Rapid wet-chemical procedures were used by Bromley (1963), Davies (1969) and Evans (1968) providing major element data for the intrusions of Tan-y-Grisiau, Manod Bach, Penmaenmawr, Foel Fras, Drosgl, Ogwen and Gyrn. High precision X-ray Fluorescence techniques, similar to that used in this study, were used by Hendry (1968) on samples from the Pitt's Head Flow and by Olver (1979) on samples of intrusive rhyolite, microgranophyre and ignimbrites from eastern Snowdonia and the Conway area. Major element data were obtained for volcanic and intrusive rocks from the Lleyn Peninsula by Matley and Heard (1930), Fitch (1967) and Tremlett (1962, 1964, 1965, 1970, 1972): Trace element determinations were additionally made by Tremlett (1972) for twenty four intrusions from Lleyn.

Bromley (1969) used various published and unpublished chemical data to plot those Snowdonian samples in a normative Quartz-Albite-Orthoclase ternary diagram. He found that the microgranites and granophyres plotted near the thermal valley of the system while hydrothermally altered samples, high level rhyolite plugs and many extrusive rocks plot towards the quartz-side of the eutectic. Davies (1968) obtained nine major element analyses for the Penmaenmawr and Dinas intrusions, which outcrop in northern Snowdonia,and he concluded that the Penmaenmawr stock was internally differentiated, with silica and the alkalis being more concentrated near the central and upper parts. Evans (1968) determined major elements and some trace elements for the intrusions of Foel Fras, Drosgl, Gyrn and Ogwen and he concluded that there were close similarities between these intrusions and Penmaenmawr, and that they belonged to the same suite.

Tremlett's studies (1962, 1964, 1965, 1970, 1972) have shown that a number of igneous suites may be recognised in the Lleyn Peninsula although their geochemical characteristics are broadly similar. He proposed that the suites are late-Caledonian (Silurian-Devonian) and on the basis of major element and some trace element data (Rb, Sr, Ba, Y, Zr, Nb, Ga, Ce, La, Li and Cs) he has shown that they are geochemically distinguishable from Ordovician intrusive material. The so-called Caledonian intrusions are poorer in SiO_2 and richer in soda, Al_2O_3, CaO, Zr, Nb, Sr, Ba and Y.

The Snowdonian granitoids are divided into microgranites, porphyritic granophyres, rhyolites and quartz-latites and they were emplaced as stocks, sheets and laccoliths. Bromley's work (1963) showed that the Tan-y-Grisiau microgranite is shaped like a truncated ellipsoid cone inclined at about 60° to the north-west. The Bwlch-y-Cywion body was mapped by Williams (1930) who identified four components: a coarse microgranite, a fine microgranite, an intrusive rhyolite and a "white type" (later stated to be a result of autometasomatic breakdown of the original granitic assemblage by Bromley, 1969). The Mynydd Perfedd porphyritic microgranite is claimed to be a wedge-shaped body which is emplaced along the Cambrian-Ordovician boundary (Harker, 1889; Williams, 1930). There is some evidence to show that the granophyres are coeval or younger than the microgranites since they show chilled margins, in some areas, against the microgranites (Bromley, 1969). The quartz-latites occur as sills or laccoliths (e.g. Foel Fras) and as high level stocks (e.g. Manod Bach) and both display signs of autobrecciation and flow-folding. The intrusion of Mynydd Mawr is considered to be a boss which shows signs of broadening downwards while the two intrusions of feldspar porphyry which outcrop across the valley, Y Garn and Tal-y-Mignedd, are laccolithic in form (Shackleton, 1959; Cattermole and Jones, 1970).

The tonalitic-granitic rocks of the Lleyn peninsula are mainly sub-circular bosses although the albite-granophyre of Nant Bodas is sill-like (Roberts, 1979).

Mineralogically the Snowdonian intrusions are quartz-, albite-, microperthite-bearing rocks with pyroxene, amphibole or biotite as the ferromagnesian minerals. Riebeckite occurs at Mynydd Mawr as small grains (< 0.5 mm), hornblende at Tan-y-Grisiau, Foel Fras, Drosgl and Gyrn and pyroxene (enstatite and augite) is found in the intrusions of the northern Carneddau, Y Garn and Tal-y-Mignedd. The ferromagnesian minerals are not uncommonly altered to chlorite although original grains of the unaltered mineral may often be found without too difficult a search. Saussuritisation of plagioclase (albite-andesine) occurs to some extent in most of the intrusions as does sericitisation and kaolinitisation of the orthoclase component of the microperthites (Bromley, 1969). The accessory minerals include zircon, allanite, apatite, magnetite and ilmenite; the last mineral occasionally shows an alteration to leucoxene. An autometasomatic roof facies has been identified at Tan-y-Grisiau and Bwlch-y-Cywion (Williams, 1930; Bromley, 1969) where it is postulated a silica- and alkali-rich vapour phase concentrated and caused the retrogression and breakdown of the original magmatic mineral assemblage.

The mineralogy of the Lleyn granitoids consists of quartz, plagioclase (albite-andesine), augite, hypersthene, biotite, hornblende and microperthite. The pyroxenes may be partly or completely converted to chlorite or hornblende and some kaolinitisation of feldspars occurs. The accessory minerals include zircon, apatite, sphene and magnetite. Detailed petrological accounts of Lleyn intrusions have been given by Tremlett (1962, 1964, 1965, 1969, 1970). Finally, it is noteworthy that a riebeckite-bearing rhyolite, which is occasionally microgranitic, occurs near Myntho Common in Lleyn.

E. The Timing of Igneous Events

There have been two views concerning the ages of the intrusive rocks of North Wales. On the one hand Shackleton (1953), Read (1961) and Tremlett (1962, 1964, 1972) have assigned them to a late stage in the Caledonian orogeny while on the other Harker (1889), Ramsay (1866), Williams (1930), Beavon (1963), Rast (1969) and Bromley (1969) considered that they were Ordovician in age and closely related to the extrusive rocks of the area. The former view was based partly on structural evidence where, for example, some of the intrusions were supposed to have been intruded, at a steep angle, into the north-western limb of the Snowdon syncline even where the limb is thought to be overturned (Shackleton, 1953). Jennings and Williams (1891) described xenoliths of cleaved Lingula Flags in the Tan-y-Grisiau microgranite and they inferred from this that the granite was post-cleavage. Fearnsides and Davies (1944) claimed that metamorphic spots, found in the contact hornfelses around the intrusion, grew in already cleaved rocks and that they were later disrupted by thrusting events. Read (1961), in his synthesis of Caledonian magmatism, thought that the Tan-y-Grisiau microgranite, and perhaps other acid intrusions of the Welsh area, occupied a similar position in the orogenic framework to the Newer Granites of Scotland (Silurian-Devonian).

The opposing view that the intrusions were emplaced prior to the main deformation was based initially on their supposed chemical and petrographic similarity to the volcanic rocks. Ramsay (1866) and Harker (1889) favoured a Bala age (Caradoc-Ashgill) for many of the intrusions and Harker proposed that some of them marked the sites of denuded necks of volcanoes which had supplied the volcanic material. This view was accepted by Williams (1930) and Davies (1959) for the Bwlch-y-Cywion and Cader Idris intrusions respectively (c.f. Ridgeway, 1976). The Mynydd Mawr riebeckitic microgranite was claimed by Harker (1889) to be "newer than the surrounding rocks but older than the cleavage" and he proposed a Bala age for its emplacement. Cattermole and Jones (1970) studied the ground around Mynydd Mawr and they found that the regional cleavage was deflected around the boss, metamorphic spots were strongly deformed in the planes of the cleavage and that the Cambro-Ordovician sediments, into which the microgranite was emplaced, were metamorphosed. Close chemical and petrographic similarities were claimed for the Bwlch-y-Cywion, Mynydd Perfedd, Tan-y-Grisiau and the "lavas" of the Lower Rhyolitic Series.

During the 1960s a considerable amonnt of work was carried out in North Wales by the Universities of Liverpool and Aberystwyth in order to elucidate some of the outstanding problems of the area. Notable among the researchers on igneous rocks were Shackleton (1959), Rast (1961, 1962, 1969), Beavon (1963), Bromley (1963, 1965, 1968, 1969, 1970), Evans (1969), Hendry (1968) and Davies (1968). Evidence was found which strongly supported a pre-cleavage emplacement for many of the granitic intrusions and this is given below. The stratigraphy of many Snowdonian areas were worked out and a correlation chart is shown in fig. 7 (page 23).

1) Thermal metamorphic spotting is deformed in the plane of the cleavage.
2) Granitic veins into country rocks are cut by the cleavage and folded.
3) Blocks of tourmalinised and spotted Glanrafon sediments are found in the Soudleyan Llyn Dinas Breccias east of Beddgelert. Similar tourmalinised and spotted rocks are found in the aureole of the Tan-y-Grisiau intrusion.
4) Around the Foel Fras intrusion, slates of Lower Ordovician age have been brecciated and spotted prior to the imposition of the cleavage.
5) Blocks of sediment in marginal intrusion breccias have differently orientated bedding planes but a similar cleavage, implying that brecciation preceded the formation of the cleavage.

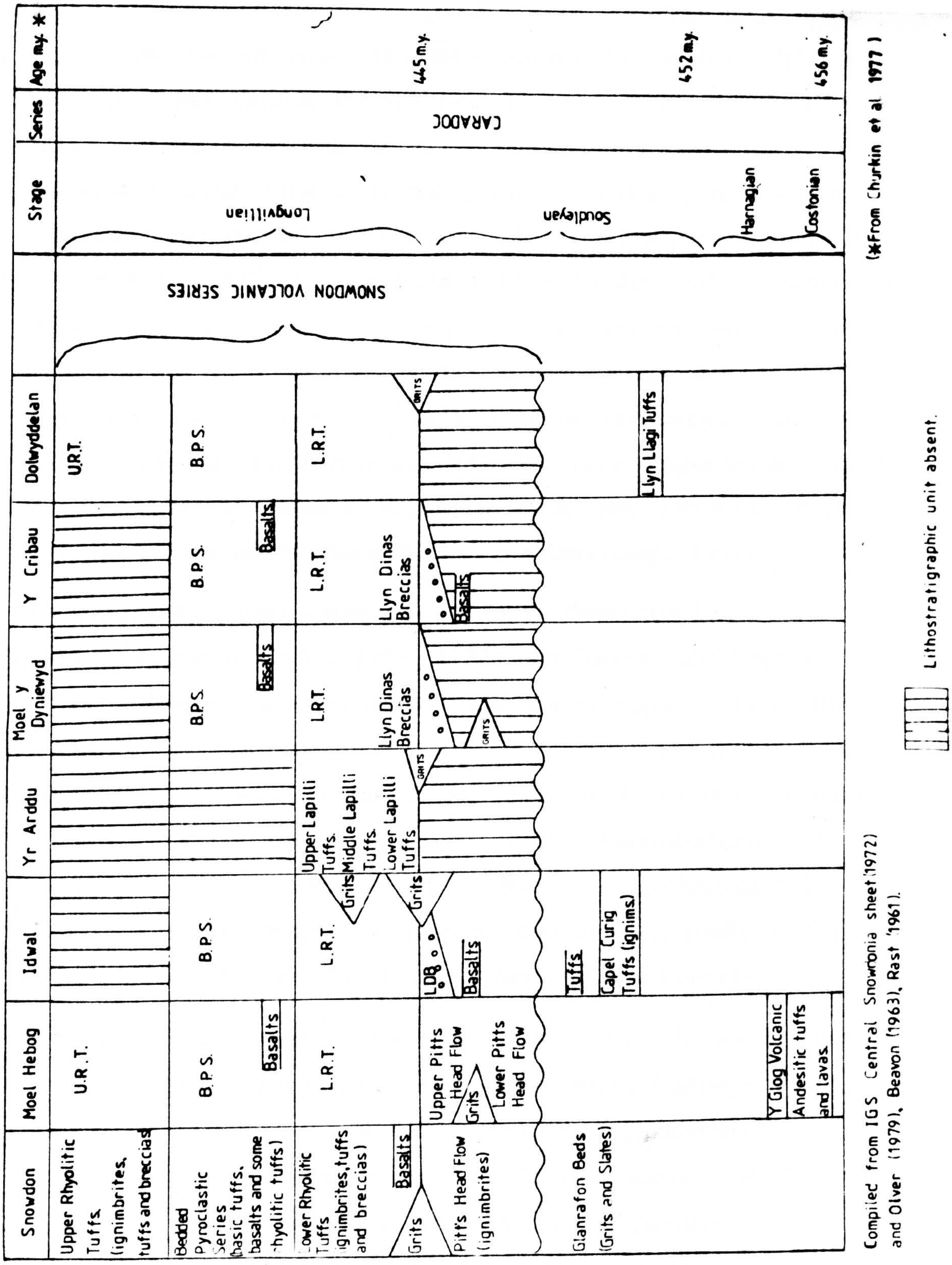
The application of radiometric dating procedures was made by Fitch et al. (1969), Thomas et al. (1966), Harper (1967) and Sabine and Watson (1965, 1966, 1967, 1971) and some apparent ages were obtained for the following intrusions.

Mynydd Mawr	410 m.y.	
Penmaenmawr	375 m.y.	Sabine and Watson (1971)
Llanbedrog	312 m.y.	
Tan-y-Grisiau	408 m.y.	Thomas et al. (1966)

Work by Fitch et al. (1969), using a greater number of samples than in their earlier study, suggested that the Tan-y-Grisiau intrusion was emplaced at 477 ± 20 m.y. (K-Ar determination), although they note that this was a preliminary result. The radiometric dates published have been criticised on the basis that many samples displayed considerable alteration (e.g. Bromley, 1969).

The ages of the basic intrusions (augite-dolerites) have caused a similar controversy to that described for the acidic rocks. They have been variously described as pre-cleavage (Harker, 1889; Williams,

Figure 7



Compiled from IGS Central Snowdonia sheet (1972) and Olver (1979), Beavon (1963), Rast (1961).

(*From Churkin et al 1977)

A lithostratigraphic correlation chart for Central Snowdonia.

1927; Williams, 1930), pre- and post-cleavage (Williams and Bulman, 1931) and post-cleavage (Shackleton, 1953, 1959). Harker found little difficulty in dating the intrusions that he examined for nowhere did they intrude Silurian rocks (which are scarce; Roberts, 1979) and they were always intruded along bedding planes and not cleavage planes. Shackleton (1959) found some dolerites in the Moel Hebog area which cut across faults and showed no cleavage and he claimed them to be late orogenic intrusions. Williams and Bulman (1931) noted that the dolerites of the Dolwyddelan area were of two types. The first showed a schistosity parallel to the local cleavage while the second type did not and they inferred that basic magma had been available for intrusion for a long period. They also found that the dolerites were emplaced as sills in Ordovician strata but as dykes in Cambrian rocks and a similar feature has been found around the Harlech Dome area (Bromley, 1969).

The timing of igneous events in the Lleyn Peninsula has been investigated by Tremlett (1962, 1964, 1972) and Thomas and Briden (1976). Tremlett has examined the volcanic and plutonic rocks of the area and on the basis of structural and geochemical evidence he claims that the tonalitic-granodioritic-granitic intrusions of Lleyn are Silurian-Devonian in age. These intrusions appear to have been disrupted or emplaced along supposed Caledonian faults and their geochemistry is distinctly different from Ordovician volcanic and plutonic rocks of the area. The intrusive and structural events are outlined below:-

1) Emplacement of the early granodiorite suite along a NNW-SSE fault belt. This includes the intrusions of Carn Fadyn, Carreg-y-Llam, Nant, Lithfaen, Garn Bach, Mynydd Nefyn, Penrhyn Bodeilas.
2) Dextral strike-slip movements along the faults causing a shift in the positions of some intrusions to their present position.
3) Sinistral faulting which disrupts the intrusions of Carreg-y-Llam, Nant, Bwlch Mawr and Gurn Ddu.
4) Disruption of the earlier faults by NNW sinistral movements.
5) Emplacement of felsites up NNW-SSE sinistral fault sets (Chwilog area) followed by the Garnfor granodiorites, the dolerite dykes and the Yr Eifl microgranite.

6) Dip-slip movements along some Caledonian faults.

Thomas and Briden (1976) sampled nine intrusions in North Wales including Penmaenmawr, Foel Fras, Penmaenbach, six Lleyn intrusions and they also obtained samples of Ordovician pillow basalts from Cader Idris. Their investigation of paleomagnetic remanence directions showed that all but one of the intrusions gave a similar direction and they explained that the deviation for that sample resulted from the rotation of the intrusion by faulting. The pole position they found for the nine intrusions and pillow basalts is approximately 90° away from published Ordovician-Devonian poles and it is claimed that an anomalous geomagnetic field had operated. They note that such fields are not unknown and their recorded duration is approximately 10^{4} years whereas 10^{7} years would be required to explain the observations for the Welsh samples. Thomas and Briden conclude that all the intrusions were emplaced during the late-Ordovician.

The preceding account has outlined the views which have prevailed and which still exist for the intrusion of the North Wales granitoids. Their relationship to the volcanic and sedimentary rocks and the regional structures demonstrates the probable Ordovician age for many of them. The well-known Tan-y-Grisiau intrusion is considered by Bromley (1969) and others to have been emplaced during the Soudleyan stage of the Caradoc. This belief is based on the observation of spotted and tourmalinised blocks of sediment, similar to those around the intrusion, in the Llyn Dinas Breccias near Beddgelert. The IGS (1972) map of Central Snowdonia shows Llyn Dinas Breccias in a number of localities although according to G. Hendry (personal communication) it is by no means certain whether these breccias may be correlated since they show marked lithological variations. The only evidence remaining therefore is structural and stratigraphic. The structural evidence indicates that the intrusions are pre-cleavage and the stratigraphic evidence shows the intrusions to be post-Tremadocian (Tan-y-Grisiau), post-Llanvirnian (Mynydd Mawr, Y Garn, Tal-y-Mignedd, Bwlch-y-Cywion, Mynydd Perfedd, Foel Fras, Penmaenmawr, Ogwen, the Yr Arddu composite minor intrusions, Lleyn intrusions, Drosgl, Gyrn, Moel Wnion), post-Bedded Pyroclastic Series (e.g. Nant Gwynant rhyolite) and post-Upper Rhyolitic Tuffs (e.g. Crib-y-Ddysgl rhyolite). The intrusions of Lleyn are generally intruded into Caradocian sediments and volcanics (Roberts, 1979).

It is noteworthy that the correlations within the Snowdon Volcanic Series are not finally established. Beavon (1963) suggested that his Lower and Middle Lapilli Tuffs on Yr Arddu were the lateral equivalent of the Pitt's Head Flow although recent work by Olver (1979) disputes this and they are considered to be time-correlated with the Llyn Dinas Breccia - Lower Rhyolitic Tuffs.

Radiometric dating has so far failed to provide what are accepted as reliable ages although modern dating methods may prove to be capable of producing such data. Considerable uncertainties remain concerning the dates of the individual intrusions and their relation to each other although it is known with confidence that the main igneous activity of Snowdonia occurred during the Caradoc for some 11 m.y. (time scale from Churkin et al., 1977).

F. Models of Formation of the Acid Intrusives

Ramsay (1881) and Harker (1889) considered that the igneous rocks of North Wales were derived from a large body of magma of intermediate composition. The acid and basic rocks were claimed to have formed by the separation of the original magma into a basic and acidic fraction while any occurrences of andesite were explained by the eruption or emplacement of the primitive intermediate melt before it had separated into the two phases.

Rast (1969), Bromley (1969), Fitch (1967), Hendry (1968) and Olver (1979) believed that the Caradocian acid volcanic and plutonic rocks were derived from the melting of crustal material. The heat required for melting was thought to be engendered by a large volume of basic magma derived from the upper mantle. The facts which led to these conclusions are:-

1) The close spatial and temporal association of acid and basic magma, exemplified by the composite minor intrusions studied by Beavon (1963) and Bromley (1968, 1969) and the spilitic pillow basalts and ignimbrites of Snowdonia.
2) The observation of widespread metamorphic spotting from Beddgelert to Trefriw suggested to Bromley (1969) that a considerable body of acidic magma lay at no great depth.
3) The regional gravity survey made by Griffiths and Gibb (1965) showed a number of gravity highs over central Snowdonia. The similar observations made over the Tertiary Igneous Centres of Scotland have been attributed to the presence of a considerable body of gabbro which lies below a low-density granitic body (Walker, 1975).
4) Hendry (1968) considered that the geochemical similarities between the Pitt's Head Flow and average crustal rocks, such as the North American Shale Composite (Haskin et al., 1966a), indicated melting of such material.

Fitch (1967) examined a sequence of Caradocian andesites, rhyodacites, ignimbrites and acid intrusions around Llanbedrog in the Lleyn Peninsula and he used these as a model for the formation of other Caradocian magmas. Basaltic rocks were considered to be mantle-derived while basaltic andesites, andesites, rhyodacites, ignimbrites and granites of calc-alkaline nature were formed by melting of the continental crust, the heat source being the basaltic magma.

The tonalitic-granodioritic-granitic intrusions of northern and central Lleyn have received detailed study from Tremlett (1962, 1964, 1970, 1972), who regarded them as late-Caledonian. On the basis of their major element chemistry, petrography and structural relationships three suites were recognised which form a time sequence.

1) The early granodiorite suite - including the intrusions of Penrhyn Bodeilas, Mynydd Nefyn, Carn Fadryn, Carreg-y-Llam, Garn Bach and Nant.
2) Hypabyssal minor intrusions.

3) Yr Eifl Felsite - considered by Tremlett (1962) to have been intruded just prior to the Garnfor Complex.
4) Garnfor Complex - three types of granodiorite porphyry; outer-, inner- and blue-type. The inner-type develops a chilled margin against the outer-type and the blue-type intrudes the inner-type.
5) Two north of west - south of east trending dolerite dykes intruded into the Garnfor Complex.
6) Intrusion of the Yr Eifl microgranite - intruded through the felsite and a chilled margin is claimed to exist on its northern contact with the felsite.

Tremlett (1970) considers that the granitoid suites display a textural evolution, developed at high crustal levels, and a chemical evolution, developed at depth.

1) Textural evolution: microgranodiorite - granodiorite-porphyry - granodiorite.
2) Chemical evolution: This was claimed to result from the progressive basification of an acidic magma at depth. Tremlett noted in his studies that:-
   a) Dolerite xenoliths increased in quantity from the acidic to the more basic granitoids.
   b) There are smooth major-element trends on Harker diagrams for samples ranging in composition from dolerite - microgranite or felsite.
   c) Mafic clots (plagioclase-hypersthene-augite-magnetite) are found, especially in the more basic granitoids, which were considered to be partially digested dolerite xenoliths.

Thus, Tremlett considered that the acid igneous rocks of Lleyn were derived from an acidic magma and that chemical variations resulted from the varying extent of assimilation or hybridisation of doleritic material. The Yr Eifl felsite was suggested to be representative of the acid magma that gave rise to the Garnfor Suite.

G. Plate Tectonic Models

Plate Tectonics theory has enabled geologists to account for many of their observations within a unified framework and a number of associations considered to be representative of a destructive plate margin with a back-arc basin have been recognised in Anglesey and North Wales. These include an ophiolite complex, an olistostrome, ocean-floor tholeiitic basalts, banded cherts and jaspers, serpentinites and gabbros, blueschist facies metamorphism, post-orogenic granites and acid volcanism, ancient continental basement and mylonite belts. These features occur in Anglesey, two tracts of land near Bangor and Bethesda (the so-called Bangor and Padarn ridges) and along the north-west coast of the Lleyn peninsula. The oldest rocks of the area are found in Anglesey and Lleyn and they constitute the Mona Complex. They consist of sedimentary, metamorphic and igneous rocks of Precambrian age and it has been suggested that they are equivalent in age to the Lower and Middle Dalradian of Scotland (Shackleton, 1969; Rast and Crimes, 1969). Greenly (1919) mapped Anglesey and produced a detailed geological map and interpretation for the area but later work by Shackleton (1969), using way-up criteria, inverted the sequence in the Bedded Succession. The succession below is after Shackleton (1969).

Anglesey	Lleyn	
Fydlyn Felsitic Group	Gwyddel felsitic beds	Bedded Succession (7000 metres)
Gwna Group	Gwna Group	
Skerries Group		
New Harbour Group		
Rhoscolyn Beds	Not exposed	
Holyhead Quartzite		
South Stack Beds		
Gneisses	Gneisses	Tectonic (Barber and Max, 1979) or gradational contact (Shackleton, 1969)

The upper parts of the Mona Complex in Anglesey and Lleyn, Gwna Group, are in the form of a melange which was originally interpreted as a tectonic breccia. Work by Shackleton (1969) and Wood (1974), however, showed that the melange was an olistostrome or a submarine slide-breccia and it is made up of over 1000 m pillow lavas, basic tuffs, quartzites, limestones, cherts, jaspers, greywackes, pelites and dolomites with a clast size ranging from less than a millimetre to over a kilometre.

Thorpe (1972) examined the geochemistry of the pillow basalts and glaucophane schists and he concluded that they possessed the characteristics of ocean floor tholeiitic basalts. More recently Beckinsale and Thorpe (1979) have studied the strontium isotope ratios of the gneisses in an attempt to resolve some of the controversy concerning them. The gneisses of Anglesey and Lleyn are ortho- and paragneisses and they have been interpreted as metamorphic basement older than the Monian supergroup (e.g. Greenly, 1919; Barber and Max, 1979) and as the metamorphic equivalent of the Bedded Succession (Shackleton, 1969; Beckinsale and Thorpe, 1979). The gneisses possess low initial strontium isotopes(0.7061) which is claimed to preclude a long history in the crust and Beckinsale and Thorpe argue that they represent the metamorphosed equivalent of the Bedded Succession. Barber and Max (1979, Discussion) however, question the geochemical results on the grounds that the samples used came from a small, isolated occurrence of gneiss which did not show any clear relationship to other gneisses or the Bedded Succession.

The Precambrian age for parts of the Mona Complex has been shown to be disputable in recent years (Muir et al., 1979) owing to the identification of Lower Cambrian microfossils in the Gwna Group. Barber and Max (1979) claim that this discovery is greatly significant for any paleogeographical reconstructions of the Irish Sea region. Greenly (1919), Jones (1938) and others were of the opinion that a large linear mass of Precambrian crust had existed between S.E. Ireland and Anglesey and this Irish Sea Horst or geanticline was an important sediment source for the Welsh Basin during Lower Paleozoic times

(Bennison and Wright, 1969; Brenchley, 1969). The possible Cambrian age for the olistostrome, and paleocurrent directions measured in Cambrian rocks around the Harlech Dome and eastern Ireland, suggested to Barber and Max that the proposed horst was not sited near Anglesey but must have lain considerably north of the area, possibly the Longford-Down Massif of Ireland.

A series of post-tectonic acid volcanic rocks, mainly ignimbrites, known as the Arvonian, succeed the Mona Complex although their base is not seen. Closely associated with the Arvonian are three granites, Coedana, Sarn and Twt Hill; the first two intrude rocks of the Mona Complex in Anglesey and the Lleyn Peninsula respectively, and the last intrudes the Arvonian near Caernarvon. Recent radiometric dating, using the Rb-Sr whole-rock isochron method, has given an age of 603 ± 34 m.y. for the Coedana granite and its initial strontium isotope ratio (0.7086) is consistent either with its derivation from a crustal contaminated mantle-derived melt or by melting of young crustal material such as the gneisses of the Mona Complex (Beckinsale and Thorpe, 1979). It is noteworthy that calc-alkaline volcanic rocks, underlying the Cambrian Dolwen Grits in the Harlech Dome, have been found in the Bryn-Teg Borehole and that they are thought to correlate with the acid volcanics of the Arvonian (Allen and Jackson, 1978). The Arvonian is considered to be a late-Precambrian - early-Cambrian formation (Challinor, 1976; Wood, 1969).

It is apparent from the foregoing account that there are features in North Wales and Anglesey which are considered representative of plate tectonics in a continental margin environment. It is also clear that considerable controversy exists concerning structural and stratigraphic relationships within the Mona Complex (see discussion in Barber and Max, 1979). Owing to the prevailing uncertainties, it is evident that very detailed plate tectonic models may not be justified, especially for the late-Precambrian - Cambrian.

One of the earliest plate tectonic models for the evolution of the British Isles was that proposed by Wilson (1966). The idea of a proto-

Atlantic ocean (Iapetus) was developed which opened during the late-Precambrian, had closed in stages throughout the Precambrian and Lower Paleozoic and subsequently re-opened at the beginning of the Cretaceous. Shelly-faunal distributions had shown for some time that two clearly marked geographical regions existed during the Lower Paleozoic. Williams (1969, 1973) demonstrated, using advanced statistical procedures, that distinct faunal communities existed during the early part of the Ordovician but by late-Ordovician times cosmopolitan communities began to appear suggesting that the ocean was closing. A general model for the evolution of the Caledonian/Appalachian orogen was proposed by Dewey (1969) which was based on supposed structural and lithostratigraphic correlations across the Appalachian and Caledonian belts. Sedimentation of Longmyndian and Torridonian rocks was said to occur on continental terraces while Dalradian, Monian and Moinian sediments accumulated on the ocean floors. Subduction towards the south-east occurred on the southern side of the ocean up to Arenig times when it ceased. During the Caradoc a new fracture developed and subduction ensued until continental collision took place during the Silurian-Devonian. Fitton and Hughes (1970) suggested that the progressive change from tholeiitic - calc-alkalic - alkaline plutonism and volcanism from the Lake District to Wales was a manifestation of the K-h relationship of Hatherton and Dickinson (1968) and that the associations in those areas could be explained by a subduction zone dipping south-east from the Southern Uplands of Scotland. Both of the above models have been criticised since recent geophysical studies have shown the absence of oceanic crust in any quantity under the Southern Uplands or the Midland Valley of Scotland (Powell, 1971; Bamford et al., 1976). The litho-stratigraphic correlations proposed by Dewey (1969) are also questioned (Bath, 1974; Rast and Crimes, 1969).

Mitchell and Reading (1971) believed that the close association of intrusive and extrusive igneous activity, vertical tectonics and low-grade regional metamorphism were consistent with the evolution of the Welsh Basin as a back-arc basin similar to that of the Japan Sea.

Baker (1973) introduced the idea that a microcontinent had existed in order to explain the sedimentation of Monian and Longmyndian rocks and that a subduction zone, lying between Anglesey and the Welsh Borders, dipped north-westwards. Wood (1974) provided a detailed model for the late-Precambrian - Lower Paleozoic evolution of Anglesey and North Wales, accounting for the presence of ophiolites, the olistostrome, blueschist metamorphism, Monian sedimentation and the development of the acid igneous activity (Arvonian, Coedana granite etc.). His proposed subduction zone dipped to the south-east from a trench situated near Anglesey. The Precambrian rocks of Anglesey, Shropshire, Pembrokeshire and the English Midlands were investigated by Thorpe (1974) who found them to be composed essentially of calc-alkaline igneous material. Although there are considerable uncertainties associated with correlating these patches of Precambrian rocks their presence is suggestive of a destructive plate margin. Thorpe presented a number of possible reconstructions and he believes that the North Wales area may have been the site of a back-arc basin.

Wider stratigraphic and structural relationships have been considered by Rast et al. (1976) and Wright (1976, 1977). Rast et al. believe that the late-Precambrian rocks of the Avalon (New England) platform are the lateral equivalent of the rocks of Anglesey, Wales, Shropshire and the English Midlands. Two phases of igneous activity have been recognised in Canada and North America and they are correlated with the Uriconian and Arvonian volcanics of Britain. The conclusions reached by Rast et al. are that the volcanicity of the Avalonian belt was generated by a north-westerly dipping subduction zone which produced an ensialic volcanic arc. The position of this arc was the site of the later proto-Atlantic ocean (Iapetus).

Wright (1976) proposed a model which attempted to explain the evolution of Britain throughout Precambrian and Lower Paleozoic times. He suggested that Iapetus was an ocean of long standing and that the recognisable events in Britain resulted from several climactic episodes caused by alternating periods of subduction to the north-west and south-east of the ocean. Five orogenic periods were identified:

1)	Morarian	$\sim$1000 m.y.
2)	Celtic	$\sim$ 600 m.y.
3)	Grampian	Tremadoc-Arenig
4)	Lakelandian	Upper Ordovician
5)	Caledonian	Silurian-Devonian

The Welsh areas were affected by the Celtic, Lakelandian and Caledonian orogenies (c.f. Rast and Crimes, 1969) while the Morarian, Grampian and Caledonian affected the northern side of Iapetus. The Celtic orogeny resulted from the closure of a marginal basin lying between Anglesey and the Welsh Borders and it produced the calc-alkaline volcanism of Anglesey and Britain (Arvonian, Charnian etc.) and it brought the slivers of ocean crust and blueschists (Mona ophiolite) to the surface. Similar events were considered to be taking place around Newfoundland. The Lakelandian episode produced a cordilleran-type orogeny which was responsible for the volcanicity of the Lake District and Wales. Wright considers that the Welsh area was never truly oceanic but that it was an incipient marginal basin possibly earmarked by the presence of the Llanvirnian Strumble Head Pillow Lavas.

A considerable number of plate tectonic theories have been presented to explain the evolution of the British Isles and some have dealt specifically with Wales and the Lake District while others have considered these areas in a much wider context. There is a consensus that the margins of Iapetus ran north-east to south-west in Britain but subduction directions dipping south-east and north-west under Wales have been proposed. The problems in identifying ancient subduction zones and their direction of dip are considerable and are not helped by the various controversies surrounding lithostratigraphic and structural correlations in Britain and the geologically important island of Anglesey.

Chapter 2

AIMS OF THE RESEARCH

The igneous rocks of North Wales have been studied and described by many workers since the early part of the 19th century and various interpretations have been made concerning their relationship to the structures of the area and more recently within the wider context of global tectonics. An appraisal of the research in the area, up until 1968, was published as a conference proceedings entitled, "The Precambrian and Lower Paleozoic Rocks of Wales" (Ed., A. Wood, 1969). Stratigraphic, structural and igneous aspects were described and notable unified accounts of the evolution of the region throughout the Ordovician were presented by Rast (1969) and Bromley (1969). Studies of the igneous rocks, prior to those by Hendry (1968), Davies (1968), Evans (1969), Tremlett (1972) and Olver (1979), were almost exclusively concerned with petrographic investigations although some major element chemical data were also made available by some workers (e.g. Bromley, 1963). No comprehensive chemical studies of either the intrusive or extrusive material has been undertaken although those investigations by Hendry (1968) and Olver (1979) provided a substantial body of major and trace element data for some volcanic and intrusive acid rocks.

Great advances have been made in the understanding of the geochemistry of igneous rocks over the last two decades and this has been facilitated in part by the development and availability of rapid and high precision instrumental analytical techniques. The acquisition of large numbers of chemical data from various volcanic and plutonic suites in different plate tectonic settings has enabled their origin to be postulated. It is also possible to recognise possible ancient plate tectonic environments by comparing the chemical data from igneous suites, particularly trace elements, with those obtained from modern areas of active or recently active plate subduction, extension, collision or within-plate activity.
The development of petrogenetic modelling equations, using trace element distribution coefficient data, has permitted the semi-quantitative assessment

of proposed petrogenetic schemes and the rare earth group of elements lend themselves to this study especially well.

A geochemical study of the granitoids of North Wales was considered timely such that some solutions could be found for the uncertainties associated with their origin and inter-relationships. To this end, the high precision and potentially accurate techniques of X-ray Fluorescence and neutron activation analysis were used and particular emphasis was placed on the rare earth elements.

Chapter 3

THE BEHAVIOUR OF THE ELEMENTS – A BRIEF ACCOUNT

Elements may be distributed throughout a rock in a number of ways.

a) As structural constituents of silicate minerals, e.g. K in biotite.
b) As structural constituents of non-silicate minerals, e.g. Fe in pyrite.
c) Distributed throughout a silicate glass.
d) As non-structural constituents of silicates, e.g. Cu and Sn in silicates.
e) As non-structural constituents in non-silicates.
f) Dissolved in fluid inclusions, e.g. CO_2, Cl.

The studies by Goldschmidt (1922, 1937) on meteoritic and terrestrial materials provided an insight into the ways in which elements distribute themselves between different minerals and phases. The results of such studies led to the classification of elements into four groups: lithophile, chalcophile, siderophile and atmophile. It was clear that some elements did not show an exclusive affinity for one group and that the physical conditions of pressure, temperature, oxygen fugacity and the chemical environments played a role in controlling element distribution. The geochemical character of an element is largely controlled by its electron configuration and Goldschmidt (1937) considered that ionic size and ionic charge were the facts which controlled an elements behaviour. This view was found to be inconsistent with some observations and later work, notably by Ahrens (1953), Ringwood (1955), Burns and Fyfe (1967) and Burns (1970, 1973), has shown that ionisation potential, electronegativity and crystal-field stabilisation energy (in transition elements) are important. Thus, there are five main points which are known to affect the behaviour of elements.

1) Elements having equal charge and ionic size will enter a mineral lattice with equal ease, e.g. Hf = Zr, Al = Ga, Ta = Nb.

2) If two elements have the same charge and similar ionic radii, the smaller ion will be preferentially incorporated into a crystal lattice, e.g. $K^+ > Rb^+$ in K-feldspar.

3) If two elements have similar ionic radii but different charges, the ion with the larger charge will enter the crystal lattice more readily, i.e. $Ba^{2+} > K^+$ in K-feldspar.

4) If two elements have the same charge and similar ionic radii, the ion with the lower electronegativity will be preferentially incorporated into the crystal lattice, e.g. $V^{3+} > Fe^{3+}$ in magnetite.

5) An ion with a higher crystal-field stabilisation energy will be preferentially accommodated in a mineral, e.g. $Ni^{2+} > Co^{2+}$ in olivine.

A further advance in the understanding of the geochemistry of igneous rocks are the determinations of distribution coefficients of trace elements between phenocryst minerals and their groundmass. The distribution coefficient, (Kd), is the ratio of the concentrations of an element between two phases in equilibrium. It is constant at fixed temperature, pressure, redox conditions and compositions of the two phases. The development of very sensitive analytical techniques over the last two decades, such as X-ray fluorescence, mass spectrometry, microprobe analysis and neutron activation, has enabled the concentrations of some trace elements to be determined well below 1 microgram, (10^{-6}g). The distribution coefficient data determined over the last twenty years have been obtained from synthetic and natural samples and a useful review of such data may be found in Irving (1978). The validity of these data depends on whether the trace element distribution was homogeneous in the melt and the growing crystals and that there was equilibrium between the groundmass and the phenocryst. Considerable variations in the published data suggest that these conditions may not be fulfilled. Most natural phenocrysts are formed under varying conditions of pressure, temperature, oxygen fugacity and groundmass composition and this is evidently demonstrated by their zoning. Such data are useful for they show how natural systems deviate from ideal silicate equilibria. Most trace element distribution coefficients are based on the assumption that the trace elements behave according to Henry's Law and work by Drake and Weill (1975) and Watson (1976), among others, has shown that this law is often obeyed up to concentrations well above those found in natural systems. Henry's Law states that, for a given dilute solution, a trace element may be considered to be surrounded by a uniform chemical environment and its activity coefficient remains constant. Its activity is therefore directly proportional to its concentration (Wood and Fraser, 1976). Because many trace elements are strongly partitioned into one phase or another it has become possible to use their concentrations to predict the dominant petrogenetic process which formed their distributions (see later discussion, this chapter).

Significant contributions to the understanding of the way elements behave in igneous systems have been made by Jensen (1973), Banno and Matsui (1973), Philpotts and Schnetzler (1970), Nagasawa and Schnetzler (1971), Ryerson and Hess (1978) and others. Jensen (1973), for example, showed that when distribution coefficients, determined from natural samples, were plotted against ionic radius, for a number of elements in a certain valence state, smooth curves with one or more well-defined maxima resulted. These maxima correspond to the optimum ionic radius for a cation in a given structural position. Jensen claims that once a mineral has started to crystallise, the charge and effective ionic radii of ions competing for a lattice site are the most important facts. The distribution coefficients for elements in a particular mineral vary systematically and if one or more coefficients are known it is possible to predict the magnitude of another for an element with the same charge and a similar ionic radius.

Watson (1976) and Ryerson and Hess (1978) have shown the effect that magma composition may have on distribution coefficients by their studies of liquid-liquid equilibria. They interpreted the variation in distribution coefficients according to the extent of polymerisation of the melts. A basaltic melt is less-polymerised than a granitic melt and therefore it possesses a greater number of possible sites for cations, particularly those with a high charge and a small size. For this reason Zr, Nb, Ta, Hf, the trivalent rare earths, Y, Ti and P are found to be strongly partitioned into the basic melt (see page 217 for a detailed discussion).

There is clearly a complex interplay of variables which may control the magnitude of distribution coefficients and for this reason it is important to realise the shortcomings of quantitative modelling of petrogenetic processes using the currently available data.

A number of collective terms have been used to describe the behaviour of trace elements such as compatible and incompatible. An incompatible element is one which possesses a low bulk distribution coefficient (see page 44 for definition of bulk distribution coefficient) because it is not readily accommodated in crystallising minerals (e.g. Th, U, K, Rb, Ta and Cs) whereas a compatible element is the converse of this (e.g. Ni, Cr, Co, V). The terminology is dependent upon the system under investigation since an element may behave incompatibly in basaltic and andesitic melts but compatibly in acidic melts. The light rare earth elements, for example, are commonly classified as incompatible elements (e.g. Saunders et al, 1980a, 1980b) but if apatite is a late crystallising phase or a partial melt residue, they may behave as compatible elements. The term hygromagmatophile has found some use in modern literature (Treuil, 1973; Wood et al., 1980) and it refers to those elements which possess a bulk distribution coefficient of less than one. Another classification of trace elements, which is independent of the magnitude of distribution coefficients, relies on their physical properties of ionic charge and radius. Elements with a low radius/charge ratio (< 0.2) are termed high field strength while those with a ratio larger than 0.2 are called low field strength. Difficulties with this classification may occur where complexing agents in a magma may cause an increase in the effective ionic radius of a cation.

Definitions

1) Incompatible element - one with a bulk distribution coefficient < 1.
2) Compatible element - one with a bulk distribution coefficient > 1.
3) Hygromagmatophile - elements with a bulk distribution coefficient < 1.
4) High field strength - elements with a radius/charge < 0.2 (Zr, Nb).
5) Low field strength - elements with a radius/charge > 0.2 (Rb, Th, K).
6) Large ion lithophile element (LILE) - K, Rb, Cs, Ba, U, Th and the light rare earths (Schilling, 1973).

The effect that various minerals have on trace element abundances depends on their modal proportion and the distribution coefficients for those elements. Some common rock forming minerals are considered below (see also Hanson, 1978).

Plagioclase

This mineral has relatively large distribution coefficients for Sr and Eu and its involvement as a crystallising or residual mineral may cause significant removal of these elements. The extent of this is dependent on the composition (Drake and Weill, 1975), oxygen fugacity and temperature of the magma. The distribution coefficients for plagioclase in basaltic, andesitic and granitic rocks are shown in table 1 (page48).

Potassium Feldspar

Potash feldspar has sizeable distribution coefficients for Sr, Eu and Ba and its involvement will reduce these elements and also K/Rb and Ba/Sr ratios.

Anorthoclase

This mineral has an effect similar to plagioclase and K-feldspar since it is a solid-solution of both.

Garnet

Garnet possesses small distribution coefficients for the light rare earths but they increase significantly for the middle and the heavy rare earths to values greater than unity (table 1). Residual or crystallising garnet will produce melts with marked fractionation of the rare earth elements.

Zircon

Zircon is similar in its effect to garnet in that it will cause markedly fractionated rare earth patterns. The distribution coefficients are, however, approximately an order of magnitude larger than those for garnet.

Apatite

This mineral possesses large distribution coefficients for the rare earths, Y and Sr and it will produce significant depletion of these elements in melts in which the crystals are in equilibrium.

Orthopyroxene

Hypersthene does not have sizeable distribution coefficients for many trace elements except for the transition metals. It does have larger distribution coefficients for the middle and heavy rare earths than for the light rare earths and its involvement as a residual or crystallising mineral may produce fractionated rare earth patterns.

Clinopyroxene

Augite may produce fractionation of the rare earths and contribute to a positive Eu anomaly since its distribution coefficient for this element is lower than those for the two adjacent elements, Sm and Gd. The transition metals are readily accommodated in the clinopyroxene lattice although the extent is temperature dependent. Zr and Nb abundances may be affected by clinopyroxene residues or crystallisation (Pearce and Norry, 1979).

Hornblende

Hornblende may produce marked fractionation of the rare earths and contribute to a positive Eu anomaly (Hanson, 1978). Y, Zr, Nb and the transition metals are appreciably accommodated by hornblende.

Olivine

Olivine does not greatly affect rare earth patterns and its crystallisation at an early stage will cause a significant reduction in Ni abundances (temperature dependent) while many other trace elements will become concentrated in the successive melts.

Petrogenic Modelling Equations

The use of modelling equations, such as that developed from Rayleigh (1896) and restated by Arth (1976) and Hanson (1978), has enabled petrologists to test their evolutionary hypotheses for igneous suites. Partial melting equations describing the behaviour of trace elements were developed by Gast (1968) and Schilling and Winchester (1967) while equations for other processes such as zone refining (Harris, 1957) and "magma plumbing" (O'Hara, 1977) have also been developed. The availability of high quality distribution coefficient data has been of great importance in the progress of modern petrogenetic theory in that it is now possible to attempt the quantitative assessment of genetic models that were hitherto difficult. The application of modelling equations is now widely used for problems in igneous petrology (e.g. Aburquerque, 1977; Arth and Hanson, 1975). Not all studies provide a unique solution and often a large number of models may be constructed which can fit the geochemical data. This situation exists because it is often impossible adequately to constrain the system under investigation. For example, the proportion of minerals in the residue after a partial melting event needs to be assumed from a current knowledge of the original source composition (e.g. lower continental crust, upper mantle). In spite of these shortcomings the advances made during the last decade in our understanding of the evolution of basaltic and granitic rocks (Arth and Hanson, 1978; Sun and Hanson, 1975; Zielinski and Frey, 1970) have been due in no small way to the application of distribution coefficient data and modelling equations.

i) Fractional Crystallisation

This process comprises two distinct variants: It can either be described by Rayleigh surface-equilibrium crystallisation (equation 1) or by total-equilibrium crystallisation (equation 2). Rayleigh fractionation involves the instantaneous equilibrium crystallisation of a mineral which is quickly covered by another layer of crystals, thus preventing further equilibration of the covered crystals with the evolving melt. Total equilibrium crystallisation is analogous with total equilibrium partial melting and the mathematical expressions of both are identical. Total equilibrium crystallisation is likely to occur in a slowly cooling magma where the whole crystals are in contact with the liquid and where the slow rate of cooling allows equilibrium to be maintained by diffusion of the elements. Rayleigh crystallisation is a more likely mechanism where cooling and settling rates are relatively high, such as in an upper-crustal magma reservoir.

$$\frac{C_L}{C_o} = F^{D-1} \text{ - - - - - - - (surface equilibrium)} \qquad \text{Equation 1}$$

where $D \ll 1$

$$\frac{C_L}{C_o} \approx \frac{1}{F} \text{ - - - - - - - - - - - - - - - - - -} \qquad \text{Equation 1a}$$

$$\frac{C_L}{C_o} = \frac{1}{D(1-F)+F} \text{ - - - - - (total equilibrium) - -} \qquad \text{Equation 2}$$

where $F < 0.4$

$$\frac{C_L}{C_o} \approx \frac{1}{D} \text{ - - - - - - - - - - - - - - - - - -} \qquad \text{Equation 2a}$$

<u>where:</u>

C_L is the concentration of a trace element in the liquid

C_o is the concentration of a trace element in the original melt

F is the fraction of melt remaining

D is the bulk distribution coefficient for an element

$$D = \sum_{i=1}^{n} X_i.Kd_i$$

n is the number of crystallising mineral phases

X_i is the modal proportion of mineral i

Kd_i is the distribution coefficient of an element in mineral i

$i = 1 \rightarrow n$

ii) Partial Melting

Three mechanisms are normally considered which Gast (1968) has formulated. These are:-

1) Fractional melting - where continuous removal of infinitesimally small quantities of melt are removed from a residual solid.
2) Batch melting - where the melt and solid are in continual equilibrium until the melt is finally removed from the solid.
3) Aggregate melting - where the melt is continuosly removed from the solid but it collects in a magma reservoir.

Batch partial melting is considered to be the most likely mechanism for producing partial melts while the other models represent possible limiting conditions. The removal of very small quantities of magma from a solid is not considered to be a likely process and this is why models 1 and 3 are not often used, except in special circumstances (see Langmuir et al., 1977).

$$\frac{C_L}{C_o} = \frac{1}{D_o+F(1-P)}$$ Non-modal batch melting Equation 3

$$\frac{C_L}{C_o} = \frac{1}{D_o+F(1-D_o)}$$ Modal batch melting Equation 4

where D_o is the bulk distribution coefficient of the original assemblage
P is the bulk distribution coefficient of the melt mineralogy
F is the fraction of melt
C_L is the concentration of a trace element in the melt
C_o is the concentration of a trace element in the solid

Equation 3 shows that as melting proceeds account is made for the change in D_o. If a mineral phase disappears during melting, however, no account is taken of this.

Equation 4 is used when the solidified melt and the parent have the same modal mineralogy and it may be rearranged according to Schilling and Winchester (1967).

$$\frac{C_L}{C_o} = \frac{1}{D(1-F)+F}$$

where D is the bulk distribution coefficient of the residue prior to the removal of the melt.

This equation demonstrates that the concentration of an element in a melt derived by partial melting is dependent on the residual mineral assemblage and not on the starting assemblage.

The equations can be simplified by limiting D and F.

a) for $D \rightarrow 0$ and < 1

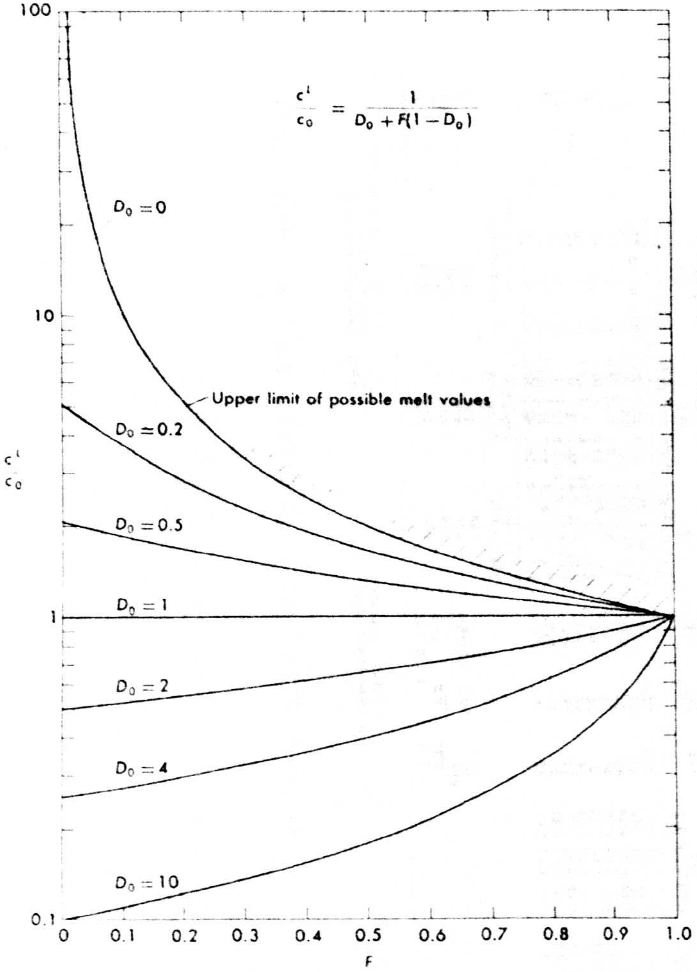
$$\frac{C_L}{C_o} \approx \frac{1}{F}$$

b) for $F \rightarrow 0$ and < 0.4

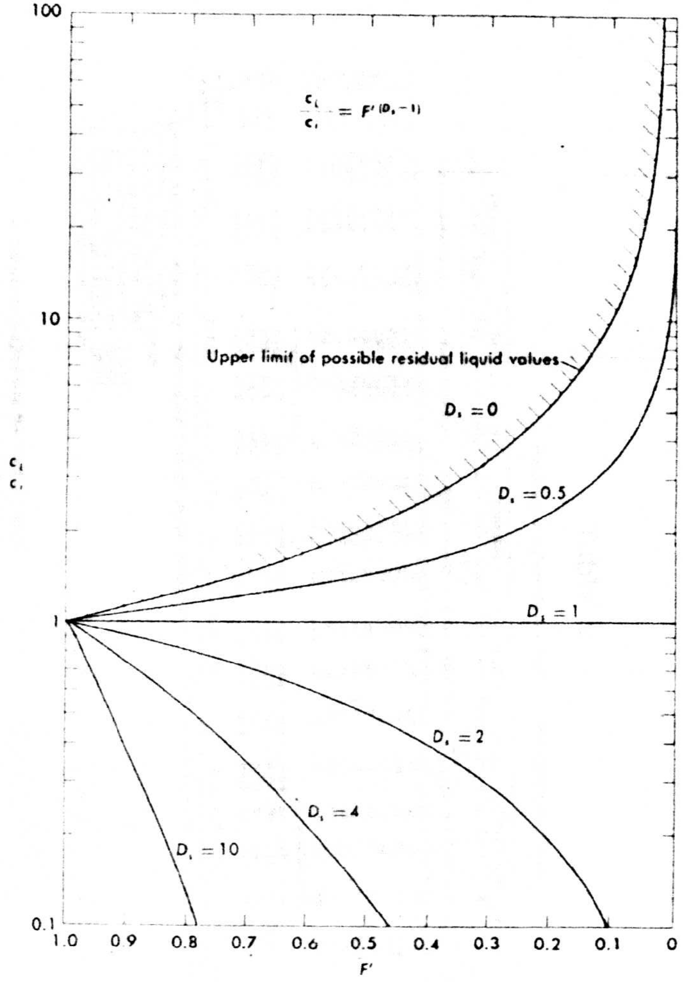
$$\frac{C_L}{C_o} \approx \frac{1}{D}$$

The two graphs fig. 8 (page 47) show how the ratio C_L/C_o (enrichment factor) changes with D and F. From these diagrams it may be seen that fractional crystallisation (Rayleigh type) is more effective at reducing the concentration of an element with a bulk distribution coefficient greater than one. Similarly for an element with $0<D<1$ fractional crystallisation may produce greater enrichment than partial melting.

Figure 8



—Illustration of the behavior of a trace element during partial melting predicted by the "modal melting" equation of Shaw (1970) for liquid which is in continuous equilibrium with residual solid until it is removed as a "batch." F, fraction of melting; c_0, initial trace-element concentration of the solid; c^L, trace-element concentration of liquid; D_0, bulk distribution coefficient for the starting assemblage.



—Illustration of the behavior of a trace element predicted by a Rayleigh fractionation model for fractional crystallization from a liquid of phases in constant proportions and having constant distribution coefficients. F', fraction of liquid remaining; c_l, concentration of the original melt; c_L, concentration in the differentiated liquid; D_l, bulk distribution coefficient for the residual solid.

Table 1

.—*Partition coefficients for basaltic and andesitic rocks*

	Olivine			Orthopyroxene			Diopside			Augite			Pigeon-ite	Hornblende			Phlogo-pite	Plagioclase			Gar-net *
	Avg	Low	High	Avg	Low	High	Avg	Low	High	Avg	Low	High		Avg	Low	High		Avg	Low	High	
	2 determinations			*3 determinations*			*2 determinations*			*5 determinations*			*1 determination*	*4 determinations*			*1 determination*	*8 determinations*			*5 determinations*
Ce	0.0069	0.0026	0.0090	0.024	0.0026	0.038	0.070	0.043	0.096	0.15	0.077	0.21	0.02	0.20	0.094	0.34	0.034	0.12	0.023	0.28	0.028
Nd	.0066	.003	.010	.033	.006	.058	.12	.065	.18	.31	.17	.43	.05	.33	.16	.56	.032	.081	.023	.20	.068
Sm	.0066	.003	.011	.054	.014	.100	.18	.090	.26	.50	.26	.74	.10	.52	.24	.93	.031	.067	.024	.17	.29
Eu	.0068	.005	.010	.054	.023	.079	.18	.091	.26	.51	.27	.75	.068	.59	.26	1.1	.030	.34	.055	.73	.49
Gd	.0077	.004	.012	.091	.032	.171	.19	.095	.27	.61	.32	.87	.16	.63	.28	1.1	.030	.063	.017	.21	.97
Dy	.0096	.006	.014	.15	.054	.293	.21	.105	.31	.68	.50	1.0	.23	.64	.31	1.0	.030	.055	.010	.19	3.17
Er	.011	.008	.017	.23	.076	.46	.17	.107	.23	.65	.46	1.0	.32	.55	.24	1.0	.034	.063	.010	.24	6.56
Yb	.014	.009	.023	.34	.11	.67	.16	.092	.23	.62	.43	1.0	.40	.49	.23	.98	.042	.067	.006	.30	11.5
Lu	.016	.009	.026	.42	.11	.84	.13	.071	.19	.56	.27	.95	.45	.43	.22	.82	.046	.060	.0045	.24	11.9
				2 determinations										*3 determinations*				*9 determinations*			
K	.0068	.0056	.0081	.014	.009	.019	.011	.0084	.014	.038	.004	.078	.0034	.96	.33	1.40	----	.17	.019	.36	.015
Rb	.0098	.0084	.011	.022	.015	.029	.015	.014	.015	.031	.015	.039	.0003	.29	.045	.43	3.06	.071	.016	.14	.042
Sr	.014	.0094	.019	.017	.010	.024	.12	.078	.15	.12	.093	.15	.0019	.46	.19	.64	.081	1.83	1.29	2.87	.012
Ba	.0099	.0086	.011	.013	.012	.014	.013	.013	.013	.026	.004	.046	.0004	.42	.10	.73	1.09	.23	.05	.59	.023
References †	1, 3, 4, 5			2, 3, 5			3, 5			2, 3, 4, 5			3, 5	1, 3, 4, 5,			3, 5	1, 3, 5			----

* Garnet values obtained by multiplying average garnet/clinopyroxene of reference 6 by average augite/liquid of this table.

† References are as follows:
1. Higuchi and Nagasawa (1969).
2. Onuma and others (1968).
3. Philpotts and Schnetzler (1970).
4. Schnetzler and Philpotts (1968).
5. Schnetzler and Philpotts (1970).
6. Philpotts and other (1972).

—*Partition coefficients for dacitic rocks*

[Data represent one determination per mineral]

	Garnet	Biotite	Plagioclase	Hornblende
Ce	0.35	0.037	0.24	0.899
Nd	.53	.044	.17	2.80
Sm	2.66	.058	.18	3.99
Eu	1.50	.145	2.11	3.44
Gd	10.5	.082	.090	5.48
Dy	28.6	.097	.086	6.20
Er	42.8	.162	.064	5.94
Yb	39.9	.179	.077	4.89
Lu	29.6	.185	.062	4.53
K	.020		.263	
Rb	.0085	3.26	.048	
Sr	.015	.12	2.84	
Ba	.017	6.36	.36	
References*	1, 2	1, 2	1, 2	3

* References are as follows:
1. Philpotts and Schnetzler (1970).
2. Schnetzler and Philpotts (1970).
3. Arth, unpub. data, 1975.

.—*Partition coefficients for rhyolitic rocks*

[Figures in parentheses indicate number of determinations]

	Hypersthene (4)			Clinopyroxene (2)			Hornblende (3)			K-feld-spar (1)	Bio-tite (1)	Phlog-opite (1)	Apatite (4)			Zircon (2)			Plagioclase (4)		
	Avg	Low	High	Avg	Low	High	Avg	Low	High				Avg	Low	High	Avg	Low	High	Avg	Low	High
Ce	0.15	0.082	0.26	0.50	0.36	0.65	1.52	1.38	1.77	0.044	0.32	0.23	34.7	18.0	52.5	2.64	2.29	3.00	0.27	0.17	0.35
Nd	.22	.12	.35	1.11	.94	1.28	4.26	4.03	4.49	.025	.29	.34	57.1	27.4	81.1	2.20	1.97	2.43	.21	.12	.29
Sm	.27	.16	.38	1.67	1.52	1.81	7.77	7.1	8.1	.018	.26	.39	62.8	29.3	89.8	3.14	2.58	3.70	.13	.084	.15
Eu	.17	.093	.27	1.56	1.11	2.01	5.14	4.5	5.9	1.13	.24	.50	30.4	20.5	50.2	3.14	1.07	5.22	2.15	.96	2.81
Gd	.34	.23	.46	1.85	1.5	2.2	10.0	9.3	10.5	.011	.28	.35	56.3	27.2	78.0	12.0	10.0	14.0	.097	.06	.13
Dy	.46	.33	.55	1.93	1.22	2.63	13.0	12.5	13.5	.006	.29	.30	50.7	25.6	69.2	45.7	37.8	53.5	.064	.04	.08
Er	.65	.53	.73	1.80	1.07	2.25	12.0	10.8	14.0	.006	.35	.17	37.2	20.0	51.2	135	119	152	.055	.038	.072
Yb	.86	.73	.99	1.58	1.14	2.01	8.38	7.45	9.0	.012	.44	.17	28.9	13.1	37.0	270	242	299	.049	.03	.07
Lu	.90	.76	1.14	1.54	1.28	1.81	5.5	4.4	6.3	.006	.33	.21	20.2	11.2	30.2	323	281	366	.046	.03	.06
	Hypersthene (1)			Clinopy-roxene (1)			Horn-blende (1)												Plagioclase (1)		
K	.0023			.037			.081			----	---	---	---	---	---	---	---	---	.10		
Rb	.0027			.032			.014			0.34(12)	2.24	.94	---	---	---	---	---	---	.041		
Sr	.0065			.516			.022			3.87	---	.672	---	---	---	---	---	---	4.4		
Ba	.0029			.131			.044			6.12	9.7	15.3	---	---	---	---	---	---	.308		
References *	1			1, 4, 5			1			4, 5, 6	2	4, 5	3	---	---	3	---	---	1		

* References are as follows:
1. Nagasawa and Schnetzler (1971).
2. Higuchi and Nagasawa (1969).
3. Nagasawa (1970).
4. Philpotts and Schnetzler (1970).
5. Schnetzler and Philpotts (1970).
6. Noble and Hedge (1970).

This table is taken directly from Arth (1976)

Chapter 4

THE DETERMINATION OF THE RARE EARTH ELEMENTS

Introduction

The rare earths constitute one of the most important groups of elements of geological interest. The reason for this is their close chemical coherence where the behaviour of an individual rare earth is closely linked with the others. This feature is clearly seen in chondrite normalised diagrams, the most commonly used graphical means of representing their abundances in igneous rocks. The rare earths cover a wide abundance range in natural materials and in igneous rocks this may be from parts per billion to the percent. A large number of analytical procedures have been developed for their determination but the most rapid and precise are those that use sophisticated instrumentation (X-ray Fluorescence, Mass-Spectrometry, Neutron activation followed by gamma spectroscopy, atomic absorption). Chemical separations of the rare earths may be required prior to the instrumental determination depending on the individual rare earth abundances or the presence of interfering elements. X-ray Fluorescence techniques are not uncommonly used to obtain the concentrations of La, Ce and Nd and the Lower Limits of Determination for these are approximately 5 p.p.m. in granitic and intermediate samples. A chemical group separation will often permit the other rare earths to be adequately determined. Neutron activation analysis has become the most widely used procedure for the determination of the rare earths owing to its high sensitivity, precision, the possibility of purely instrumental analysis and its relatively low overall cost compared with other high precision techniques.

Neutron activation was originally proposed in the 1930s, but it was not until 1957 that it was used in the modern sense for the determination of sodium in ultrabasic rocks (Salmon, 1957). The method has found considerable application in chemistry, the life sciences, applied physics and the earth sciences for the determination of a wide range of elements. Some 20-30 elements may be determined in a single sample by the so called instrumental neutron activation analytical method INAA of which the rare earths are an important group. The pioneering study by Gordon et al. (1968) has demonstrated the strengths of the technique when high quality semiconductor detectors are used. Hertogen and Gijbels (1971) considered the application of low-energy photon detectors LEPD to the non-destructive or instrumental INAA analysis of geological materials and they found that many of the rare earth elements were determined better with the low-energy detector than with a high-energy coaxial detector.

Destructive or radiochemical neutron activation analysis RNAA may provide higher sensitivity and accuracy than instrumental activation analysis and it is used accordingly for specialised studies. The radiochemical procedures may involve a group separation, the separation of individual elements or the removal of one or more elements which may cause serious interferences or high backgrounds if present. Special facilities may be required such as a laboratory designed for the handling of radioactive materials. Destructive procedures have been used for the analysis of meteoritic, ultrabasic,lunar and other materials where the element abundances are very low or where it is desired to remove interferences (Porrit, Porrit,1977; Filby et al., 1970; Laul et al., 1970; Haskin et al., 1968; Denechaud et al., 1970; Zielinski, 1975).

The present study has involved a considerable amount of radiochemical and neutron activation analysis. In view of the time spent on these operations and the importance of the rare earth group of elements to the geological interpretations it is considered appropriate to discuss the methodologies in detail.

A. Neutron Activation and Counting

The activation of an element by neutrons may be achieved using nuclear reactors, small accelerators or isotopic neutron sources, although the determination of most of the rare earth elements requires the high fluxes found in a reactor. The thermalised neutron fluxes obtained from accelerators and isotopic sources are not uncommonly about five or more orders of magnitude lower than the fluxes obtainable from nuclear reactors.

The neutrons produced in a nuclear reactor result from the fission of ^{235}U by thermal neutrons which are those having a most probable energy of 0.025 eV (velocity = 2200 ms^{-1}). More neutrons are generated than are required to cause fission and these make up the fission spectra where neutron energies range from 0-15 MeV and the most probable energy is 1 MeV. Absorption, scattering, spallation, fragmentation and fission may occur when a neutron interacts with matter although the first and second processes are the most probable at neutron energies below 1 MeV and it is these that concern the activation analyst. A number of neutron induced reactions may occur e.g. (n,γ), (n, p), (n,α), (n, 2n) but the radiative capture reaction or (n, γ) is the most likely to occur. Here the neutron is absorbed by the target nucleus to form a product nuclide with an atomic mass increase of one. Gamma radiation (prompt gammas) are ejected until the product nuclide is de-excited to the ground state, hence the notation (n,γ). The product nuclide may be stable or radioactive and it is the formation of the latter which is normally of interest to the activation analyst. The radiative capture reaction is associated with the emission of gamma radiation (prompt gamma) which facilitates the deexcitation of the product nuclide from its so called virtual and bound states to its ground state. These gamma rays are not those that are measured in activation analysis for their life time is very short. The gamma radiation which is measured results from the radioactive decay of the product nuclide and it may be associated with alpha or beta emission.

The likelihood of a nuclear reaction occurring, or its cross-section, (σ) is the reaction probability expressed as an effective area within which target and neutron will interact (σ, 1 barn $= 10^{-24}$ cm^2). In the thermal region most nuclides have cross-sections which are inversely proportional to the neutron velocity but in the epithermal region (0.1 - 10^5 e V) the cross-section for some nuclear reactions may change rapidly as a function of the neutron energy and resonances may be seen. Examples of the former case are $^{23}Na \rightarrow ^{24}Na$ and $^{58}Fe \rightarrow ^{59}Fe$ while $^{113}Cd \rightarrow ^{114}Cd$ and $^{197}Au \rightarrow ^{198}Au$ exemplify the latter (see fig. 8a, page 52a). During a routine irradiation the neutron flux consists essentially of thermal and epithermal neutrons although some advantages have been found when samples are irradiated without thermal neutrons. This is achieved by enclosing the samples in cadmium boxes because this element has a very large capture cross-section for thermal neutrons ($^{113}Cd \longrightarrow ^{114}Cd$ (stable), $\sigma \approx 20{,}000$) which are thus effectively filtered (see Brunfelt and Steinnes, 1969; Baedecker et al., 1977).

Production of radioactive nuclides

The induced activity for a particular nuclide may be calculated from:-

$$A_t = \frac{6.023.10^{23}.\sigma.\Phi.G.g}{100\ M} \quad 1 - e^{-\frac{0.6931t}{T}}$$

where:
A_t	activity produced during irradiation time t (disint. s^{-1})
Φ	neutron flux (n cm^{-2}s^{-1})
σ	activation cross-section (10^{-24}cm^2)
G	isotopic abundance %
g	wt. of element (g)
t	irradiation time
T	half-life of nuclide
M	Atomic weight of nuclide

The above equation is not used to determine the element abundances in the comparator method of analysis used in this study although it serves to show that the induced activity in a sample is dependent upon the

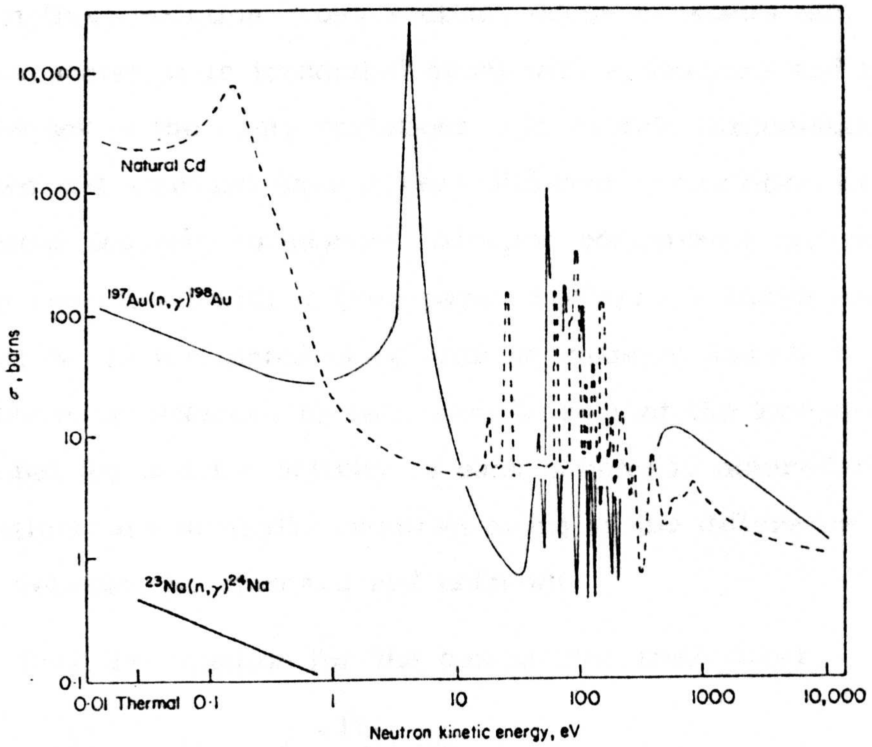


FIG. 8a Neutron capture cross-sections in barns as a function of neutron kinetic energy for natural Cd, Na and Au.

number of target atoms, their reaction cross-sections, the integrated neutron flux and the decay of the product nuclei during the irradiation and after. The comparator method eliminates the uncertainties in the neutron flux, reaction cross-section, decay constants etc. since the unknown material is irradiated along with a standard and both samples are subject to the same variations. In certain circumstances where the unknown and standard have a very different composition or where anomalous isotopic abundances exist,the comparator method may have errors associated with it (see pages 91-93). A known amount of an element W_s is irradiated along with an unknown sample W_u. Flux monitors are commonly attached to each sample so that the variations may be corrected for and the activity of each sample is determined. Half-life corrections are normally required owing to the difference in decay times between the standard and unknown.

Thus the equation for the comparator method is:

$$\frac{W_u}{W_s} = \frac{A_u}{A_s} \cdot \frac{(e^{-\lambda T_1}).\Phi_1}{(e^{-\lambda T_2}).\Phi_2}$$

where	A_u	measured activity in the unknown
	A_s	measured activity in the standard
	T_1	elapsed time after irradiation
	T_2	elapsed time after irradiation
	Φ_1	neutron flux correction factor
	Φ_2	neutron flux correction factor
	W_s	weight of element in standard
	W_u	weight of element in unknown

For most irradiations the number of atoms of a particular nuclide does not change appreciably although some nuclides with very large activation cross-sections may "burn-up" (e.g. ${}^{151}\mathrm{Eu} \xrightarrow{(n,\gamma)} {}^{152m}\mathrm{Eu}, {}^{152g}\mathrm{Eu}$; $\sigma = 9000$ barns). After the samples have been removed from the reactor their activity is allowed to diminish for a few days before they are counted. The nuclides likely to cause high activities in the present study are the short lived isotopes ${}^{152m}\mathrm{Eu}$, ${}^{165m}\mathrm{Dy}$, ${}^{165g}\mathrm{Dy}$, ${}^{140}\mathrm{La}$ and ${}^{153}\mathrm{Sm}$.

The radioactivity of product nuclides is caused by the emission of alpha particles, beta particles (electron and positron) gamma radiation and X-rays.

i) Alpha particles are monoenergetic helium nuclei and their relatively large mass prevents much penetration of matter. Their range is a function of the energy lost per unit path length and this in turn is a complex function of Z (atomic number of absorber) and the energy of the α-particle.

ii) Beta (β^-) decay occurs when the product nuclide has a neutron excess relative to its number of protons. The decay causes an increase in the atomic number by one but the atomic mass remains unchanged e.g.

$$^{232}_{90}\mathrm{Th} \xrightarrow{(n,\gamma)} {}^{233}_{90}\mathrm{Th} \xrightarrow[22\text{ mins}]{\beta^-} {}^{233}_{91}\mathrm{Pa} \xrightarrow[27\text{ days}]{\beta^-} {}^{233}_{92}\mathrm{U} \xrightarrow[10^5\text{ years}]{\alpha} {}^{229}_{90}\mathrm{Th} \xrightarrow{\hspace{2em}} \text{etc}$$

The above decay scheme continues until a stable nuclide is reached.

iii) β^+ (positron) decay occurs when the product nuclide has a proton excess relative to its number of neutrons. Positron emission results in a nuclide with an atomic number decrease of one and an unchanged atomic mass, e.g.

$$^{168}_{70}\mathrm{Yb} \xrightarrow{n,\gamma} {}^{169}_{70}\mathrm{Yb} \xrightarrow[31\text{ days}]{\beta^+} {}^{169}_{69}\mathrm{Tm}\ \text{(stable)}$$

Both types of beta decay are often accompanied by the emission of gamma rays if the daughter nuclide is in an excited state after the emission of the charged particle. The gamma radiation carries away the excess energy until the nuclide reaches its ground state. Analogous with positron decay is the phenomenon of electron-capture. Electron-capture results in the generation of characteristic X-rays of the daughter element. Alpha and beta particles are readily absorbed by matter depending on their energies, owing to their relatively high charge and mass. Special detection systems and sample preparations are required for their measurement.

iv) Gamma radiation frequently accompanies alpha and beta decay where it serves to de excite nuclei by a single gamma ray or a cascade of emissions between a number of excited levels until the ground state is reached. Gamma rays are monoenergetic, unlike beta radiation, and their highly penetrating nature enables their ready detection. The nucleus may also interact directly with orbital electrons of the K, L or M shells. The electron may be ejected from its orbital position with an energy equivalent to the energy of the gamma ray minus the binding energy of the electron. The orbital electrons are rearranged such that the missing electron site is filled. This process is associated with the production of characteristic X-radiation and the whole process is termed internal conversion. The degree of internal conversion is dependent on the atomic number of the nucleus and the energy and type of gamma transitions. An example of this process if found for the decay of $^{233}\mathrm{Pa} \xrightarrow{\beta^-} {}^{233}\mathrm{U}$ where uranium $K\alpha_1$ and $K\alpha_2$ X-rays are produced (94 + 98 KeV).

Interaction of gamma radiation with matter

Electromagnetic radiation reacts with matter by three main processes:

1) Photoelectric effect
2) Compton effect
3) Pair production

1) Photoelectric absorption occurs when a photon interacts with a bound electron and transfers all of its energy to that electron. Virtually all interactions occur with K and L electrons and their energies are equal to the difference in energy of the incident photon and the binding energy of the electron. The photoelectric effect occurs mainly with elements with a medium to high atomic number and with low photon energies. The probability of the process is proportional to Z^4 of the absorber and to E^{-3} (photon energy).

2) Compton interactions (incoherent scattering) occur when a photon collides with a free or weakly bound electron and transfers some of its energy. The energy transfer varies from zero to a maximum value defined by $E_{max} = E_o / 1 + (511/2E_o)$, where E_o is the photon energy in KeV and 511 KeV represents the energy equivalent to the rest mass of the electron. Compton scattering increases with the atomic number of the absorber and decreases with the energy of the incident photon.

3) Pair production can only occur with gamma rays having energies greater than 1.02 MeV and it results from the creation of an electron-positron pair. The positron eventually gives up its kinetic energy and it annihilates so that two 0.511 MeV gamma rays are produced.

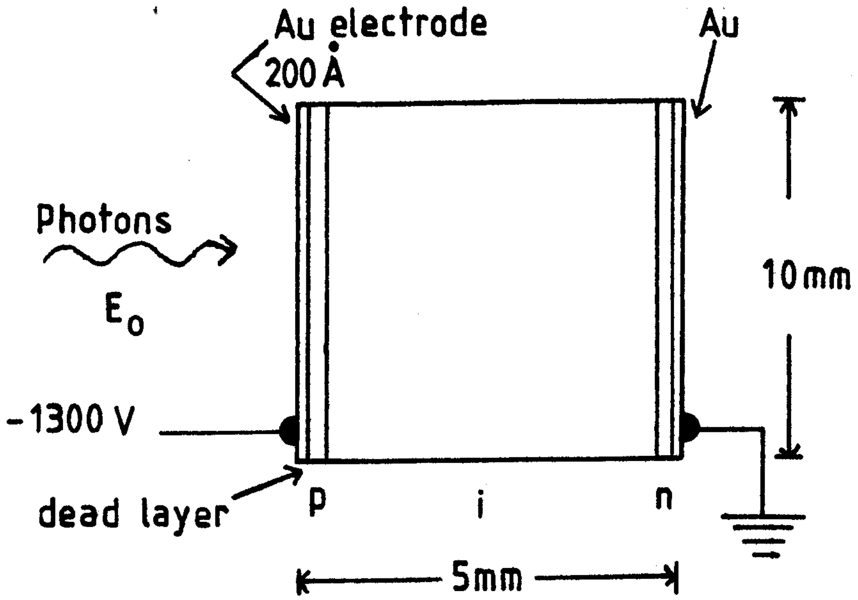
The behaviour of radiation as it encounters matter is clearly the basis for its detection and the effects of electromagnetic radiation on semiconductor detectors will be described. Such detectors respond to ionisation rather than the radiation and a photon enters the detector creating a cloud of electron-hole pairs. The number of these pairs is proportional to the energy of the photon.

$$E = n\varepsilon$$

where	E	is the photon energy
	n	the number of electron-hole pairs
	ε	the average energy required to produce an electron-hole pair

In semiconductor detectors the value of ε is about 2.9 eV for Ge and 3.6 eV for Si and its magnitude is partly responsible for the resolution capabilities of the detector. Early semiconductor detectors were constructed in a number of ways owing to the problems in obtaining pure materials. The impurities were capable of charge carrying and this resulted in a loss of detector proportionality. A means of correcting for this was to produce a compensated or intrinsic layer between the n-type material (electron acceptor) and the p-type germanium or Si (electron donor) where there is an effectively neutral charge. This type of detector is termed a p-i-n junction diode (see fig. 9 below) where negative acceptor ions are compensated for by the positive charge of lithium ions. Modern methods have enabled ultrapure Ge detectors to be produced without any need for charge compensation and such devices are called intrinsic germanium detectors. In order that the highly mobile lithium ions are contained within the crystal of a compensated detector and to reduce electronic noise it is necessary to operate semiconductors at very low temperatures. Cryostatic control is obtained with the aid of a copper rod, immersed in a dewar of liquid nitrogen in contact with the detector.

Figure 9



Diagrammatic cross-section of a reverse bias p-i-n junction planar Ge (Li) diode.

B. Theory of Cation Exchange Chromatography

Cation exchangers may be defined as materials which may exchange ions reversibly from an electrolyte solution (eluant). This analytical technique for separating elements has a considerable history although it was not until 1935 that a great development in the field occurred with the production of synthetic organic ion-exchangers. In recent years the number of organic based ion-exchange resins has increased although the most commonly used are the polystyrene-DVB type (DVB = divinyl benzene). The advantage of this type of resin is that it is monofunctional, that is its functional group is of a single type and may be for example, sulphonate (cation exchanger) or alkylamino (anion exchanger) although many other groups may be used. The divinyl benzene is an important structural constituent of the polystyrene framework since it affects a number of physical properties of the resin. Many resins contain about 8% DVB although other proportions are available and are specified by the manufacturers (e.g. Dowex 50W-X8 - the W designates the resin as being white and the X8 as containing 8% DVB).

General Properties (from Bockris, 1959 and Kitchener, 1957)

The sulphated* polystyrene resins, usually marketed in the sodium or hydrogen form, behave as strong acids and they may exchange their H^+ or Na^+ for the cations of other elements.

$$R_1SO_2OH + NaCl \rightleftharpoons R_1SO_2ONa + HCl$$

where R is the polystyrene matrix.

Thus the resin may take up cations from a solution under appropriate conditions and release an equivalent number of ions. Some important properties of cation exchange resins are as follows:-

1) Colour and density

Most of the commercially available resins are yellow or brown depending on the degree of cross-linkage (i.e. proportion of DVB). The more highly cross-linked resins are brown while the less crossed-linked may be almost colourless.

* sulphonated

2) Grain-size

Most polymerisation type resins are formed as small beads and manufacturers distribute them in a range of grain-sizes. 100-200#, for example, refers to grain diameters of 0.074-0.149 mm and the measurement is made prior to the addition of the functional group. Some fine resins are made simply by crushing larger grained beads followed by sieving to grade the particles.

3) Ion-exchange capacity

This is expressed as meq g^{-1} (milligram equivalents - meq) and it refers to the number of exchangeable sites which the resin possesses and it does not depend on the experimental conditions. A strong acid type resin (sulphonated polystyrene bead type) has an approximate exchange capacity of 5 meq g^{-1} (dry resin) or 2 meq cm^{-3}. The capacities of resins are determined by acid-base titrations or by the sulphur content of a given weight of resin. Thus, 2.0 meq of a univalent metal may be absorbed onto 1 cm^3 of conditioned resin and this could be displaced under suitable conditions by 1.0 meq of a divalent metal and so on.

4) Selectivity

Multivalent ions are more strongly absorbed from dilute solutions than ions of lower valence. The order of absorption on a strongly acidic cation exchange resin of elements of the same valence depends partly on the extent of hydration and other complexing in the eluting agent and the resin of ions since these facts may affect the effective size of the ions. In concentrated solutions the effect of valency is reversed and the multivalent ions are more readily dispelled from the resin than divalent or univalent ions.

5) Degree of cross-linking

Highly cross-linked resins have smaller pore-sizes, lower swelling capacities, lower exchange capacities and lower rates of ion exchange. As a result of these features highly porous resins (low cross-linking or DVB) are less selective since their porosity allows ions of various sizes into the resin structure. Thus a compromise between resin capacity and selectivity has to be made and for this reason resins of medium porosity are manufactured for general purposes with a cross-linking of about 8% DVB.

6) Operation rate

Cation exchangers reach equilibrium fairly rapidly and the rate controlling stage is not the chemical reaction but the diffusion rate. Diffusion of large ions is slower than that of smaller ions and therefore it is important that the rate of flow of eluant is not so great as to prevent approximate equilibrium being attained.

7) Chemical resistance

The polymerisation type resins have a high chemical resistance to strong non-oxidising acids and a moderate resistance to strong alkalis and oxidising acids.

8) Temperature

Polymerisation resins may withstand prolonged operating temperature of 100-120^{o}C.

A number of criteria need to be considered when setting up an operating cation exchange column for a particular separation scheme. In the present study the rare earth elements are required to be quantitatively separated from a solution containing many elements of variable concentration. For the separation of the REE the resin should have a large number of exchangeable sites, be chemically inert and adaptable to a wide range of experimental conditions.

The facts which may affect the performance of the resin are as follows:-

1) Column size

The column should be long and narrow so that the slight variations in chemistry between the lightest and heaviest REE may be accommodated. Owing to the "lanthanide contraction" and hydration-complexing effects the light rare earth elements are held more strongly than the heavy REE.

2) Resin particle size

The rare earth elution peaks are partly dependent on the resin mesh size and it is advisable to use as small a mesh size as possible consistent with obtaining adequate flow rates.

3) Cross-linkage

A X8 cross-linkage is found to be adequate for the separation of the REE since it is reasonably selective and has a high capacity.

4) Flow-rate

The width of an elution peak or curve (plot of percentage elution versus eluate volume) is a discontinuous function of the flow rate i.e. at very low flow rates the width of the peak is invariant but at very high flow rates the peak is absent since equilibration is not achieved.

5) Temperature

The widths of peaks vary inversely with the temperature since equilibration is achieved more rapidly at higher temperatures. Temperatures of $< 90^{o}C$ are in practice required since at higher temperatures bubbles may form due to boiling of the eluant.

6) Sample mass

Peturbation of elution peaks is noticeable when large amounts of an element are present. Elements present in trace amounts may be completely separated from one another but when one of the elements is present in relatively large quantities the elution peaks become very broad.

C. RNAA versus INAA

The technique used for the determination of the rare earth elements involves their group-separation using ^{144}Ce as a chemical yield monitor. The procedure may be classified as radiochemical neutron activation analysis although most descriptions of this method involve a post-irradiation separation of the elements of interest whereas the present technique employs a pre-irradiation separation (Denechaud et al., 1970; Haskin et al., 1968; Zielinski, 1975). The more commonly used non-destructive analytical procedure, such as that used by Gordon et al. (1968) and Hertogen and Gijbels (1971), possesses advantages and disadvantages and these are listed below along with those for the destructive technique.

Advantages

RNAA	INAA
1) Useful for determinations of very low - high abundance elements	1) Useful for routine determinations of elements at low -high abundances
2) Many interfering elements removed	2) Multi-element determination possible
3) High peak/background ratio	3) High precision data obtainable
4) Spectra are fairly simple	4) The sample is effectively unchanged after the irradiation and it may be used for subsequent studies if required
5) Reasonable precision and high accuracy	
6) The spectral data can often be reduced without large computers	

Disadvantages

RNAA	INAA
1) Restricted range of elements may be determined, generally < 10	1) Interfering elements may be numerous resulting in very complex spectra
2) Well-equipped laboratory required	2) A large computer is generally required to reduce the spectral data
3) The sample is effectively destroyed	3) Some peaks may be obscured by the commonly high background
	4) Absorption of energies below 150 KeV by the sample may be appreciable

Thus, it is clear that both methods have their merits although if an analyst is interested in only a small group of elements, such as the rare earths, and the expertise for the chemical manipulations has been developed then high quality data may be obtained more rapidly through RNAA than INAA. The use of a pre-irradiation separation technique is not very common although it does have a number of interesting aspects.

1) Shielding effects due to the presence of elements with high thermal neutron absorption cross-sections or high resonance absorption integrals are greatly reduced.

2) Matrix elements which activate readily (e.g. sodium) are removed and therefore special handling precautions are not required.

3) The reagent blanks may require consideration whereas they are insignificant with post-irradiation separation (see page 69a).

D. The Radiochemical Procedures

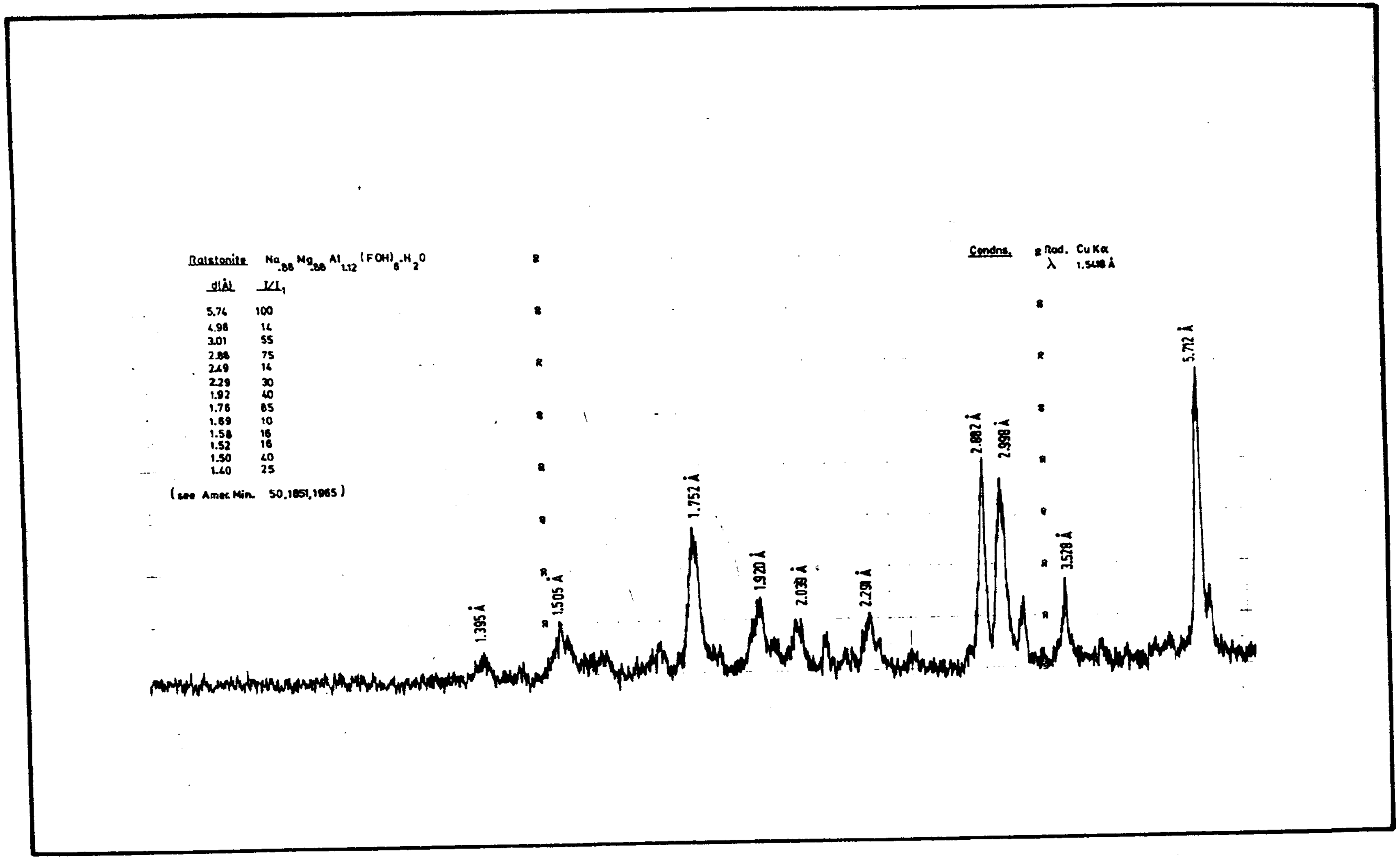
The chromatographic method used for the separation of the rare earths has been used for a number of years (Edge and Ahrens, 1962; Towell, 1963; Zielinski, 1975). The particular method employed was described and supplied on request by R.A. Zielinski (1975) and it is to be found in the appendix (page 317). A number of modifications were made and the complete method is shown in the flow chart (fig. 11, page 66) and described in this section. Essentially the technique involves a sample digestion, cation-exchange chromatography and sample collection and preparation ready for neutron activation.

1. Hydrofluoric-perchloric acid digestion

This technique is a well established method in the wet-chemical analysis of silicate material and a detailed description is considered unnecessary. A useful observation was made during the course of the digestions which does not appear to be cited in the literature. During the evaporation of SiF_4 it was found to be essential that the residue did not dry out and that repeated damping with a few drops of perchloric acid was required. This ensures that all traces of fluoride are removed and that the residue is converted to perchlorates. If the residue dries out at an early stage of the evaporation (the dense, white fumes) of SiF_4, complex aluminium fluorides are formed which prove to be practically impossible to dissolve. A sufficient quantity of this white insoluble material was obtained for analysis by X-ray diffraction and the trace obtained is shown in fig. 10, page 65. An examination of the d-spacings of the material, corresponding to the peaks obtained, shows that a close comparison may be made with those of the mineral Ralstonite, which is a hydrated sodium magnesium aluminium fluoride.

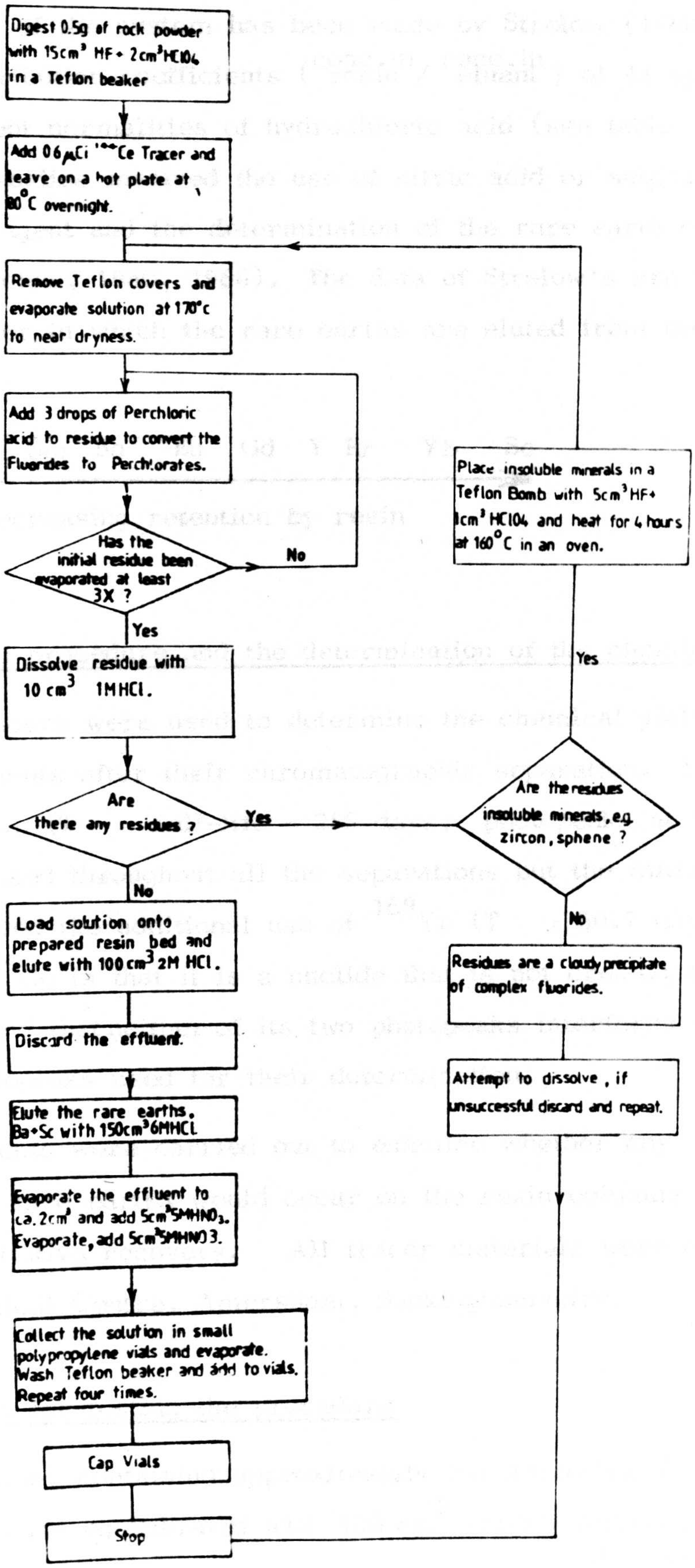
This observation is clearly very important since neglecting the precipitate may produce erroneous results and any sample which showed the precipitate was discarded.

Figure 10



An X-ray diffraction chart recording of the insoluble residue that may be formed from improper digestion procedures. The material is closely similar to the naturally occurring mineral ralstonite.

Figure 11



A flow chart showing the radiochemical procedure for the separation of the rare earth elements.

2. The ion-exchange of the rare earths

A useful study of the system has been made by Strelow (1960) who determined the distribution coefficients ($\frac{\text{conc. in resin}}{\text{conc. in eluant}}$) of 43 species of cations at different normalities of hydrochloric acid (see table 2 , page 68). Later studies involved the use of nitric acid or sulphuric acid as the eluting agent and the determination of the rare earth elements in carbonatites (Strelow, 1960, 1966). The data of Strelow's are useful for showing the order in which the rare earths are eluted from the resin column.

La Ce Sm Ba Eu Gd Y Er Yb Sc

$$\xrightarrow{\hspace{12em}}$$

decreasing retention by resin

Testing experimental procedure and the determination of the chemical yield

Radioactive tracers were used to determine the chemical yield of the rare earth elements after their chromatographic separation. The fission product ^{144}Ce (T = half-life = 285 days; photopeaks at 80 KeV and 134 KeV) was used throughout all the separations but the initial testing of the method involved the additional use of ^{169}Yb (T = 30.7 days). The advantage of ^{144}Ce is that it is a nuclide that is not created during neutron activation and that neither of its two photopeaks interferes with any rare earth photopeaks used for their determination.

Early experiments were carried out to examine whether any fractionation of the rare earths would occur on the resin columns and to test for their quantitative recovery. All tracer materials were obtained from the Radiochemical Centre, Amersham, Buckinghamshire.

Experimental Method for testing the procedure

1) The resin column, containing approximately 5 g Amberlite CG 120 (100-200 mesh), is equilibrated with 100 cm^3 6MHCl followed by 100 cm^3 2 MHCl at a flow rate of approximately 1 cm^{3}min^{-1}.

Table 2

A selectivity scale for various species of cations, Strelow (1960, 1966)

	Equilibrium Distribution Coefficients in Hydrochloric Acid						
Cation	0.1*N*	0.2*N*	0.5*N*	1.0*N*	2.0*N*	3.0*N*	4.0*N*
Sc(III)	$>10^4$	3200	500	120	28.8	14.9	11.7
Sm(III)	$>10^4$	$>10^4$	1330	217	39.0	15.4	8.6
Gd(III)	$>10^4$	$>10^4$	1220	183	30.2	11.4	6.1
Er(III)	$>10^4$	$>10^4$	990	165	27.2	10.7	6.0
Yb(III)	$>10^4$	$>10^4$	960	153	27.4	12.2	7.4
ZrO^{+2}	$>10^5$	$>10^5$	$\sim10^5$	7250	489	61	14.5
Th^{+4}	$>10^5$	$>10^5$	$\sim10^5$	2049	239	114	67
La^{+3}	$>10^5$	10^5	2480	265.1	48	18.8	10.4
Ce^{+3}	$>10^5$	10^5	2460	264.8	48	18.8	10.5
Y^{+3}	$>10^5$	$>10^4$	1460	144.6	29.7	13.6	8.6
Ba^{+2}	$>10^4$	2930	590	126.9	36	18.5	11.9
Hg^{+} •	$>10^4$	7600	640	94.2	33	19.2	13.6
Al^{+3}	8200	1900	318	60.8	12.5	4.7	2.8
Sr^{+2}	4700	1070	217	60.2	17.8	10.0	7.5
Ga^{+3}	$>10^4$	3036	260	42.58	7.75	3.2	0.36
Ca^{+2}	3200	790	151	42.29	12.2	7.3	5.0
Pb^{+2} •	$>10^4$	1420	183	35.66	9.8	6.8	4.5
Fe^{+3}	9000	3400	225	35.45	5.2	3.6	2.0
Cr^{+3}	1130	262	73	26.69[b]	7.9	4.8	2.7
Tl^{+} •	173	91	41	22.32	9.9	5.8	3.3
Ni^{+2}	1600	450	70	21.85	7.2	4.7	3.1
Co^{+2}	1650	460	72	21.29	6.7	4.2	3.0
Mg^{+2}	1720	530	88	20.99	6.2	3.5	3.5
Mn^{+2}	2230	610	84	20.17	6.0	3.9	2.5
Fe^{+2}	1820	370	66	19.77	4.1	2.7	1.8
Cs^{+1}	182	99	44	19.41	10.4	...	...
UO$_2^{+2}$	5460	860	102	19.20	7.3	4.9	3.3
Ag^{+} •	156	83	35	18.08	7.9	5.4	4.0
Cu^{+2}	1510	420	65	17.50	4.3	2.8	1.8
Hg^{+2} •	4700	1090	121	16.85	5.9	3.9	2.8
Zn^{+2}	1850	510	64	16.03	3.7	2.4	1.6
Rb^{+}	120	72	33	15.43	8.1	...	...
K^{+}	106	64	29	13.87	7.4	...	...
Be^{+2}	255	117	42	13.33	5.2	3.3	2.4
Ti^{+4}	$>10^4$	297	39	11.86	3.7	2.4	1.7
V^{+4}		230	44	7.20	...	...	...
Na^{+}	52	28.3	12	5.59	3.6	...	...
Li^{+}	33	18.9	8.1	3.83	2.5	...	...
Sn^{+4}	$\sim10^4$	45	6.2	1.60	1.2	...	...
Cd^{+2}	510	84	6.5	1.54	1.0	0.6	...
V^{+5}	13.9	7.0	5.0	1.10	0.7	0.2	0.3
Mo^{+6}	10.9	4.5	0.3	0.81	0.2	0.4	0.3
Se^{+4}	1.1	0.6	0.8	0.63	1.0	...	0.7
Bi^{+3}	Ppt.	Ppt.	<1.0	1.0	1.0	1.0	1.0
As^{+3}	1.4	1.6	2.2	3.81	2.2	...	...
Sb^{+3}	Ppt.	Ppt.	Ppt.	Ppt.	2.8	...	...
Pt^{+4}	...	...	...	1.4	...	...	...
Au^{+3}	0.5	0.1	0.4	0.84	1.0	0.7	0.2
Hg^{+2}	1.6	0.9	0.5	0.28	0.3	0.2	0.2

• Done in nitric acid.

[b] More than one cationic species present.

2) 100 $\mu\lambda$ (microlitres) of ^{144}Ce solution corresponding to 1.2 μCi (1 μCi = 3.7 . 10^4 disintegrations per second) is added to a solution containing 50 mg $FeCl_3$. This solution is intended to mimic the solution obtained after the sample digestion with hydrofluoric acid.

3) The tracer solution is loaded and allowed to flow into the resin, care being taken not to allow the resin bed to drain dry.

4) The column is eluted with 100 cm^3 of 2MHCl at a flow rate of approximately 1 $cm^3 min^{-1}$. The iron begins to appear, as a yellow solution, after 25 cm^3 of eluant has passed through the resin.

5) The resin column is scanned slowly with a small radiation monitor which is fitted with a lead sheet cowling around its barrel to limit the radiation that may enter the detector.

6) The rare earth tracer is removed from the column by elution with 150 cm^3 6M HCl.

The same procedure described above was employed with the ^{169}Yb tracer. A final study involved measuring the advance of the point of maximum activity and the results of all three tests are shown in fig. 12 (page 70). The tracer investigation has shown that the furthest advance for ^{144}Ce is 10 cm from the top of the resin bed and for ^{169}Yb the furthest advance is 14 cm after 100 cm^3 2MHCl has passed through the resin. The rate of advance of an elution peak is slow when using 2MHCl and greater than 300 cm^3 of this strength of acid would be required before ^{169}Yb began to pass out of the column (see fig. 12). The cerium and ytterbium tracers were removed from the column by eluting with 150 cm^3 of 6MHCl. No evidence was found for the tracers being retained by the resin after this volume of eluant had been passed.

The conclusions from the preceding account and from the data of Strelow (1960, 1966 see table 2) are that the experimental conditions described by Zielinski (1975, appendix III) are appropriate for the separation and quantitative recovery of the rare earths from geological material.

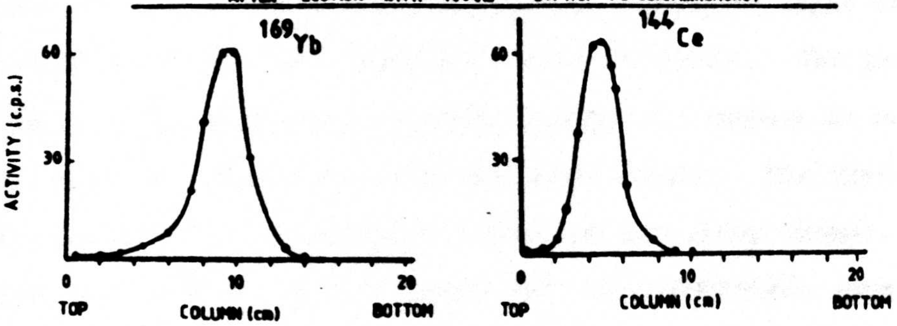
Blanks

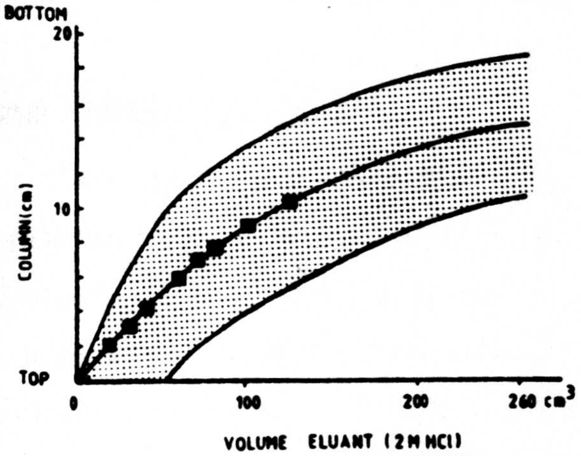
A potential source of positive systematic error, when using pre-irradiation group separations, is the extent of the reagent blanks. Zielinski (1975) found the REE blanks in his study to be less than 0.1% for BCR-1. In this study two determinations were made to assess the significance of the reagent blanks. Two "separations" were carried out without there being a sample present. The reagents were evaporated to dryness after passing through the ion exchange columns and the residues were irradiated. No rare earth peaks were observed in spectra accumulated over 10,000 seconds and therefore the blanks are below the detection limit for the analytical procedure used.

Figure 12

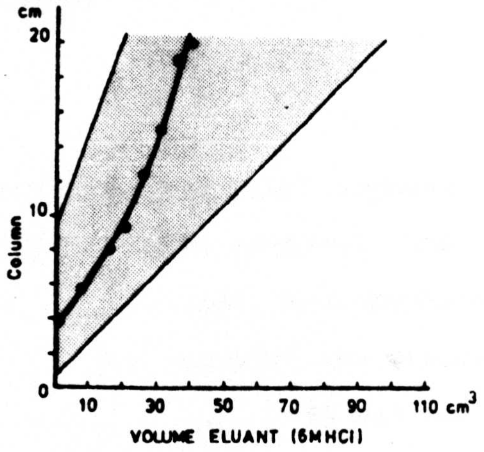
RESULTS OF THE TRACER EXPERIMENTS TO TEST THE ION-EXCHANGE PROCEDURE.

THE GRAPHS REPRESENT THE DISTRIBUTION OF THE TRACERS IN A RESIN COLUMN AFTER ELUTION WITH 100 cm³ 2M HCl (5 determinations)





THE SQUARES DEFINE THE MAXIMUM RADIOACTIVITY OF ^{169}Yb IN RELATION TO ELUANT VOLUME AND POSITION. THE FIELD DELIMITS TRACER DISTRIBUTION.



THE SOLID CIRCLES DEFINE THE MAXIMUM ACTIVITY OF ^{144}Ce AND THE STIPPLED FIELD DELIMITS ITS DISTRIBUTION IN THE RESIN BED.

Note: It is not uncommon in column chromatography to attach a separating funnel to the top of the burette so that it may act as a reservoir for the eluting agent. This technique was not used in this study. A system was devised where the elution could take place and stop after approximately 100 cm^3 of 2M HCl (or 150 cm^3 6M HCl) had passed through the resin. A peristaltic pump with a twelve channel capacity was used to deliver the eluant via small bore plastic tubing to eight resin columns (Watson-Marlow H.R. Flow Inducer; Type MHRE22). The pump was connected to a timer-switch and this enabled the device to be turned off after the required volume of acid had been eluted. The flow rate of the acid was controlled by a tumbler switch on the pump motor. This system permitted easy control of flow rates and semi-automatic elution of up to twelve columns at one time although it was found that eight was the largest number that could be readily handled.

Final Sample Preparation

The rare earth elements, along with barium and small amounts of scandium, were collected in 150 cm^3 6M HCl in teflon beakers. The solutions were evaporated to dryness and the chlorides were converted to nitrates by addition of 10 cm^3 3M HNO_3. This solution was evaporated to about 3 cm^3 before it was transferred to a 14 O.D. x 16 mm polypropylene vial. The teflon beaker was rinsed with deionised water and placed on a hot-plate operating at 110°C. The small vials were placed in depressions machined into a 1 cm thick slab of aluminium the purpose of which was to distribute the heat evenly around the vials thus facilitating rapid evaporation. The rinse from the teflon beaker was poured gently into the vial and this was repeated until all signs of radioactivity disappeared from the beakers. All vials were filled with pure cellulose powder after their solutions had evaporated to dryness and they were then capped and sealed.

The rare earths cannot be irradiated as chlorides since ^{35}Cl activates to the long-lived, beta emitting ^{36}Cl.

E. Sample Counting and Instrumentation

Detector System and Operating Conditions

The use of high quality electronic equipment is an essential requirement for neutron activation analysis where Ge (Li) or intrinsic Ge detectors are used. The typical instrumentation layout and specifications are shown below.

Detectors

i) Ortec 8000 series planar Ge (Li) spectrometer with cooled
FET: active volume = 0.4 cm^3
Operating bias - 1300 Volts
Window material 0.13 mm beryllium
Resolution at 5.9 KeV = 254 eV
Resolution at 122 KeV = 600 eV

ii) Ortec 8000 series coaxial Ge (Li) spectrometer
Active volume = 43.5 cm^3
Nominal efficiency = 9.3 %
Peak/Compton = 33:1
Resolution at 1332 KeV = 1.91 KeV
Operating bias = + 2800 Volts

Bias Supply

i) Ortec 459
ii) Ortec 459

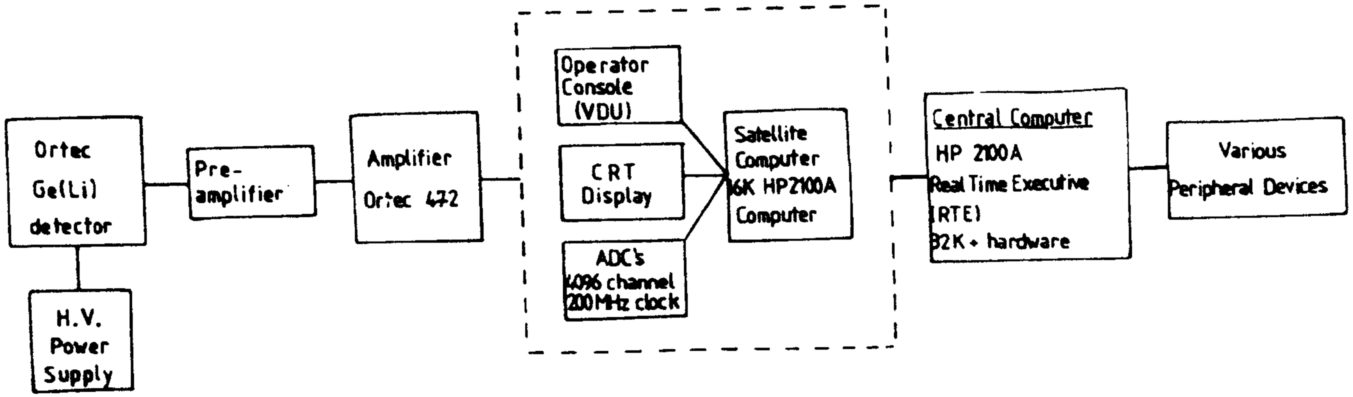
Amplifier

Ortec 472 using 2μsec shaping time constant and base line restorer at LO

Analogue to Digital Converter

Hewlett-Packard H-P5416B ADC was used along with a 16K H-P2100A Computer. 4096 channels were used to accumulate all spectra.

Figure 13



Instrumentation layout for NAA data accumulation

Sample Counting Procedure

The separated materials, after having been irradiated at the University of London Reactor Centre for 16-22 hours in a flux of approximately $1.6 \times 10^{12}\, n\, cm^{-2} s^{-1}$, were allowed to cool for three days. Counting was carried out at a number of times using a coaxial and a planar Ge (Li) spectrometer at the Radiation Centre of the University of Birmingham. Samples were placed in constant geometry counting devices attached to both detectors and they were counted in a position such that the ADC deadtime indicator was less than 10 %. Counting times varied from 1000 sec to 15,000 sec and all spectra were stored on magnetic tape so that they could be recalled, using the Radiation Centre's computer, for close examination.

Three different phases of counting were carried out in order to provide the information for element determinations in the various samples.

1)	Chemical yield determination	(1 count)
2)	Neutron Flux monitors	(1 count)
3)	Samples	(3 counts)

1) The chemical yields of the group separated samples were determined prior to irradiation by counting the activity of the 133 KeV photopeak of ^{144}Ce with a NaI (Tl) scintillation detector. Since all measurable activity was derived from the tracer there were no problems of resolving interferences and the high efficiency of the scintillation detector allowed over 40,000 counts to be accumulated in 100 secs.

The yields were calculated by dividing the counts obtained from a group separated sample by the counts obtained from the same quantity of tracer which had not been subjected to a chromatographic separation. Samples with a chemical yield better than 95 % were submitted for irradiation although only fifteen samples out of approximately one hundred had incurred losses greater than 5 %.

Table 3

Low Energy Photon Detector Measurements

Time after irradiation	Countset	Isotope	Energies measured (KeV)	Counting time
3-7 days	I	^{153}Sm	103	1000 secs
		^{239}Np	106	
14-17 days	II	^{141}Ce	145	10,000 secs
		^{147}Nd	91	
		^{152}Eu	122	
		^{169}Yb	63.5	
		^{177}Lu	208	
30-35 days	III	^{141}Ce	145	10,000 secs
		^{152}Eu	122	
		^{160}Tb	87	
		^{233}Pa	98	
		^{169}Yb	63.5	

High energy photon detector measurements

3-7 days	I	^{140}La	1596	1000 secs
14-17 days	II	^{141}Ce	145	10,000 secs
		^{147}Nd	91, 531	
		^{152}Eu	122, 243, 1408	
		^{160}Tb	298, 879	
		^{169}Yb	177	
		^{208}Lu	208	
		^{233}Pa	312	
30-35 days	III	^{141}Ce	145	10,000 secs
		^{152}Eu	122, 1408	
		^{160}Tb	298, 879	
		^{233}Pa	312	
		^{169}Yb	177	

2) The reactor's neutron flux variation was monitored by attaching a disc of 'Specpure' iron foil (99.9 % pure, Johnson Matthey) to each sample. After irradiation the foils were removed from the samples and counted using a NaI(Tl) scintillation detector. The 1099 KeV and 1291 KeV photopeaks of ^{59}Fe (T = 44.6 days) were integrated to obtain their peak areas and over 80,000 counts could usually be collected in two minutes. A correction factor for all samples was calculated by correcting the flux monitors for their weight differences followed by normalising the flux monitor counts to the monitor with the largest counts. These correction factors effectively remove the neutron flux variations from each sample.

3) The sample spectra were accumulated using both the planar and coaxial Ge(Li) detectors and three counts were carried out with both devices. The spectra obtained from the group separated samples are shown for the international reference sample NIM-G and the reference sample BOB-1 at different times after their irradiation (figs 14,15,16,17). The spectra were accumulated with both detectors although none of them has been corrected for variations in neutron flux, sample weight, or decay times but qualitative information may be gleaned from them. The spectra of figure 17 show clearly how the high background associated with non-separated material may obscure many small peaks. Peaks due to Ba, Sc and Pa (from Th) appear in some separated materials and these result from either limitations of the chromatographic procedure or the collection of an excessive amount of the 6 MHCl eluent. No serious problems have been encountered where these elements are present and Sc and Pa are generally present in small quantities. The spectra of fig. 15 shows the effects of sample decay on the granitic rock, NIM-G. The relatively smooth baseline results from the very low Sc content of this rock. Figs 14 and 16 show the spectra accumulated using the planar detector for both separated and non-separated material. The chromatographically purified samples have considerably more simple spectra owing to the removal of Ta, Hf, Th and Fe and their lower activities are due to the fact that they received a smaller neutron flux than the non-separated samples.

Figure 14

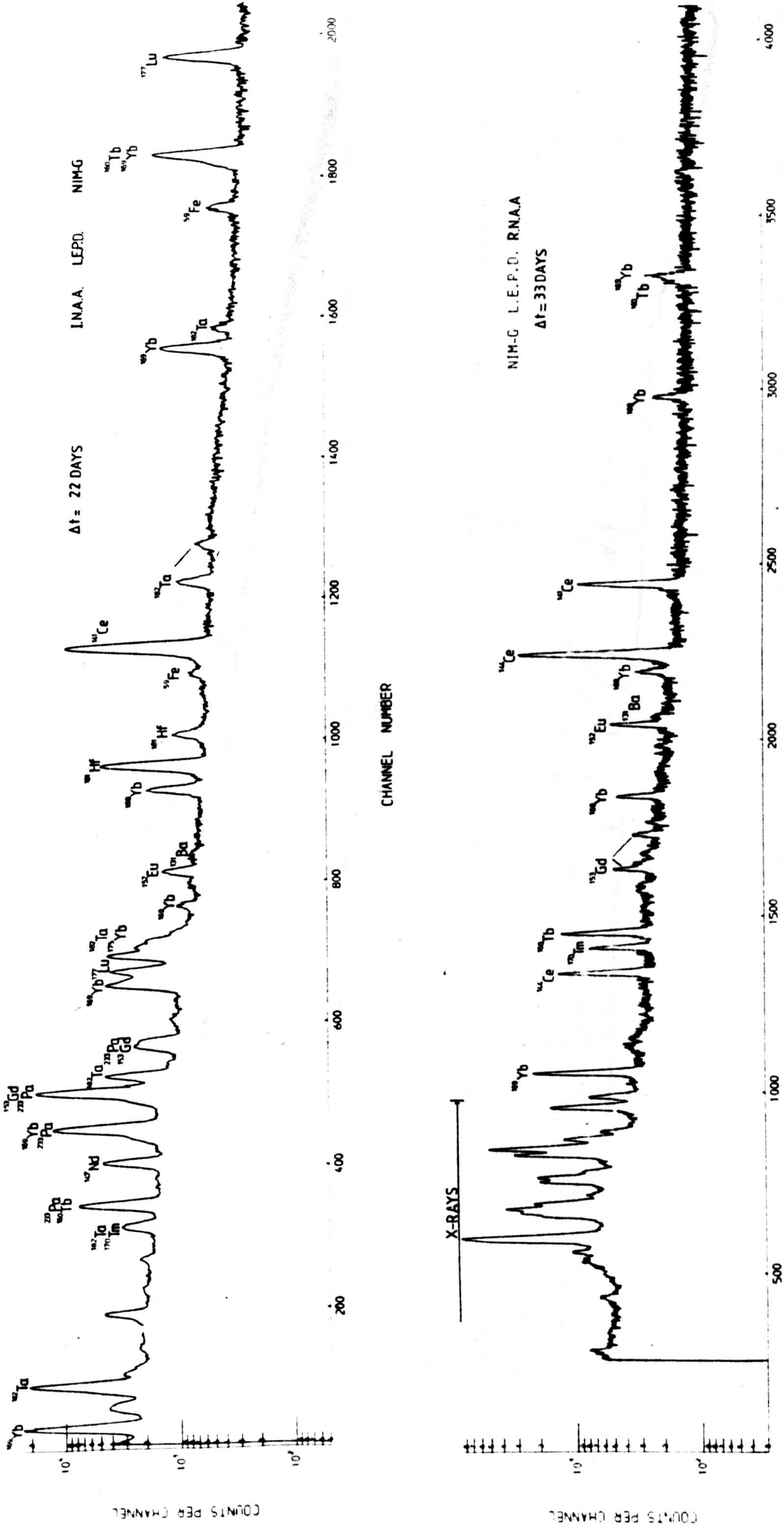
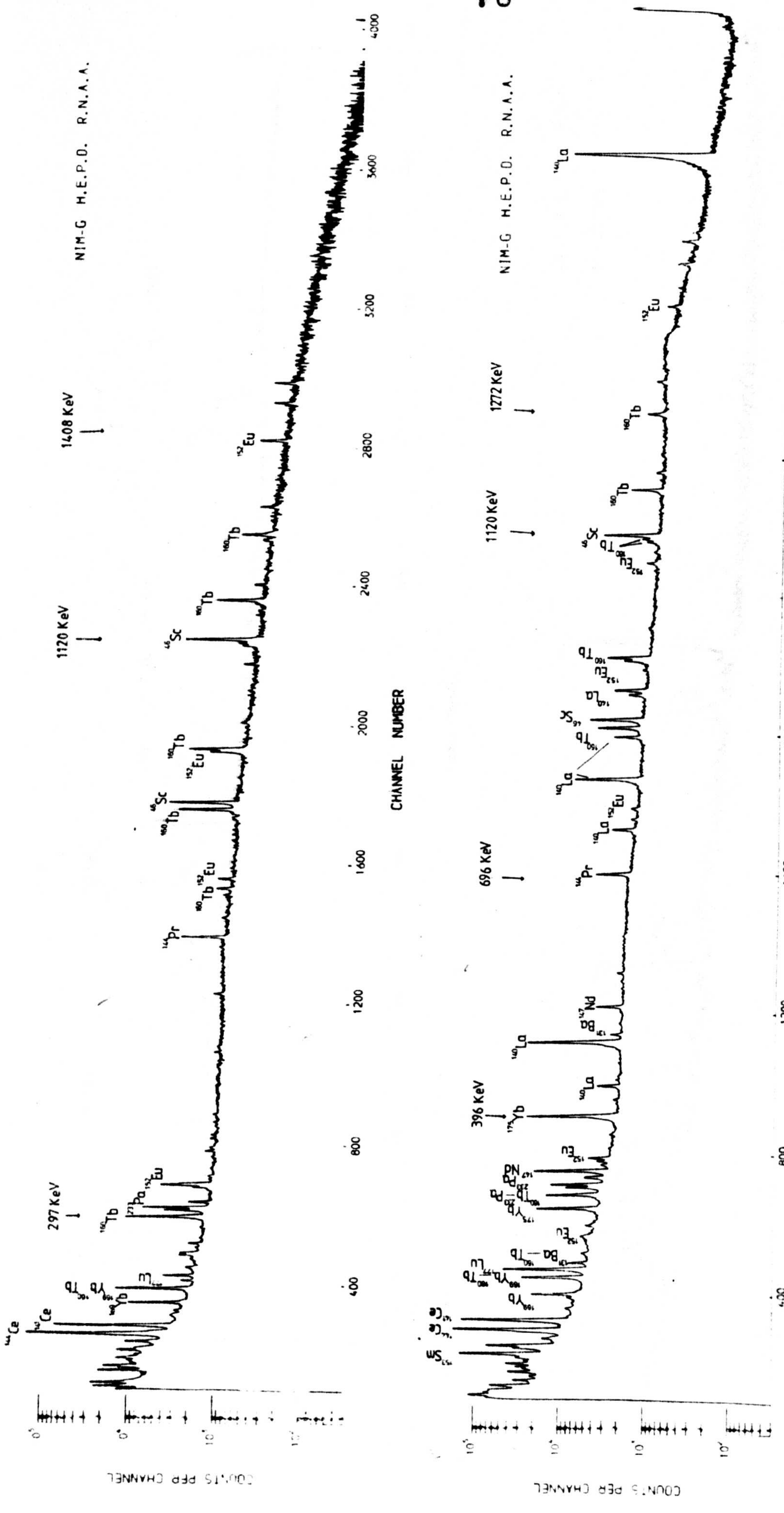

I.N.A.A. L.E.P.D. NIM-G
Δt = 22 DAYS
169Yb
182Ta
182Ta 170Tm
233Pa 160Tb
147Nd
169Yb 233Pa
153Gd 233Pa
182Ta
233Pa 153Gd
169Yb 177Lu
182Ta 175Yb
169Yb
152Eu
131Ba
169Yb
181Hf
181Hf
59Fe
141Ce
182Ta
182Ta
169Yb
59Fe
160Tb 169Yb
177Lu
200
400
600
800
1000
1200
1400
1600
1800
2000
CHANNEL NUMBER
COUNTS PER CHANNEL
NIM-G L.E.P.D. R.N.A.A
Δt = 33 DAYS
X-RAYS
169Yb
141Ce
170Tm
160Tb
153Gd
169Yb
152Eu
131Ba
169Yb
144Ce
143Ce
169Yb
160Tb
169Yb
500
1000
1500
2000
2500
3000
3500
4000
CHANNEL NUMBER
COUNTS PER CHANNEL

Figure 15


NIM-G H.E.P.D. R.N.A.A.
297 KeV
1120 KeV
1408 KeV
144Ce
141Ce
160Tb
169Yb
177Lu
131Ba
152Eu
144Pr
46Sc
CHANNEL NUMBER
COUNTS PER CHANNEL
400
800
1200
1600
2000
2400
2800
3200
3600
4000
NIM-G H.E.P.D. R.N.A.A.
396 KeV
696 KeV
1120 KeV
1272 KeV
153Sm
175Yb
140La
147Nd
CHANNEL NUMBER
COUNTS PER CHANNEL

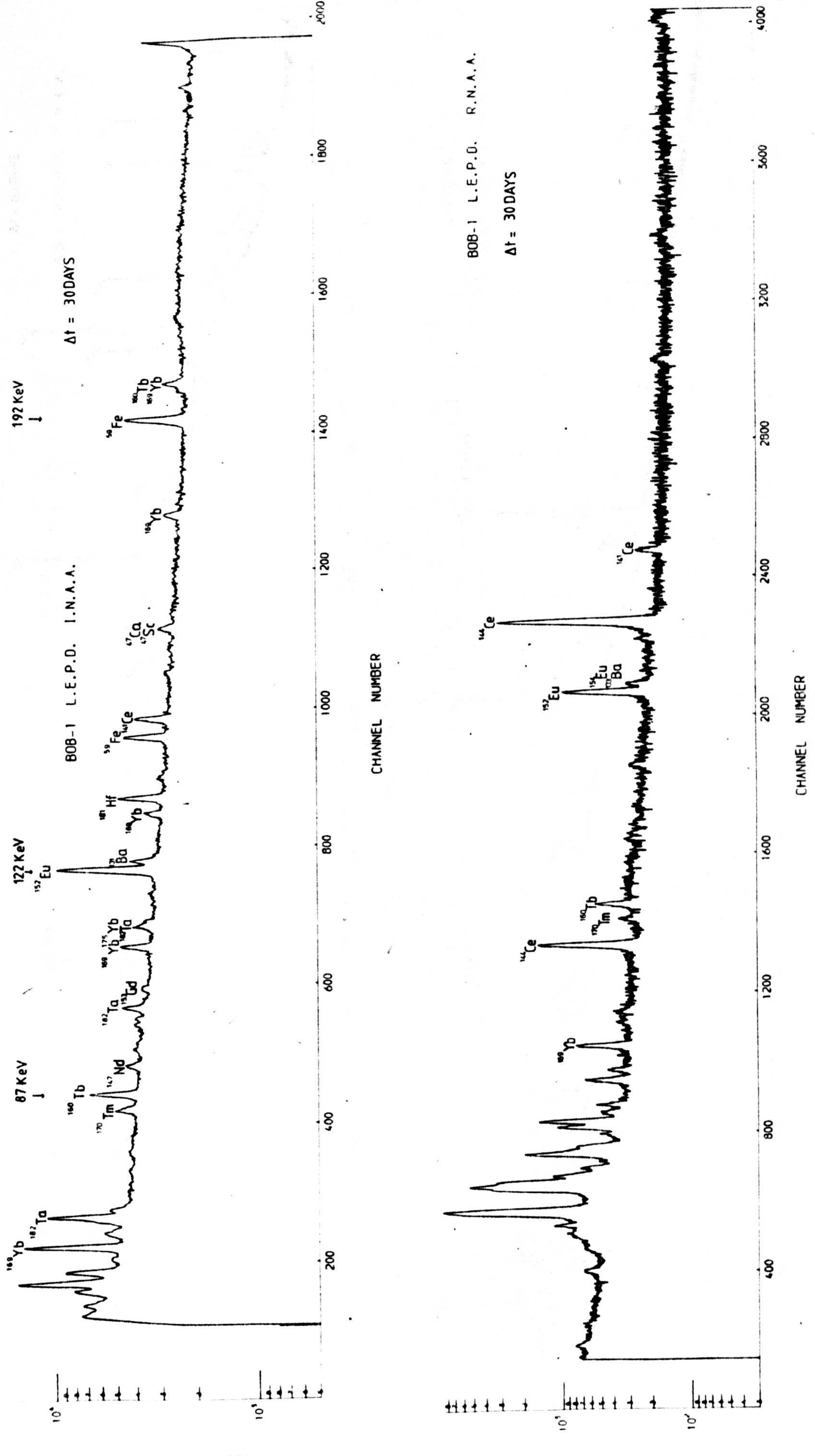

BOB-1 L.E.P.D. I.N.A.A.
Δt = 30DAYS
87 KeV
122 KeV
192 KeV
169Yb
182Ta
170Tm
160Tb
147Nd
182Ta
153Gd
169Yb
175Yb
182Ta
152Eu
131Ba
169Yb
181Hf
59Fe
141Ce
47Ca
47Sc
169Yb
59Fe
160Tb
169Yb
200
400
600
800
1000
1200
1400
1600
1800
2000
CHANNEL NUMBER
10⁴
10³
COUNTS PER CHANNEL
BOB-1 L.E.P.D. R.N.A.A.
Δt = 30DAYS
169Yb
144Ce
170Tm
160Tb
152Eu
154Eu
133Ba
144Ce
141Ce
400
800
1200
1600
2000
2400
2800
3200
3600
4000
CHANNEL NUMBER
10³
10²
COUNTS PER CHANNEL

Figure 16

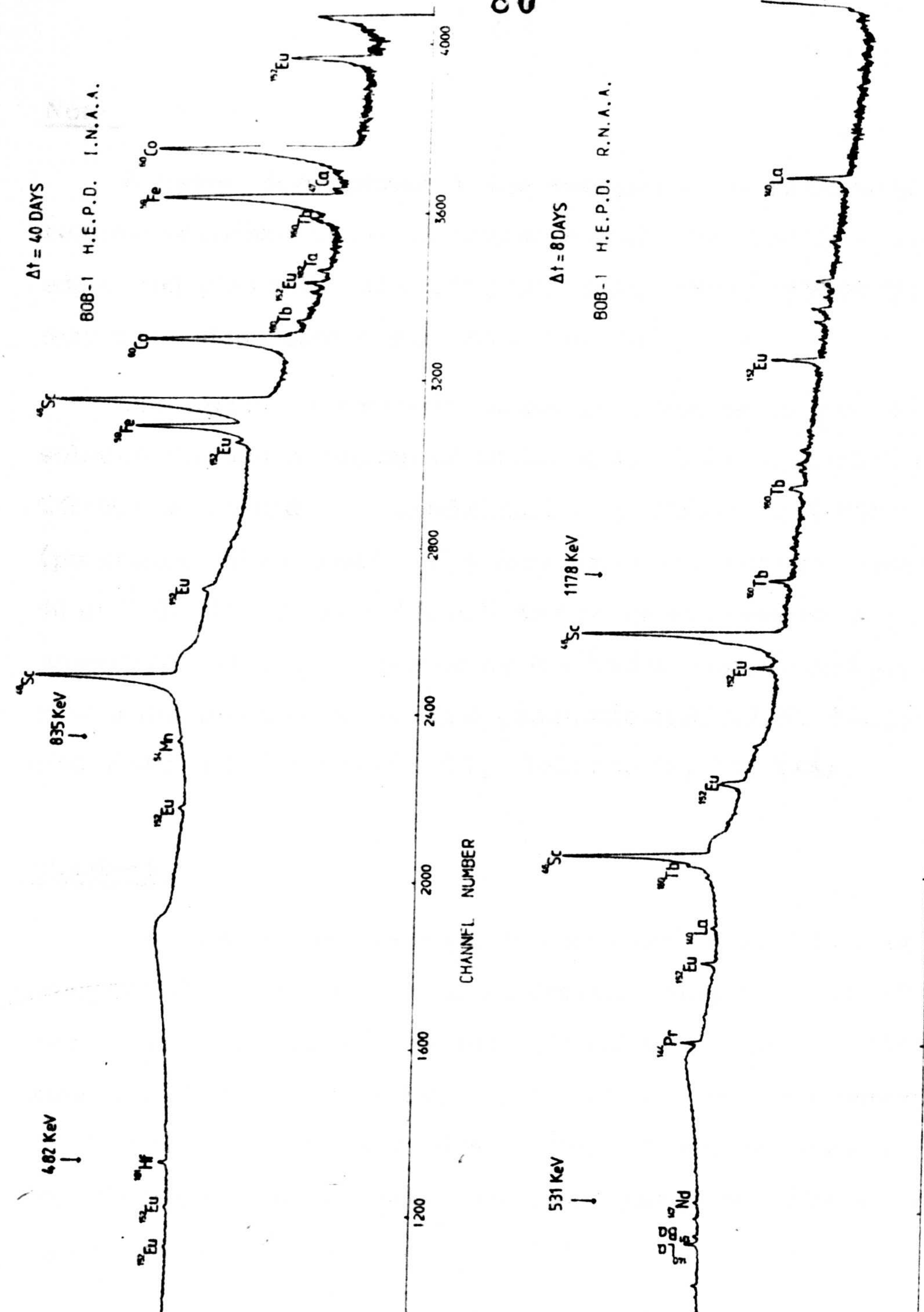

Δt = 40 DAYS
BOB-1 H.E.P.D. I.N.A.A.
192 KeV
482 KeV
835 KeV
CHANNEL NUMBER
COUNTS PER CHANNEL
Δt = 8 DAYS
BOB-1 H.E.P.D. R.N.A.A.
531 KeV
1178 KeV
CHANNEL NUMBER
COUNTS PER CHANNEL
400
800
1200
1600
2000
2400
2800
3200
3600
4000
10^5
10^4
10^3
10^2
^{152}Eu
^{59}Fe
^{181}Hf
^{141}Ce
^{169}Yb
^{160}Tb
^{51}Cr
^{54}Mn
^{46}Sc
^{60}Co
^{140}La
^{47}Ca
^{144}Ce
^{153}Sm
^{147}Nd
^{131}Ba
^{144}Pr

Figure 17

Note

A useful development of the analytical procedure would be to remove scandium since its presence may give rise to sizeable Compton edges and plateaux. Element peak areas determined in these regions may have significant errors associated with them.

One means of removing scandium would be to pass the initial solution through a column of Dowex-1 X8, 200-400 mesh (or Amberlite CG400) which had been conditioned with 100 cm^3 0.5 MHCl - 0.5 MKSCN (potassium thiocyanate). The rare earth elements are eluted with about 40 cm^3 0.5 MHCl - 0.5 MKSCN and Sc is retained on the column. This procedure has been employed by the United States Geological Survey and it was disclosed in a personal communication (J.W. Morgan, 1979; see also Fritz and Kaminski: 1971, Talanta, 18, 541-548).

Standards

The comparator technique is commonly applied to neutron activation analysis where an unknown and reference sample are irradiated together and element abundances are proportional to the ratio of the counts in the standard after all corrections have been applied. An important requirement of the comparator method is that all samples have a similar matrix and abundances of elements such that neutron shielding or gamma ray absorption are equivalent.

The standards used for the rare earth determinations were the international references NIM-G (granite), BCR-1 (basalt), the reference sample BOB-1 (basalt) and a synthetic standard that was prepared by the author. All standards were subjected to the same chemical treatment as the unknowns to avoid differences in neutron shielding and matrix absorption of gamma energies.

The synthetic multi-element standard was prepared by spiking solutions of known concentration into Vitreosil silica. The solution strengths were determined by a titrimetric procedure using $Cu(NO_3)_2$ and EDTA (ethylene diammine-tetra-acetic acid) and details of the method may be found in Haskin et al. (1968). The silica was prepared by crushing silica tubing in an agate TEMA until it was about 200 mesh followed by acid washing and ignition to 1100°C. All rare earth element abundances in the standard materials may be found in the section on analytical results (pages 94-98).

Element energies used for determinations T = half-life

^{140}La (T = 40.2 hrs) There are a number of useable energies for the determination of this element but 1596 KeV was used since it is not interfered with and it lies on a region of low background. The photopeak was only measurable using the large coaxial detector. No correction for ^{235}U fission products was required.

^{141}Ce (T = 32.5 days) The 145.5 KeV photopeak is the only one for this nuclide and no serious interferences were found using either detector. Since iron was removed during the cation-exchange process no ^{59}Fe peaks existed which could have caused interferences. Some background placement problems may occur when using the large detector because the low energy region of the spectra are crowded with lines. The coaxial detector provided similar cerium results to those found with the planar detector although they were generally higher with the former. No corrections for ^{235}U fission products were necessary.

^{147}Nd (T = 11.1 days) The 91 KeV and 531 KeV energies were used for the planar and coaxial detector determinations. Neither peak is interfered with but there are relatively large counting errors associated with the 531 KeV peak owing to its low intensity. No corrections for ^{235}U fission products were necessary.

^{153}Sm (T = 46.8 hrs) The photopeak at 103 KeV was used for the determinations of this element and results of high precision are obtained because of the high intensity of the energy. The planar detector was used for measurements and the only possible interferences are from

^{153}Gd (103 KeV) and ^{239}Np (103.6 KeV). The contribution from gadolinium was insignificant at the time of counting since the Gd/Sm peak area ratio was less than 1 %. The interference from ^{239}Np (from ^{239}U) was not usually significant but where a ^{239}Np peak at 106 KeV was found, resulting initially from the escape of uranium from the cation-exchange column, it was necessary to apply the following correction.

Peak area (^{239}Np, 103.6 KeV) = 0.77 * Peak area (^{239}Np, 106 KeV)

The contribution from ^{239}Np to the ^{153}Sm photopeak at 103 KeV could therefore be subtracted.

The factor 0.77 represents the relative intensity ratio of (^{239}Np, 103.6 KeV/^{239}Np, 106 KeV) and it was found by counting a sample of uranium (Uranium oxide, 99.97 %; Koch-Light Laboratories) after it had been irradiated in the thermal neutron facility of the Radiation Centre's Dynamitron accelerator.

^{152}Eu (T = 12.7 yrs) This element was determined using the 122 KeV and the 1408 KeV photopeaks of the ^{152}Eu isotope. No serious interferences were found and the computer program, used for processing the spectra, was able to resolve the 122-123 KeV partial overlap from the 124 KeV peak of ^{131}Ba.

^{153}Gd (T = 236 days) This element cannot be satisfactorily determined using a coaxial detector and the low intensity of the 103 KeV photopeak, and its interference from ^{153}Sm, requires that it is counted at least a month after irradiation with the planar detector. No determinations were made for this element owing to the large errors associated with its measurement which result from the very poor counting statistics.

^{160}Tb (T = 72.1 days) Terbium is not determined with high precision by the coaxial detector since all of its peaks are interfered with although acceptable results were obtained using the 298 KeV and 879 KeV peaks. ^{233}Pa peaks were observed in some spectra owing to the collection of an excessive amount of 6 MHCl eluting agent during the chromatographic separations. Where these peaks were seen it was necessary to correct the ^{160}Tb peaks at 87 KeV and 298 KeV since they are both interfered with by ^{233}Pa at 86.6 KeV and 299.9 KeV . The relative intensities of the ^{233}Pa peaks at these energies were found by irradiating a sample of thorium oxide (99.9 % purity, Koch-Light Laboratories) in the Radiation Centre's Dynamitron neutron facility. It was found that the 86.6 KeV peak of ^{233}Pa was 0.165 times as intense as the 98 KeV ^{233}Pa peak. The 98 KeV peak is a $UK\alpha_1$, x-ray energy formed by internal conversion as ^{233}Pa decays by beta emission to ^{233}U. The 299.9 KeV peak of ^{233}Pa was found to be 0.17 times as intense as the photopeak at 312 KeV. Thus where ^{233}Pa (from ^{233}Th) peaks were observed their contributions to the ^{160}Tb peaks could be removed by the use of the determined correction factors.

^{170}Tm (T = 130 days) This nuclide has one peak at 84.3 KeV and no serious interferences were found since ^{182}Ta (84.7 KeV) was not seen in any of the spectra. The peak intensity was generally too low for acceptable results to be obtained and the element was not determined.

^{169}Yb (T = 30.7 days) Ytterbium is favourably determined using either detector although the coaxial detector gave slightly higher values than the planar detector. The 63.5 KeV and 177 KeV energies were used and no interferences were found for either peak. Tantalum and Hafnium are the elements most likely to have caused overlaps but their presence was not noted.

^{177}Lu (T = 6.74 days) Lutetium may be determined by its peaks at 113 KeV or 208 KeV although the latter is preferable since there are no serious interferences associated with it and the background is less complex than that found for the 113 KeV peak. Both detectors provided similar results although higher precision was obtainable using the coaxial detector owing to the better counting statistics.

F. Data Reduction

The spectral data for all samples, counted six times each, were stored on magnetic tape using the Birmingham Radiation Centre's hardware and software. The data were transferred, via a special data link at the Radiation Centre, to the large ICL 1906A computer which serves the University. Spectra could be read back from magnetic tape into the Centre's Hewlett-Packard 2100A computer, if desired, and displayed or analysed using one of three satellite stations equipped with its own computer, visual display units and data accumulation facilities but linked to the real-time executive (RTE).

The computer program, MEGRASPEC, was used for the reduction of all spectral data and it was provided by K. Randle of the Radiation Centre. The original program, called BRUTAL, was written at Livermore Laboratory, modified and described by workers at the Brookhaven National Laboratory and further modified by K. Randle. Digital or non-iterative mathematical procedures are used in the program to search for peaks, determine their complexity and calculate peak areas corrected for background and discernible overlaps. An example of the output produced by MEGRASPEC and a copy of its description and operating procedures may be found in appendix D. Peak areas are determined by a similar method to the total peak area or YULE technique (Yule, 1968) where the contents of all channels in the peak are summed. The program fits a Gaussian to the upper part of all peaks to define their characteristics more accurately.

A number of other digital methods of peak integration have been devised and Baedecker (1971) has discussed the advantages of five methods other than the total peak area technique. His conclusions concerning the use of total peak areas were that they were less precisely determined than the peak areas found using the five other methods. However, where large differences in sample dead-time existed or where changes in resolution occurred during the data acquisition the YULE technique was superior to the others. Neither of these effects were found to occur during the collection of the present data. The differences between the various methods are in the choice of baseline, linear or quadratic form, and the peak integration limits. Some procedures, for example, ignore the channels situated near peak boundaries since they add to the overall uncertainty of the peak areas but do not contribute significantly to its net area.

Photopeak areas may be determined by iterative or fitting procedures where a mathematical function is fitted to the data. The program SAMPO (Routti and Prussin, 1969) for example, fits a Gaussian with an appended exponential tail to photopeaks, the latter accounting for the deviation from a Gaussian on the lower part of the peak. Baedecker (1977) and Yule and Rook (1977) have studied the reproducibility and accuracy between the digital and non-digital methods of photopeak integration. Yule and Rook examined the precision of peak area determinations using the program SAMPO (non-digital) and programs incorporating the total peak area method (digital). Their results show that the fitting method is slightly superior but that neither technique works well for small peaks. The program SAMPO requires over an order of magnitude more computer time than a program using a digital procedure. In view of these facts it is uncertain whether the use of iterative or fitting programs with their slightly higher precision can justify the costly computer time.

An unknown and a standard were counted for 10^5 seconds and the spectra were processed by SAMPO and MEGRASPEC in order to determine whether significant differences in the ratio unknown/standard existed. The table below shows that although the computed area may differ the ratio is approximately the same.

The variation between ratios is generally less than 2%, although 5% for ^{231}Pa, and these errors are within the overall analytical precision of the techniques employed (see following section, page 89). Thus for the described analytical technique there does not seem to be any significant advantage in using the program SAMPO although for very complex spectra with unresolved peaks there may be some advantage.

Peak Areas

Peak	MEGRASPEC Unknown	MEGRASPEC Standard	SAMPO Unknown	SAMPO Standard	Megraspec Unk/Std	Sampo Unk/Std
^{141}Ce	34301	67654	34920	67516	0.5070	0.5172
^{144}Ce	37398	36695	37930	36977	1.0191	1.0257
^{147}Nd	15387	22312	15560	22205	0.6896	0.7007
^{160}Tb	23291	41951	23310	42882	0.5552	0.5435
^{170}Tm	5334	9843	5592	10344	0.5419	0.5406
^{169}Yb	79038	141986	78830	142099	0.5566	0.5547
^{233}Pa	7870	81187	6895	75061	0.0969	0.0918

G. Analytical Results

The results of the rare earth determinations in the samples from North Wales are shown in table 4 (page 99a). Four unknown samples were included in a polyethylene irradiation tube with a reference sample (BCR-1, NIM-G, BOB-1 or the synthetic sample, page 97). Six irradiations were obtained (1 at ICI, Billingham; 1 at Aldermaston; 4 at the University of London Reactor Centre) and a total of 43 unknown samples along with seven standards were analysed. The granitic reference NIM-G was analysed in quadruplicate to estimate the precision of the techniques and seven reference samples (BCR-1, NIM-G, BOB-1, SY-2, JB-1, MRG-1 and the synthetic standard) were irradiated at the same time in order that the accuracy could be assessed. The reference sample BCR-1 was used as the standard to calculate the rare earth element abundances of the six other reference materials.

a. Random Errors in NAA

Random errors determine the reproducibility of a result and in the present study their most probable source is the chemical yield determination, counting and also peak area determinations.

1) Chemical yield determination. The transferring of $50\mu\lambda$ (microlitres, 10^{-6} litre) of ^{144}Ce tracer using a micropipette is clearly a source of error and the combined uncertainty of this procedure and the subsequent counting of the activity was determined. An aliquant of ^{144}Ce tracer was added to ten counting vials and the activity was counted. The relative standard deviation was found to be 3 % and this uncertainty must be associated with all samples.

2) Counting statistics. Since radioactive decay and its measurement are statistical processes it is possible to apply statistical laws to estimate their associated uncertainties. Detailed statistical treatments may be found in De Soete et al. (1972).

The uncertain ty or standard deviation of a particular measurement is the square root of the number of counts accumulated in the peak and backgrounds:

$$\sigma = \sqrt{N}$$

but since errors are associated with peak and two background determinations:

$$\sigma = \sqrt{N_{PK}} + \sqrt{N_{bK1}} + \sqrt{N_{bK2}}$$

where N is the number of counts.

The overall uncertainty of the analytical technique is thus,

$$\sigma^2 = \left[\frac{\sqrt{N_{PK}} + \sqrt{N_{bK1}} + \sqrt{N_{bK2}}}{N_{PK}}\right]^2 + (0.03)^2$$

where the last term represents the error of the yield determination.

Element	R.S.D. % (1) counting stats.	R.S.D. % (2) Analysis
La	1.2	3.2
Ce	1.5	3.3
Nd	3.6	4.7
Sm	1.1	3.2
Eu	1.5	3.3
Tb	2.0	3.6
Yb	1.6	3.4
Lu	1.4	3.3

R.S.D. = relative standard deviation (%)

(1) Relative standard deviation due to counting statistics.

(2) Relative standard deviation due to counting statistics and chemical yield determination.

The peak and background characteristics of sample TYM were used for the determination of the precision. Some samples may therefore have higher or lower precision.

Four samples of the granite NIM-G were irradiated together and one of them was used as the standard for the remaining three. The rare earth data given by Jackson and Strelow (1975)* were used to compute the abundances.

Standard* - Chem. Geol., 15, 303-307 n = 4 samples

	NIM-G	NIM-G	NIM-G	NIM-G	Mean (ppm)	Std.dev. (ppm)
La	105	103±3	110±3	108±3	107	3
Ce	195	203±7	205±7	198±7	200	5
Nd	73	75±3	71±3	76±3	74	2
Sm	15.5	16.2±.5	14.7±.5	16.1±.5	15.6	0.7
Eu	0.39	0.41±0.01	0.38±0.01	0.36±0.01	0.39	0.02
Tb	2.10	2.24±0.08	1.99±0.07	2.18±0.08	2.1	0.1
Yb	13.3	14.2±0.5	13.9±0.5	12.9±0.5	13.6	0.6
Lu	2.1	2.36±0.08	2.17±0.08	2.06±0.08	2.2	0.1

(1) (2)

Two remaining samples were analysed in duplicate.

	A7	A7
La	20.2	20.3
Ce	48.3	45.1
Nd	30.0	26.6
Sm	8.52	8.44
Eu	1.79	1.74
Tb	1.5	1.5
Yb	5.1	4.9
Lu	0.8	-

N.B. The errors quoted in column (1) are those from counting statistics and the yield determination whereas those of column (2) represent the standard deviation calculated from a population of four samples

$$\text{S.D.} = \sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}}$$

b. Systematic Errors

Systematic errors are those which affect the accuracy of the analytical technique and they may arise in a number of ways.

1) Anomalous isotopic abundances
2) Variable neutron fluxes induced by shielding effects
3) Matrix absorption of gamma rays
4) Interfering nuclear reactions
5) Dead-time corrections
6) Line overlaps
7) Variable neutron spectra

1) Anomalous abundances of some nuclides have been noted and De Soete et al. (1972) state that isotopes of Ce, Nd and Yb may fractionate under some natural conditions. This possibility can be investigated only by mass spectrometry and in the absence of such data the extent is uncertain.

2) Variable neutron flux doses may be received by two samples if they contain variable amounts of nuclides with very high absorption cross-sections. These nuclides may effectively cause neutron shielding. This problem is not likely to be serious for samples which have undergone a pre-irradiation group separation although some of the rare earth isotopes possess very large cross-sections and with such materials shielding may occur, e.g. Samarium.

3) The absorption of gamma energies below 150 KeV may be appreciable for certain matrices. Where standards and unknowns are almost identical the effects of matrix absorption become unimportant since photopeak areas are ratioed. It is difficult to achieve this close control of samples and a number of precautions will be necessary for samples greater than about 200 mg in weight (see Croudace, 1979). Where small sample weights are chosen to obviate or minimise matrix effects the problems of inhomogeneity and sensitivity loss become important. Samples which have been chemically separated are unlikely to suffer from mass absorption differences.

4) Interfering nuclear reactions may be primary or secondary. Primary reactions of potential importance are the fission of ^{235}uranium by thermal neutrons to produce a number of fission products which will include La, Ce, Pr and Nd. Since uranium was removed, or was present in very minor amounts, by the chromatographic technique, the (n,f) reaction is not likely to occur.

The cross-sections of (n,p), (n,α), (n,2n) etc. reactions in a nuclear reactor are considerably smaller than the (n,γ) reaction and they may be ignored.

Secondary nuclear reaction may occur where samples are irradiated for very long periods or subjected to a very high neutron flux and where the concentration of elements of adjacent atomic number are appreciable. The reactions are also largely dependent on the cross-section of the primary reaction and the half-life of its daughter.

$$^{139}\mathrm{La} \xrightarrow[9\ \text{barns}]{(n,\gamma)} {}^{140}\mathrm{La} \xrightarrow[40\ \text{hrs}]{\beta^-} {}^{140}\mathrm{Ce} \xrightarrow{(n,\gamma)} {}^{141}\mathrm{Ce}$$

$$^{164}\mathrm{Dy} \xrightarrow[5000\ \text{barns}]{(n,\gamma)} {}^{165}\mathrm{Dy} \xrightarrow[2.35\ \text{hrs}]{\beta^-} {}^{165}\mathrm{Ho} \xrightarrow{(n,\gamma)} {}^{166}\mathrm{Ho}$$

The two reactions shown above are two which may occur during long irradiations and the second reaction is more likely to produce significant errors if holmium is to be determined. De Soete et al. (1972, p. 487) have presented a table to show the magnitude of second-order reactions. For a flux of 10^{12} n cm^{-2} s^{-1} and an irradiation time of 10^5 seconds, ^{141}Ce from ^{139}La may be about 70 pp.b. whereas Ho from ^{164}Dy may be as high as 35 p.p.m. Generally, second-order interferences are not significant for most rare earth element determinations.

5) Dead-time corrections are not considered to be a serious source of error since all samples were counted within 10 % deadtime and the amplifier used is easily capable of correcting for this scale of deadtime.

6) Line overlaps may be a significant source of error although most if not all possible interfering element energies which coincide with rare earth element energies are known. Partial overlaps are usually removed quite adequately by the computer programs used to process spectral data. Complete overlaps require a knowledge of the intensity of the interfering peak and this may often be calculated after the peak area of a single uninterfered peak at another energy is found. Secondary x-rays formed by the excitation of elements in the samples or in the vicinity of the detector by β or gamma-rays of high energy may introduce errors. The gold-electrode of the planar detector is excited by intense beta emitters or by gamma energies which are close to the gold K absorption edge and energies corresponding to the $K\alpha_1$, $K\alpha_2$, $K\beta_1$ and $K\beta_2$ lines may be found. No rare earth photopeak energies of interest corresponded to the gold x-rays and therefore this feature is not important in the present study.

Total or partial energy absorption may occur in a detector and where there is partial absorption the photoelectric effect may operate along with Compton interactions and pair production. The detector material may be excited by the photoelectric effect to produce characteristic x-rays and these may escape from the detector. In Ge(Li) detectors the escape peaks occur about 10 KeV below the photopeak (Ge $K\alpha = 9.9$ KeV; $K\beta = 11$ KeV) and should be observable up to 1 MeV. However, since high energy photons may penetrate deeply into germanium, the escape probability becomes practically negligible so escape peaks can hardly be observed. Escape peaks may be produced after pair production where they occur at 511 KeV and 1022 KeV below the photopeak with an energy greater than 1022 KeV. The interferences produced by escape peak phenomena due to the photoelectric effect are not appreciable above 40 KeV with the planar detector (Baedecker et al., 1977; Hertogen and Gijbels, 1971) and escape peaks associated with other processes were not found to occur in the spectra obtained with the coaxial detector.

c. Results of Reference Materials Compared with Other Reported Values

A "true" analytical value is rarely if ever attainable and an assessment of the "true" value may only be made by many determinations in different laboratories using different analytical techniques. A mean of all the available data is not always chosen as the recommended value since some analytical techniques are considered superior to others and the data may be weighted accordingly. The international reference sample BCR-1 (Columbia river basalt) is perhaps the best known of all the materials analysed in this study and for this reason it has been used as the ultimate standard for the other reference samples.

BCR-1 USGS REFERENCE

La	26	25.1 (5)	23.8 (5)	23.8 (3)
Ce	53.9	54.1 (1)	48.8 (12)	-
Nd	29	29.3 (4)	30.0 (13)	29.6 (4)
Sm	6.6	6.77 (5)	6.52 (10)	6.51 (3)
Eu	1.94	1.95 (2)	1.92 (7)	1.86 (6)
Tb	1.0	1.03 (*)	1.06 (10)	-
Yb	3.36	3.52 (4)	3.17 (8)	-
Lu	0.55	0.57 (8)	00.52 (15)	0.48 (12)
	(1)	(2)	(3)	(4)

* interpolated value

(1) Flanagan (1973) recommended values.

(2) Seifert et al. (1977) average of 7 isotope dilution results.

(3) Seifert et al. (1977) average of 5 NAA results.

(4) Brunfelt and Steinnes (1973) ENAA.

Figures in brackets are the relative standard deviations (%) of interlaboratory results.

NIM-G (Granite) National Institute of Mining, South Africa

La	110	3.2	105	114	107	-
Ce	190	3.3	195	192	198	195
Nd	72	4.7	73	60	-	-
Sm	15.28	3.2	15.5	18.6	-	-
Eu	0.40	3.3	0.39	0.38	-	0.47
Tb	2.62	3.6	2.1	3.4	2	-
Yb	13.08	3.4	13.3	13.3	14	14.2
Lu	2.04	3.3	2.1	1.7	-	-
	(1)	(1a)	(2)	(3)	(4)	(5)

(1) This work, RNAA, analyst I. Croudace.

(1a) Relative standard deviations for this work in %.

(2) Jackson and Strelow (1975) Isotope Dilution.

(3) Erasmus et al. (1977) INAA.

(4) Recommended values; Steele et al. (1978); NIM Report 1945.

(5) Pal and Terrell (1978), INAA.

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SY-2 (Syenite) Canmet, Canada

La	71	53	85	75	74
Ce	144	130	210	215	200
Nd	79	71	70	110	100
Sm	17.11	14	16	16	14
Eu	2.42	2.0	2.2	2.4	1.9
Tb	2.44	2.2	-	2.7	5.0
Yb	17.97	18.0	17	16	14
Lu	2.55	2.5	3	2.7	11
	(a)	(b)	(c)	(d)	(e)

(a) This work, RNAA, I. Croudace.

(b) Strelow and Jackson see Abbey et al. (1975)

(c) Abbey et al. (1975), Recommended values.

(d) Pal and Terrell (1978), INAA.

(e) Rosenberg and Zilliacus (1977), INAA.

Analytical errors for this work are the same as those above.

MRG-1 (Gabbro) Canmet, Canada

La	11	8.6	10	9.2	10	8.1
Ce	27	26	25	25	25	24.6
Nd	19	23	20	19	-	18.0
Sm	5.58	5	6.4	4.3	-	4.2
Eu	1.59	1.5	1.3	1.39	1.4	1.3
Tb	0.54	0.53	0.5	0.58	-	0.46
Yb	0.79	0.82	0.7	0.78	1.0	0.44
Lu	0.11	0.09	0.31	0.15	-	0.065
	(1)	(2)	(3)	(4)	(5)	(6)

(1) This work, RNAA, analyst I. Croudace

(2) Strelow and Jackson (see Abbey et al., 1975), Isotope Dilution

(3) Pal and Terrell (1978) INAA

(4) Rosenberg and Zilliacus (1977) INAA

(5) Abbey et al. (1975) Recommended values

(6) Jackson (1975) (see Abbey et al., 1975), Isotope Dilution

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JB-1 (Alkali basalt) Geological Survey of Japan

La	37	37.1	36	36	37	36
Ce	68	68	65	67	67.5	67
Nd	29	27.7	30	21	26.8	25
Sm	5.21	5.6	4.7	4.8	5.13	4.8
Eu	1.59	1.6	1.5	1.5	1.55	1.52
Tb	0.8	0.73	-	-	0.77*	0.5
Yb	2.09	2.21	1.2	2.1	2.14	2.1
Lu	0.31	0.23	0.33	0.3	0.308	0.3
	(a)	(b)	(c)	(d)	(e)	(f)

*interpolated

(a) This work RNAA

(b) Open University (Pers. Comm.) (1979)

(c) Randle (1974) INAA

(d) Abbey (1976)

(e) Tanaka (1975) I.D.

(f) Flanagan (1973)

BOB-1 (ocean-floor basalt) Birmingham University,
Geology Department

	(1)	(2)	(3)	(4)	(5)	(6)
La	5.85	5.1	5.82	-	5.01	5.6
Ce	15.6	14.8	16.8	16.1	13.6	14.6
Nd	12.0	10.7	10.7	11.1	10.8	11.2
Sm	3.31	3.4	3.5	3.3	3.38	3.36
Eu	1.25	1.3	1.19	1.25	1.25	1.25
Tb	0.71	0.71	0.7	0.6	0.77*	0.71
Yb	2.74	2.89	2.59	2.87	2.76	2.76
Lu	0.39	0.44	0.38	-	-	0.43

* interpolated

(1) This work, RNAA, Ian Croudace

(2) P. Potts, Open University (Pers. Comm.) INAA

(3) P. Henderson, Bedford College London (Pers. Comm.) INAA

(4) C.J. Hawkesworth et al. (1977) Isotope Dilution

(5) R. Pankhurst (1979) IGS (Pers. Comm.) Isotope Dilution

(6) Mean of seven INAA determinations

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<u>Synthetic standard</u>, prepared by I. Croudace, 1978

	(a)	(b)
La	-	-
Ce	143	140
Nd	70.0	79
Sm	10.51	10.50
Eu	3.88	3.93
Tb	3.13	3.10
Yb	5.71	5.20
Lu	1.03	1.03

(a) Calculated values after spiking silica with rare earth solutions.

(b) Observed values, RNAA, I. Croudace.

Comparison of RNAA and INAA results on sample YFB, a Felsite from the Lleyn Peninsula

La	29	32
Ce	74	70
Nd	28	28
Sm	6.19	5.58
Eu	0.69	0.66
Tb	0.72	0.77
Yb	2.99	2.93
Lu	0.48	0.49
	(a)	(b)

(a) Analyst: N. Donnellan,1979, INAA; Birmingham University.

(b) Analyst: I. Croudace, 1978, RNAA.

Lower Limits of Detection and Determination

The terminology and mathematical expressions for estimating the lower limit of detection and the lower limit of determination are profuse and Currie (1968) has shown that the various definitions may provide values which may differ from one another by three orders of magnitude. Currie has provided formulae based on Poisson statistics which permit the ready calculation of the lower limit of detection and the lower limit of determination. The former term refers to the smallest true signal which will be detected although such detection can only be qualitative. The latter term refers to the smallest true signal which will permit a quantitative evaluation of the signal. The determination limit is about three times the detection limit.

$$\text{Detection limit} = \left[\frac{2.71 + 4.65 \; N_{bK}}{Np} \right] * \text{concentration (ppm)}$$

$$\text{Determination limit} = \frac{50\left[1 + \left[1 + \frac{N_{bK}}{12.5}\right]^{1/2}\right]}{N_{pK}} * \text{concentration (ppm)}$$

where N_{bK} is the counts in the background

N_{pK} is the counts in the peak

Both quantities were determined using the spectral data for BCR-1.

	Lower Limit of Detection (ppm)	Lower Limit of Determination (ppm)
La	0.55	1.70
Ce	1.67	5.00
Nd	1.95	6.00
Sm	0.04	0.13
Eu	0.04	0.14
Tb	0.06	0.19
Yb	0.06	0.19
Lu	0.03	0.10

Table 4

	LA	CE	ND	SM	EU	TB	YB	LU	$(Ce/Yb)_N$	$(Ce/Sm)_N$	$(Tb/Yb)_N$	Eu/Eu^*
TG11	118.00	200.00	90.00	17.11	3.31	2.37	8.15	1.12	6.43	2.72	1.30	0.61
TG13	59.00	107.00	52.00	10.40	1.50	1.36	5.60	0.81	5.00	2.40	1.08	0.46
TG3	51.02	116.51	53.30	12.28	1.52	2.45	7.73	1.08	3.95	2.21	1.41	0.36
TG4	35.75	76.61	44.23	10.42	2.00	2.50	9.41	1.43	2.13	1.71	1.18	0.53
TG6	35.10	73.42	40.82	9.86	1.79	1.94	7.81	1.15	2.46	1.74	1.10	0.53
BC2	36.40	78.20	35.15	8.18	0.97	1.29	4.83	0.76	4.24	2.23	1.19	0.37
BC7	19.82	40.70	23.81	6.14	0.90	1.31	4.18	0.65	2.55	1.55	1.40	0.42
IC9	48.75	95.76	44.79	9.49	1.17	1.36	5.23	0.91	4.80	2.35	1.16	0.39
COMP1	50.37	101.35	47.06	10.60	1.48	1.54	6.90	1.03	3.85	2.23	0.99	0.44
NGWY	52.00	95.76	39.12	7.81	1.04	1.15	5.02	0.74	5.00	2.86	1.02	0.42
FF2	30.87	75.01	30.62	7.07	2.17	1.12	3.76	0.56	5.22	2.47	1.33	0.94
DR2	31.00	64.64	35.15	9.23	2.35	1.83	5.85	0.88	2.89	1.63	1.39	0.74
GYRN	45.50	95.76	41.39	9.86	1.86	1.50	5.23	0.74	4.80	2.26	1.28	0.59
MB6	24.37	57.46	34.02	9.80	2.62	1.55	5.64	0.98	2.67	1.37	1.22	0.82
MP3	41.60	76.61	31.75	7.44	2.35	1.09	3.76	0.60	5.34	2.40	1.29	0.99
YGARN	39.00	72.62	31.75	7.07	2.14	1.04	3.03	0.44	6.28	2.39	1.52	0.95
TYM	39.65	79.80	32.93	7.25	2.04	1.11	3.24	0.51	6.45	2.57	1.53	0.87
PENM2	26.00	57.00	30.00	7.94	2.12	1.74	6.26	0.90	2.38	1.67	1.23	0.75
PENMA	28.93	61.45	30.62	8.37	2.21	1.70	5.85	0.77	2.75	1.71	1.29	0.76
PENGD	26.00	59.05	31.65	7.81	2.21	1.65	5.76	0.81	2.68	1.76	1.27	0.81
PENDG	22.75	55.81	29.00	7.64	2.33	1.60	5.40	0.79	2.71	1.70	1.32	0.87
PENMF	27.30	60.65	31.19	8.18	2.42	1.76	5.85	0.81	2.72	1.73	1.34	0.84
MM4	28.28	68.63	40.82	14.88	0.24	4.81	12.75	1.61	1.41	1.08	1.68	0.04
MM2	27.30	53.47	34.59	11.90	0.18	3.81	13.59	2.20	1.03	1.05	1.25	0.04
MM6	3.41	9.97	7.94	4.28	0.14	1.87	12.75	1.96	0.20	0.54	0.65	0.07
YFA	29.90	63.84	25.52	5.10	0.72	0.79	2.93	0.45	5.71	2.92	1.20	0.44
YFB	32.50	70.22	28.35	5.58	0.66	0.78	2.93	0.49	6.28	2.93	1.18	0.38
IC50	46.75	86.38	38.69	7.60	1.52	1.00	3.14	0.49	7.20	2.65	1.42	0.64
GARN1	43.12	85.77	38.69	9.40	3.04	1.50	3.28	0.53	6.85	2.13	2.03	0.99
GARN3	46.25	88.79	38.42	9.32	3.09	1.49	3.44	0.52	6.76	2.22	1.92	1.02
PANB	52.00	107.73	60.21	15.62	5.18	2.44	5.12	0.75	5.51	1.61	2.12	1.02
YFC	57.25	116.34	50.46	9.67	2.45	1.36	4.10	0.79	7.43	2.80	1.48	0.80
MN2	52.65	111.72	51.60	11.16	2.97	1.51	4.10	0.60	7.14	2.33	1.64	0.85
PBX	61.75	127.68	56.70	10.60	2.97	1.56	3.55	0.70	9.42	2.81	1.96	0.88
PBH	58.50	104.54	47.79	10.97	3.31	1.57	3.97	0.60	6.90	2.22	1.76	0.95
IC30	55.25	108.73	45.36	8.18	2.28	1.19	3.76	0.53	7.57	3.10	1.40	0.88
CBACH	58.50	111.72	47.63	9.24	2.62	1.35	4.18	0.61	7.00	2.82	1.44	0.89
CROD	51.50	103.74	51.03	8.33	2.53	1.25	3.45	0.45	7.88	2.90	1.61	0.95
PBH	58.50	104.54	47.79	10.97	3.31	1.57	3.97	0.60	6.90	2.22	1.76	0.95
MOELP	57.52	115.71	56.70	13.40	3.45	1.91	4.99	0.70	6.04	2.01	1.69	0.81
GGOCH	101.40	175.56	90.72	17.86	3.11	2.51	5.50	0.74	8.36	2.29	2.02	0.55
NBOD	91.00	183.59	77.28	18.55	1.06	2.62	10.80	1.64	4.45	2.31	1.08	0.18
LB6	73.00	186.02	73.71	16.93	1.24	2.37	6.48	0.86	7.52	2.56	1.63	0.23
IC37	26.32	50.27	22.11	5.23	0.51	1.08	6.53	0.74	2.00	2.22	0.74	0.27
PY6	14.62	32.72	19.85	5.39	1.73	1.01	2.19	0.35	3.91	1.41	2.06	0.95

Chapter 5

PETROGRAPHY

Introduction

Short petrographic descriptions are provided for samples of the granitoids from North Wales. The descriptions are confined to unaltered or the least altered samples since many of the intrusions, particularly those of Snowdonia, possess hydrothermal or metasomatic facies (see Bromley, 1969).

Detailed petrographic studies of most of the intrusions sampled in this study have been made by Bromley (1963), Beavon (1960), Tremlett (1962, 1964, 1965), Davies (1969) and Evans (1968). It is not considered necessary, therefore, to repeat their observations in such depth.

In general the granitic rocks are porphyritic microtonalites, microgranodiorites, microgranites and granophyres. Equigranular, medium-grained and fine-grained varieties are also found. All samples are holocrystalline although some such as the Yr Eifl felsite, some intrusive rhyolites of Snowdonia and the quartz-latites of Manod Bach and Foel Fras may have been emplaced as glasses containing phenocrysts of plagioclase. The unaltered samples may be classed as hypersolvus granitoids following the classification proposed by Tuttle and Bowen (1958). They applied this term to low-calcium, felsic plutonic rocks in which albite occurs only as a component of perthitic feldspar. This is in contrast to subsolvus granitoids where discrete grains of albite and orthoclase are found. Experimental and field work indicates that hypersolvus granites are expected from relatively anhydrous liquids and they are commonly found in near surface environments. A number of experimental studies on the granite system (e.g. Luth et al., 1964; Harris et al., 1970) have shown that wet granitic liquids cannot move far from their source of origin before they freeze, unlike dry magmas. During their ascent hydrous magmas begin to exsolve water and crystallise and it is unlikely that they will penetrate far into the crust. Although the liquidus temperatures are higher for granitic melts containing little or no water such melts may not intersect their solidus until they have reached high crustal levels. Thus the mineralogy of a granite may provide some information concerning its environmental origin, its water content and its depth of origin. It should be realised that hypersolvus granites may acquire water as they enter high crustal levels or water may become concentrated during fractionation and a subsolvus mineral assemblage may result (see Martin and Bonin, 1976, for a fuller discussion).

A Glossary of the technical terminology used

Granophyre:	fine-grained intergrowths (<2 mm) of quartz and alkali feldspar.
Micropegmatite:	As for granophyre.
Myrmekite:	An intergrowth of vermicular quartz in plagioclase.
Pilotaxitic:	The texture of the groundmass of a holocrystalline igneous rock in which lath-shaped microlites (often plagioclase) are arranged in a felty mesh.
Holocrystalline:	Wholly crystalline.
Glomerocryst:	An aggregate of crystals of the same mineral.
Glomeroporphyritic:	The texture of porphyritic igneous rocks containing closed clusters of equant crystals, usually the same mineral.
Cumulophyric:	The texture of a porphyritic igneous rock in which the phenocrysts, not necessarily the same mineral, are clustered in irregular groups.
Saussuritisation:	The replacement, especially of plagioclase, by a fine-grained aggregate of epidote minerals, albite, calcite, sericite and zeolites. It is a metamorphic process.

A. SNOWDONIA

1) Tan-y-Grisiau (Plate 1)

Macrospcopic description

A medium-grained, porphyritic microgranite with a white or pinkish appearance.

Microscopic description

Quartz occurs as sub-circular grains 1-2 mm, small grains $<$1 mm, and intergrown with perthite, antiperthite and less commonly with plagioclase. Plagioclase occurs as subhedral-anhedral crystals, 0.5-2 mm, of albite-oligoclase composition. Alkali feldspar exists as a component of micropegmatite (granophyric intergrowth) and perthitic and antiperthitic feldspars, 0.5-2 mm. The ferromagnesian minerals include biotite, chlorite and hornblende. These are generally found as small anhedral grains or interstitial crystals up to 2 mm. The accessory minerals are magnetite, zircon and allanite and the last two named are often included as euhedral grains in biotite or chlorite where pleochroic haloes are produced. The zircon and allanite may also be partially metamict.

2) Bwlch-y-Cywion, Ogwen and composite minor intrusions

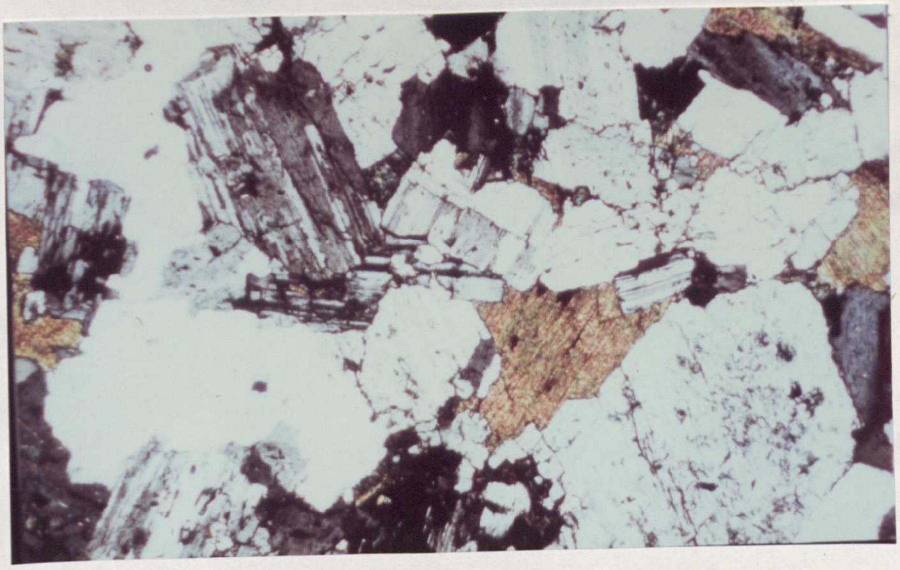
The physical and microscopic appearance of samples from these intrusions are closely similar to those described for Tan-y-Grisiau. Some variations in texture (e.g. much or little granophyric intergrowth), grain-size and extent of chloritisation of ferromagnesian minerals are evident although they are not sufficiently different to warrant separate descriptions. They may all be classified as medium-grained porphyritic microgranites.

3) Mynydd Mawr (Plate 2)

Macroscopic description

Fine-grained riebeckite-microgranite with a white-pink appearance.

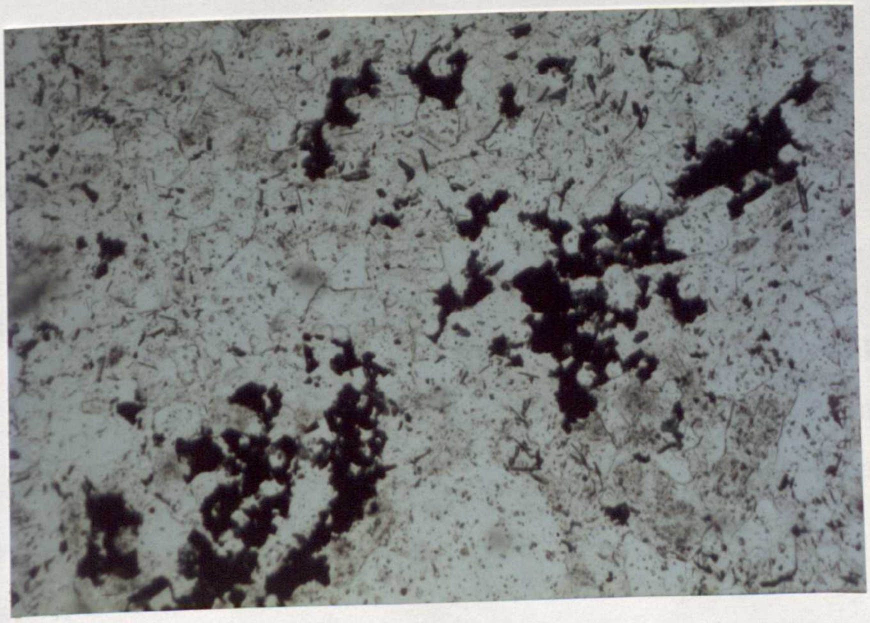
Plate 1



x 35 X Nichols

Tan-y-Grisiau microgranite- South-eastern Snowdonia. Biotite-plagioclase-perthitic feldspar-quartz-zircon may be seen. Zircon is north-east of centre.

Plate 2



x 65 P.P.L.

Mynydd Mawr microgranite - Central Snowdonia. Micropoikilitic riebeckite and small acicular prisms of acmite are set in a quartz-feldspar mosaic.

Microscopic description

Thin-sections of this intrusion show that the rock has an equigranular, microcrystalline ($<$ 0.1 mm) texture. Small patches of micropoikilitic riebeckite are found in most thin-sections although occasionally they are completely replaced by chloritic material.

4) Manod Bach

Macroscopic description

A fine-grained porphyritic quartz-latite which is dark grey in appearance resulting from the grain-size.

Microscopic description

Samples consist of euhedral-subhedral plagioclase phenocrysts (0.5 - 2 mm) set in a microcrystalline groundmass which may be spherulitic. All original ferromagnesian minerals have been converted to chloritic material displaying anomalous interference colours (penninite). Plagioclase crystals, commonly showing Carlsbad twinning, may occur as glomerophenocyrsts up to 4 mm. Apatite, and titanomagnetite are the main accessory minerals.

5) Drosgl

Macroscopic description

A grey, porphyritic microgranodiorite.

Microscopic description

The samples examined consist of a mass of plagioclase phenocrysts (0.5 - 1 mm) and glomerophenocrysts (1 - 2.5 mm) set in a groundmass of quartz, orthoclase and plagioclase. Intergrowths between these minerals are common,particularly between orthoclase and quartz (granophyre). Perthitic felspars are seen and many plagioclase phenocrysts have a thin mantle of perthite which is in turn intergrown to form granophyre (micropegmatite). Hornblende and augite occur as subhedral-euhedral crystals within the groundmass and the latter mineral is occasionally found poikilitically enclosed in plagioclase. Partial chloritisation of the ferromagnesian minerals is found. Magnetite is a minor mineral while apatite and zircon occur in accessory amounts.

6) Penmaenmawr (Plates 7 and 8)

Macroscopic description

The rocks of this intrusion may be described as microtonalites and fine- and medium-grained varieties are found. Samples vary in colour from dark grey to light grey depending on their grain-size.

Microscopic description

The sections examined from this intrusion show a variety of grain-sizes. The southern part of the intrusion is made up of a fine-grained porphyritic microtonalite containing phenocrysts, with zoned cores, of plagioclase (andesine). The groundmass consists of a felty mesh of plagioclase laths and small grains of augitic pyroxene; such a texture may be called pilotaxitic. The coarser-grained samples are equigranular and they consist of plagioclase feldspar (andesine-labradorite), augite, occasional enstatite, magnetite and ilmenite. Ilmenite is often partially altered to leucoxene. These crystals are set in a granophyric groundmass which is beautifully developed in some thin-sections. Hornblende crystals ($<$0.5 mm) occur sporadically along with chlorite. The chlorite partially replaces some ferromagnesian minerals and in some localities it is seen to replace the orthoclase component of the micropegmatite. In these same localities green and white veins ($<$ 4 cm wide) are found and they are composed of altered micropegmatite and patches of augite-diopside.

7) Foel Fras

Macroscopic description

A porphyritic quartz-latite which is light grey to greenish grey in appearance.

Microscopic description

The samples from this intrusion consist of euhedral-subhedral phenocrysts (0.5-1.5 mm) and glomerophenocrysts ($<$ 3 mm) of plagioclase feldspar set in a fine-grained - microcrystalline groundmass.

Plate 3

x 35 P.P.L.

Gyrn microgranodiorite - Northern Snowdonia.

Plate 4

x 35 P.P.L.

Penrhyn Bodeilas - Lleyn.
Hornblende with regions of alkali amphibole and two zircon crystals.

The plagioclases, commonly of andesine composition, are surrounded by a rim of microperthite which may be intergrown with quartz. Small (<1 mm) prismatic crystals of augite and hornblende and rare biotite represent the ferromagnesian minerals. The groundmass is made up of quartz, orthoclase and plagioclase and the first two minerals may be intergrown to form interstitial granophyre. Magnetite and ilmenite are minor phases and apatite and zircon occur as accessory minerals.

All samples collected show some alteration of plagioclase (saussuritisation) and ferromagnesian minerals (chloritisation).

8) Moel Wnion and Gyrn (Plate 3)

Macroscopic description

Samples from these intrusions may be described as porphyritic microgranodiorites and they are buff to light grey in colour.

Microscopic description

Euhedral-subhedral plagioclase phenocrysts (<2 mm) with perthitic rims are found along with prismatic hornblende (<0.4 mm) in a felsic groundmass. The groundmass consists of intergrown quartz and orthoclase and anhedral plagioclase. Magnetite is scattered throughout the rock and apatite and zircon are the main accessory minerals. The samples from Moel Wnion are in the main finer-grained than those collected from Gyrn.

9) Y Garn and Mynydd Tal-y-Mignedd

Macroscopic description

Petrologically and chemically the samples collected from these intrusions are almost identical. They are medium-grained, porphyritic microgranodiorites.

Microscopic description

The rocks collected consist of euhedral, elongated plagioclase phenocrysts (<1 mm) and occasional glomerophenocrysts set in a fine-grained groundmass of quartz and feldspars. Some minor epidotisation of the larger phenocrysts and clusters is seen. The original ferromagnesian minerals are replaced by chloritic material showing anomalous interference colours. Ilmenite and magnetite are minor ore phases and apatite is the main accessory mineral.

10) Mynydd Perfedd

Macroscopic description

A light grey, porphyritic microgranite.

Microscopic description

Petrographically the samples from this intrusion are not greatly dissimilar to those of Y Garn and Tal-y-Mignedd although the last two named have a finer grained groundmass. Feldspar phenocrysts (<2 mm) and occasional glomerophenocrysts are found, both possessing thin perthitic rims. Orthoclase occurs as microperthite but more commonly as granophyre. No original ferromagnesian minerals are seen since they have been completely altered to chlorite. Magnetite and ilmenite are minor phases and apatite is the main accessory mineral.

B. THE LLEYN PENINSULA

11) Gurn Goch

Macroscopic description

A medium-grained, porphyritic microgranite.

Microscopic description

This rock consists of euhedral phenocrysts of plagioclase (<3 mm) and clusters of microperthitic feldspar (<3 mm). Where the two are juxtaposed a tesselated margin results and all plagioclase crystals are surrounded by a thin mantle of microperthitic feldspar. The groundmass consists of quartz and perthitic feldspar which may be intergrown. All feldspars are turbid in plane polarised light and original ferromagnesian minerals are chloritised. Small grains of euhedral apatite are found associated with the chloritic patches and magnetite and ilmenite occur scattered throughout the rock.

12) Nant Bodlas

Macroscopic description

A medium-grained, leucocratic granophyre.

Microscopic description

The samples collected consist of equigranular (1 mm) crystals of microperthitic feldspar which are intergrown with quartz. A spectacular development of this granophyre is frequently seen. All the feldspar shows a turbid appearance in plane polarised light although some sections show an associated structural feature. This is commonly formed by a series of lines at right angles and it resembles cleavage although there are no openings. The lines possess a different extinction direction from the rest of the crystal and it is probable that they result from volume changes associated with the kaolinitisation of the potassium feldspar. Their orientation and regularity may have been controlled by the cleavage and twinning of the original feldspars.

13) Llanbedrog (Plate 9)

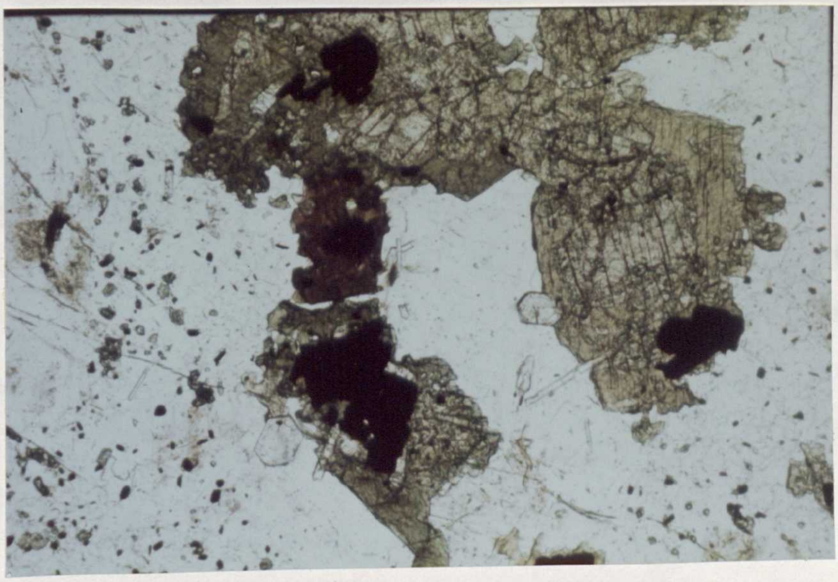
Macroscopic description

A medium-grained, leucocratic, porphyritic granophyre.

Microscopic description

The porphyritic nature of this rock results from clusters (2-3 mm) of euhedral plagioclase and subhedral microperthitic feldspars. These are surrounded by myrmekitic and granophyric intergrowths. Single, large euhedral phenocrysts are surrounded by a mantle of microperthite which grades into granophyric intergrowths. Biotite is the only original ferromagnesian mineral. Alterations include chloritisation and kaolinitisation (turbid feldspars). Zircon and small amounts of apatite are the accessories.

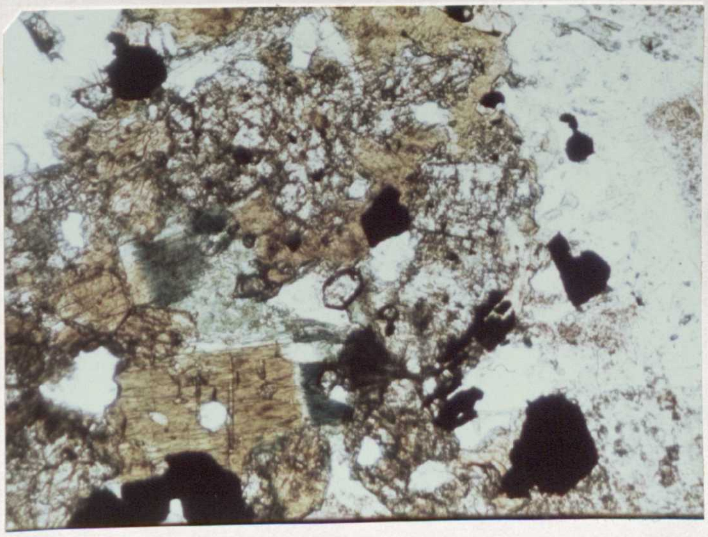
Plate 5



x 35 P.P.L.

Penrhyn Bodeilas microtonalite - Lleyn.
An amphibole (after augite) - magnetite - apatite cluster.

Plate 6



x 35 P.P.L.

Penrhyn Bodeilas microtonalite - Lleyn.
Hornblende (and augite) -apatite-magnetite cluster. The edges of some hornblende crystals are of sodic amphibole.
A zircon crystal is seen at the centre of the picture.

14) Moel-y-Penmaen (Plate 19)

Macroscopic description

A fine-grained holocrystalline andesitic rock.

Microcrystalline description

The sample from this locality possesses a pilotaxitic texture. Its small grain-size prevents any detailed petrographic investigation although small pyroxenes, probably augite, and plagioclase can be made out. The pyroxenes are occasionally poikilitically enclosed in plagioclase phenocrysts.

15) Yr Eifl

Macroscopic description

A fine-grained felsite which is pink, green or grey in appearance.

Microscopic description

Occasional glomerophenocrysts (1-2 mm) composed of subhedral plagioclase and microperthitic feldspar are set in a microcrystalline groundmass. Thin rims of microperthite/orthoclase commonly surround the feldspar clusters and both have a turbid appearance. Chloritic material and magnetite are scattered throughout the rock.

16) Garnfor (Plates 11, 13, 15, 16, 17, 18)

Two textural and chemical varieties are identified from this intrusive complex.

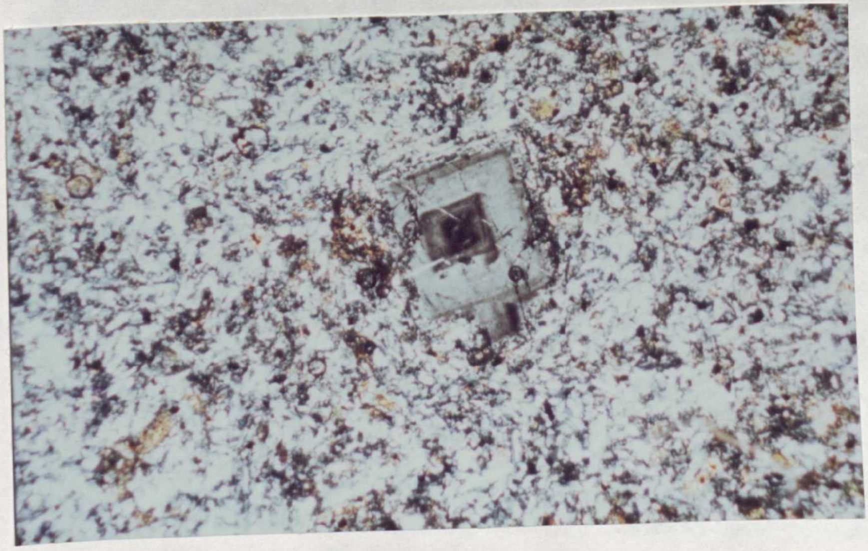
a) Macroscopic description

A medium-grained porphyritic microgranodiorite which has a pinkish appearance.

Microscopic description

This rock-type consists of euhedral-subhedral feldspar phenocrysts (< 2 mm) and glomerophenocrysts (< 4 mm) set in a groundmass of microperthitic feldspars, quartz and anhedral grains of hornblende, biotite, chlorite and magnetite. Some feldspars show zoning and possess

Plate 7



x 35 X nichols

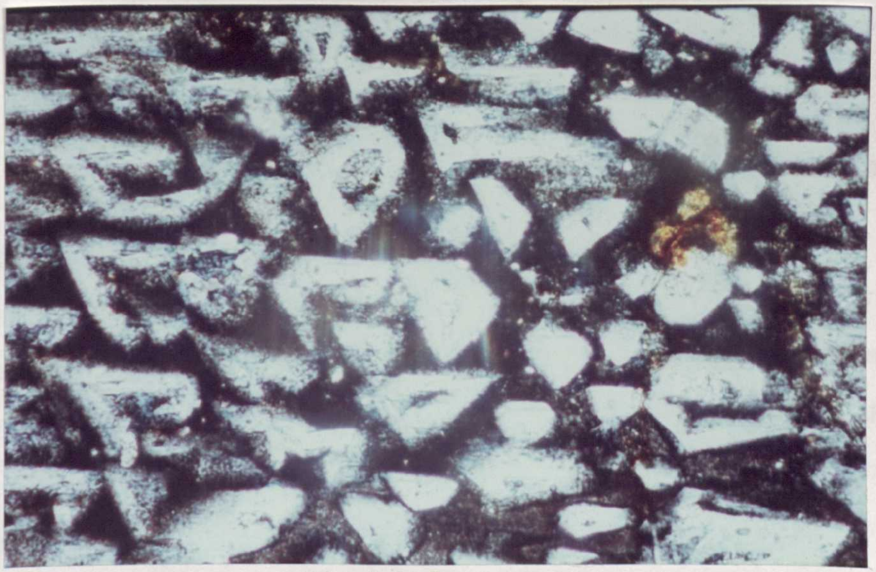
Penmaenmawr microtonalite -Northern Snowdonia.
A zoned plagioclase feldspar phenocryst set in a fine-grained pilotaxitic groundmass.

Plate 8

x 35 P.P.L.

Penmaenmawr microtonalite - Northern Snowdonia.
Granophyric intergrowths varying from vermicular to cuneiform in habit. The orthoclase component is often chloritised.

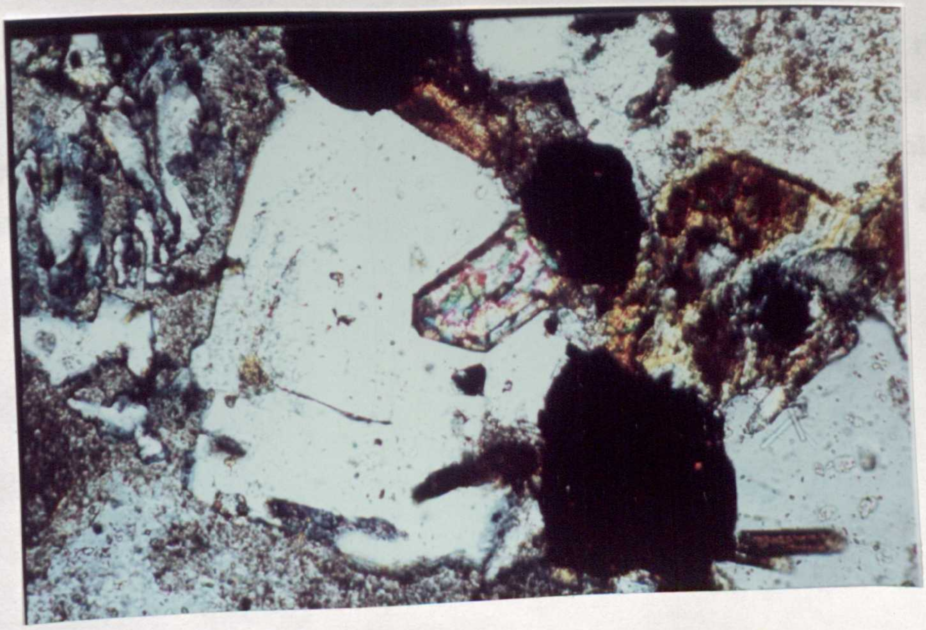
Plate 9



x 100 X nichols

Llanbedrog granophyre - Lleyn.
Cuneiform quartz in micropegmatite.

Plate 10



x 65 X nichols

Penrhyn Bodeilas - Lleyn.
A zircon crystal and magnetite. Granophyric intergrowths on the left.

turbid margins. The plagioclase varies in composition from oligoclase to andesine. The accessory minerals are zircon and apatite.

b) Macroscopic description

A porphyritic microtonalite which is light grey in appearance.

Microscopic description

This rock-type consists of phenocrysts, glomerocrysts and cumulocrysts (mafic clots), up to 5 mm in size, set in a fine-grained felsic groundmass. The groundmass is made up of quartz, plagioclase and occasional clinopyroxene. The plagioclase crystals that form the glomerocrysts and parts of the cumulocrysts have clearly had a complex history. Some show normal or oscillatory zoning while others may have cores which have oscillatory zoning and rims with normal zoning. The feldspar compositions vary generally from oligoclase - andesine although occasionally cores of labradorite are found. Many of the plagioclase phenocrysts and glomerocrysts are surrounded by a thin rim of orthoclase. Crystals of pyroxene, mainly augite, occur as phenocrysts, in the groundmass and as part of the cumulocrysts. In the cumulocrysts they are associated with plagioclase, magnetite and apatite and this will be shown, in a later chapter, to be of petrogenetic importance. Hornblende is found as a mineral partially replacing augite. Hypersthene is found in a number of thin-sections although it is subordinate to augite. The main accessory minerals are apatite and zircon.

17) Penrhyn Bodeilas (Plate 4, 5, 6, 10)

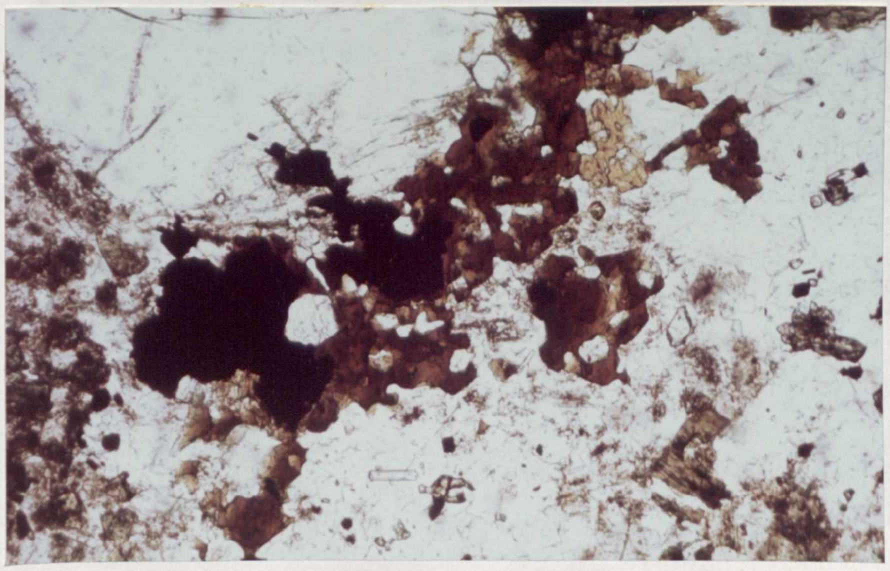
Macroscopic description

A grey or pink porphyritic microtonalite.

Microscopic description

Samples consist of large phenocrysts, glomerocrysts and cumulocrysts up to 4 mm. The pyroxenes show a greater amount of alteration to hornblende and chlorite compared with the Garnfor sample previously described. Primary igneous hornblendes are also found and some of

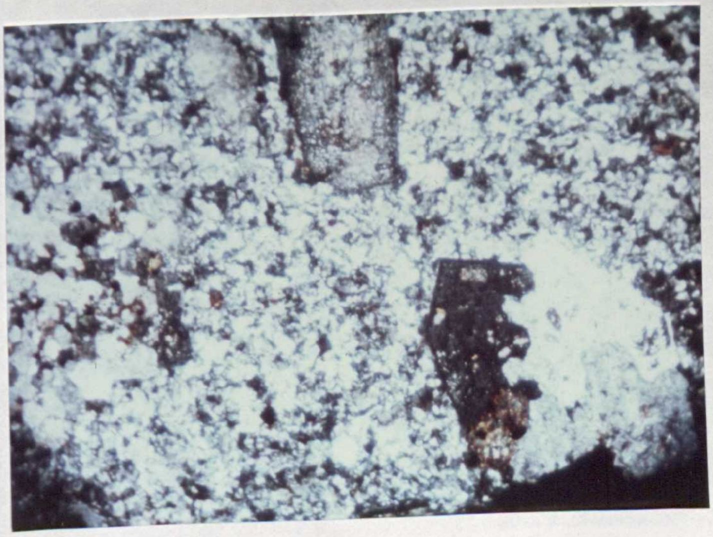
Plate 11



x 65 P.P.L.

Inner Garnfor - Lleyn.
Apatites in close association with hornblende-biotite-magnetite.

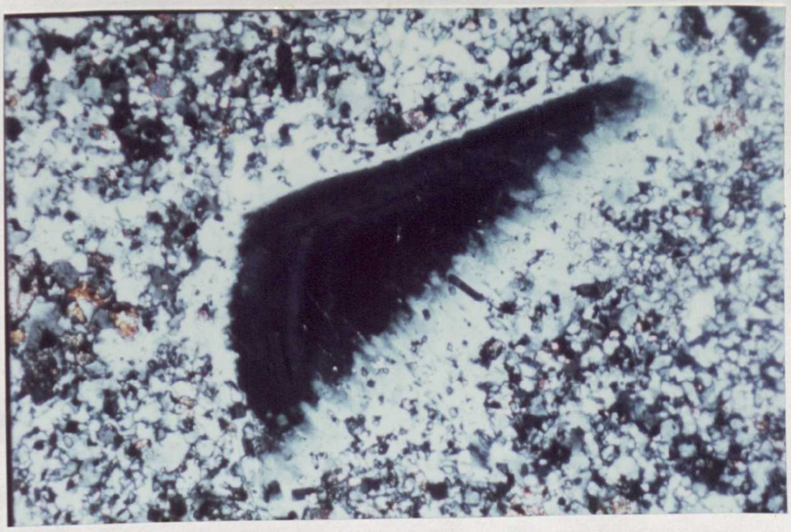
Plate 12



x 35

Moel Penllechog - Lleyn Peninsula.
A plagioclase glomerocryst showing an embayed margin where it is intergrown.

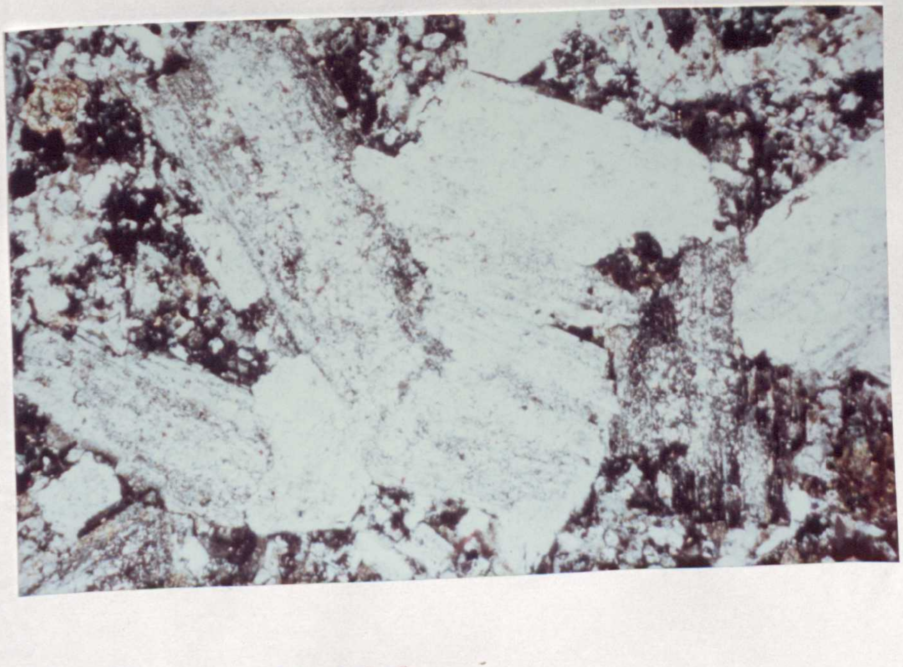
Plate 13



x 65 X nichols

Inner Garnfor - Lleyn.
An oscillatory-zoned and resorbed plagioclase (oligoclase-andesine)

Plate 14



x 35 X nichols

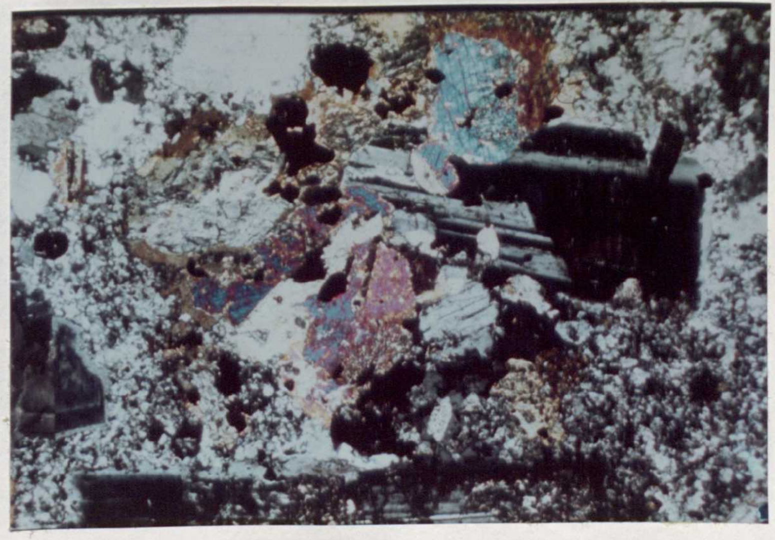
Mynydd Nefyn microgranodiorite - Lleyn.
Glomerophenocryst of plagioclase made up of five grains.

them possess regions of an alkalic-amphibole. This may suggest that the physico-chemical conditions changed sufficiently for growth (or reaction) of the alkali amphibole. The feldspars are often rimmed by microperthite and this is commonly intergrown with quartz to produce interstitial granophyre. Apatite and zircon are the main accessory phases.

Conclusion

Since the aim of this study is to investigate the petrogenesis of the granitoids of North Wales it is clearly appropriate to present a summary describing the crystallisation sequences of the various suites. It is not possible to present a very detailed petrographic account, owing to possible subsolidus changes in the mineralogy of some samples and the fine grain-size of others, but a simplified picture is available. The information given below is derived partly from petrographic studies made by the author and from previous studies (Bromley, 1963; Davies, 1969; Evans, 1968). Although the evidence has not yet been presented, the sample population of North Wales granitoids may be divided into three groups. On this basis three crystallisation series are presented below which will prove to be of importance during the petrogenetic discussions of Chapters 7 and 8.

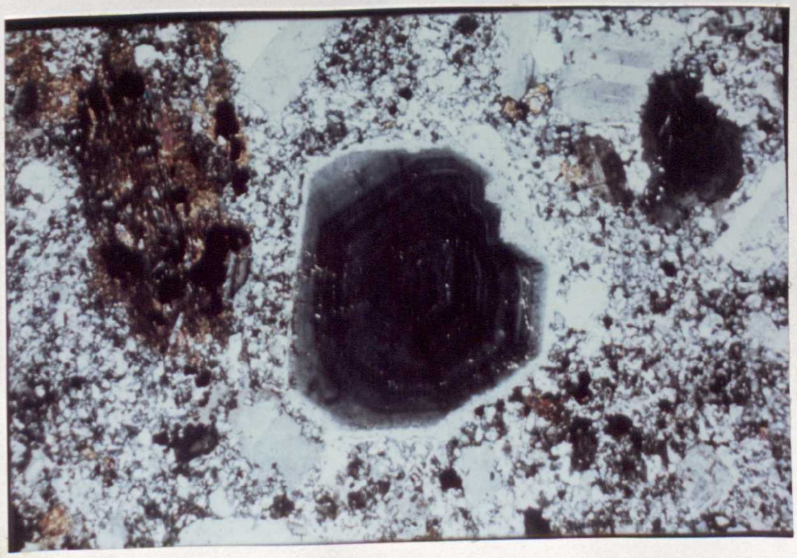
Plate 15



x 35 X nichols

Inner Garnfor microtonalite - Lleyn Peninsula.
Augite-plagioclase-magnetite cumulocryst set in a fine-grained felsic groundmass.

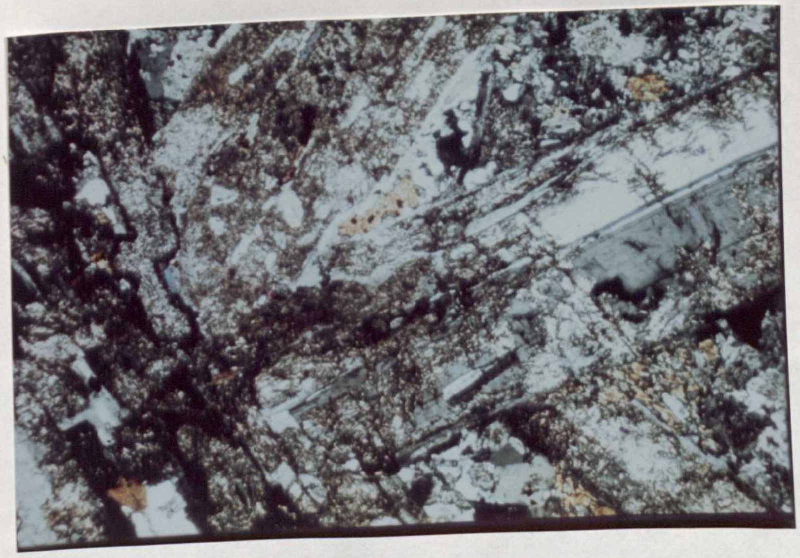
Plate 16



x 35 X nichols

Inner Garnfor microtonalite - Lleyn.
An oscillatory-zoned plagioclase phenocryst showing resorbed edges and a thin orthoclase mantle.

Plate 17



x 35 X nichols

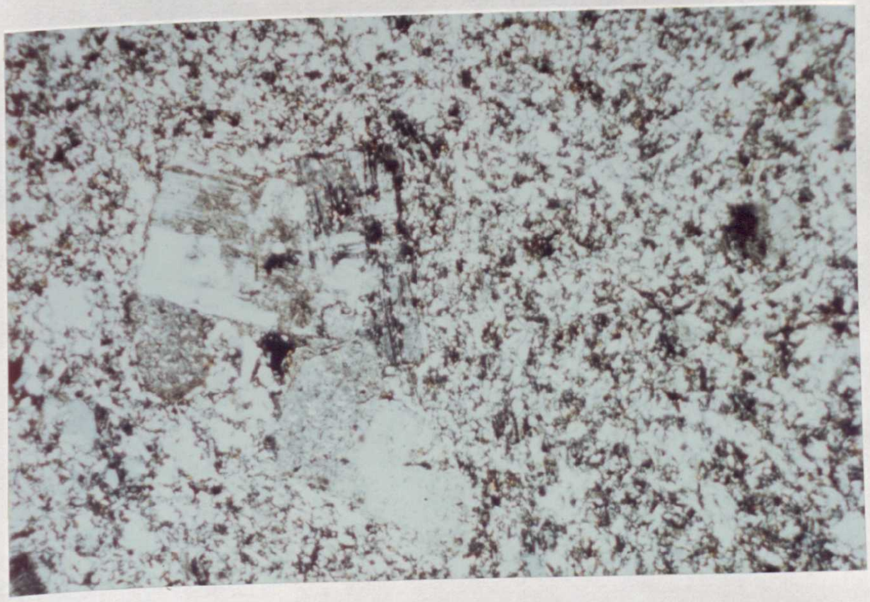
Inner Garnfor - Lleyn.
Two plagioclase phenocrysts with the development of interstitial hornblende (probably after augite).

Plate 18

x 35 X nichols

Inner Garnfor - Lleyn.
A zoned plagioclase feldspar showing signs of resorption. The crystal is rimmed by kaolinitised microperthite.

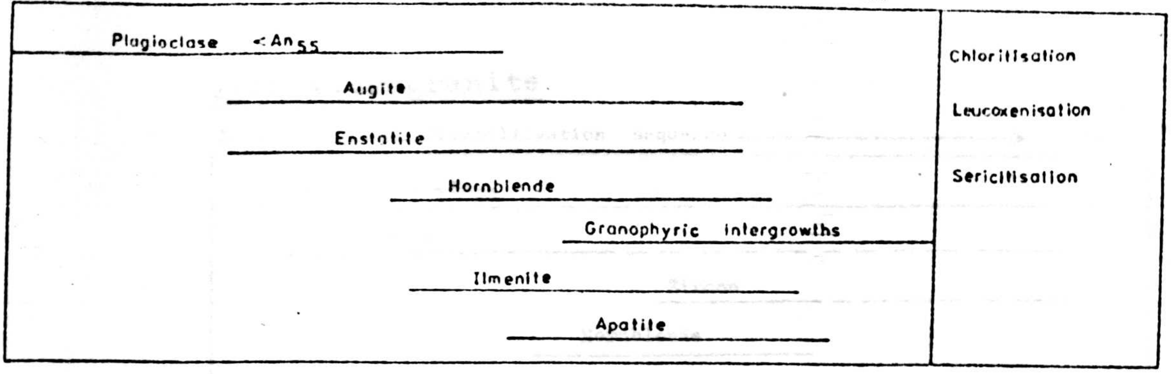
Plate 19



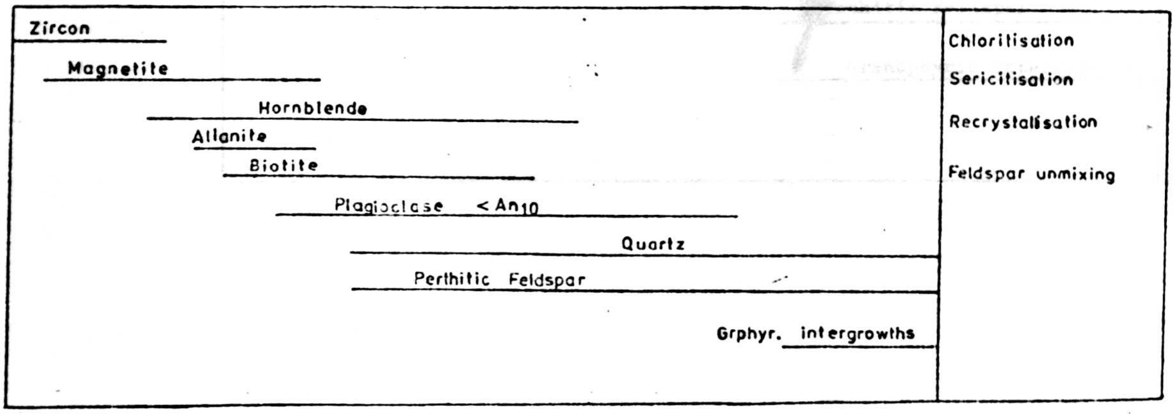
x 35 X nichols

Moel-y-Penmaen Andesite - Lleyn.
Glomerocryst of plagioclase set in a pilotaxitic groundmass.

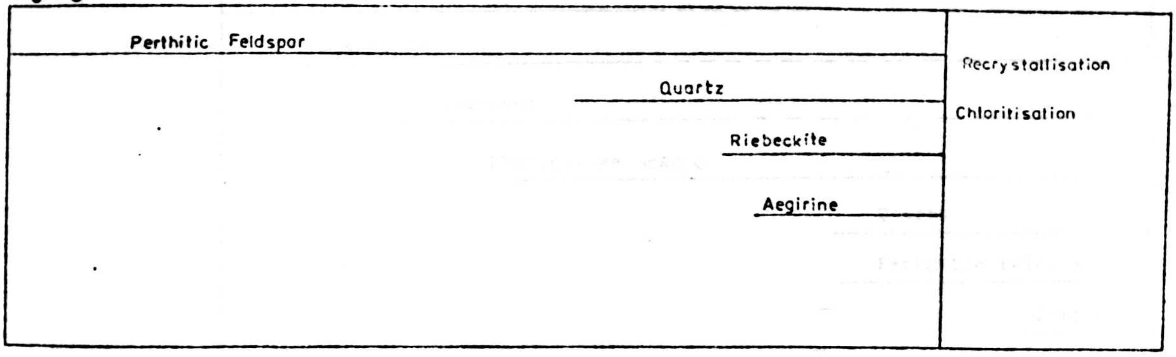
Penmaenmawr microtonalite



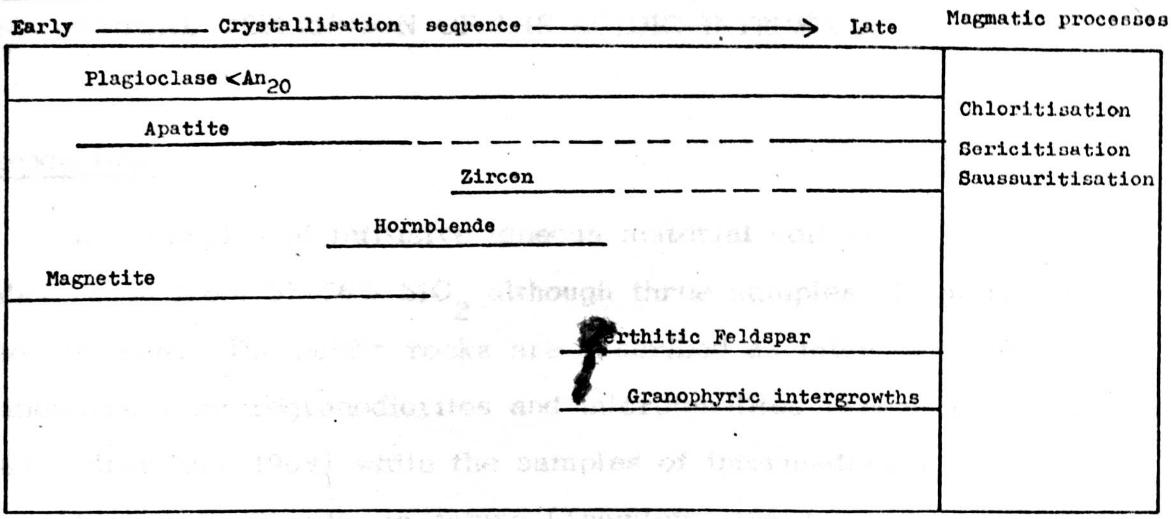
Tan-y-Grisiau microgranite



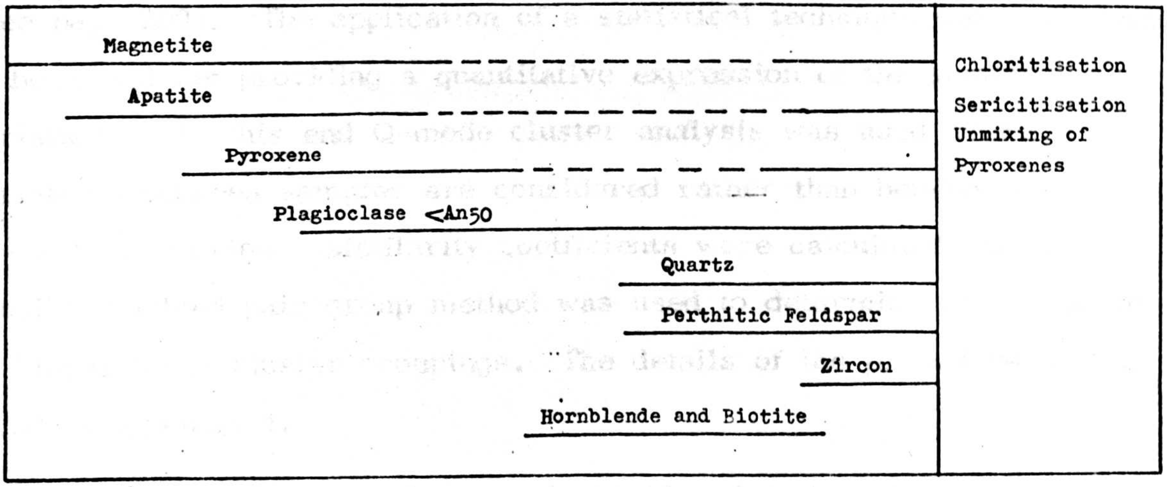
Mynydd Mawr microgranite



Gyrn microgranite



Garnfor microtonalite



Chapter 6

GEOCHEMICAL DESCRIPTION OF THE ACIDIC INTRUSIVES OF NORTH WALES

Introduction

The samples of intrusive igneous material collected from North Wales range from 57-76% SiO_2 although three samples of dolerite were also obtained. The acidic rocks are described as microgranites, granophyres, microgranodiorites and microtonalites (Tremlett, 1962, 1964; Bromley, 1969) while the samples of intermediate composition from Lleyn are andesitic in nature (Tremlett, 1962).

An examination of the chemical data obtained by X-ray fluorescence analysis and neutron activation techniques show that there are differences among the sample population. Some of these differences were noted by Tremlett (1972) who separated the intrusions of Lleyn into Ordovician and Caledonian groups depending on various geochemical parameters (see page 209). The application of a statistical technique was considered to be useful for providing a quantitative expression of the sample variations. To this end Q-mode cluster analysis was used where variations between samples are considered rather than between variables (R-mode). Cosine similarity coefficients were calculated and an equally weighted pair group method was used to determine the sequence or hierarchy of cluster groupings. The details of the procedure may be found in appendix 1.

The clustering procedure used considered major elements, trace elements and major-trace elements separately. The cluster dendrograms are shown in figures 18, 19, 29 (pages 123-125). The interpretation of such diagrams is open to a certain amount of subjectivity and the level of similarity chosen depends largely on the nature of the study. For example it may be considered important that individual intrusions be separated, assuming that they are chemically homogeneous, in which case a high level of similarity is chosen. If it is desired to identify whether different igneous suites exist in a particular investigation it is probably safe to use a lower level of similarity. However, if there is evidence that a suite of rocks, with a broad composition range, is comagmatic, the cluster dendrograms produced may show a number of discrete clusters. This will most likely be related to the compositional members of the suite (acid, intermediate, basic) and not to the absence of a genetic relationship. Thus great care is required when interpreting cluster dendrograms and their use may have more of a corroborative than a diagnostic importance.

a) Major elements (figure 18, page 123)

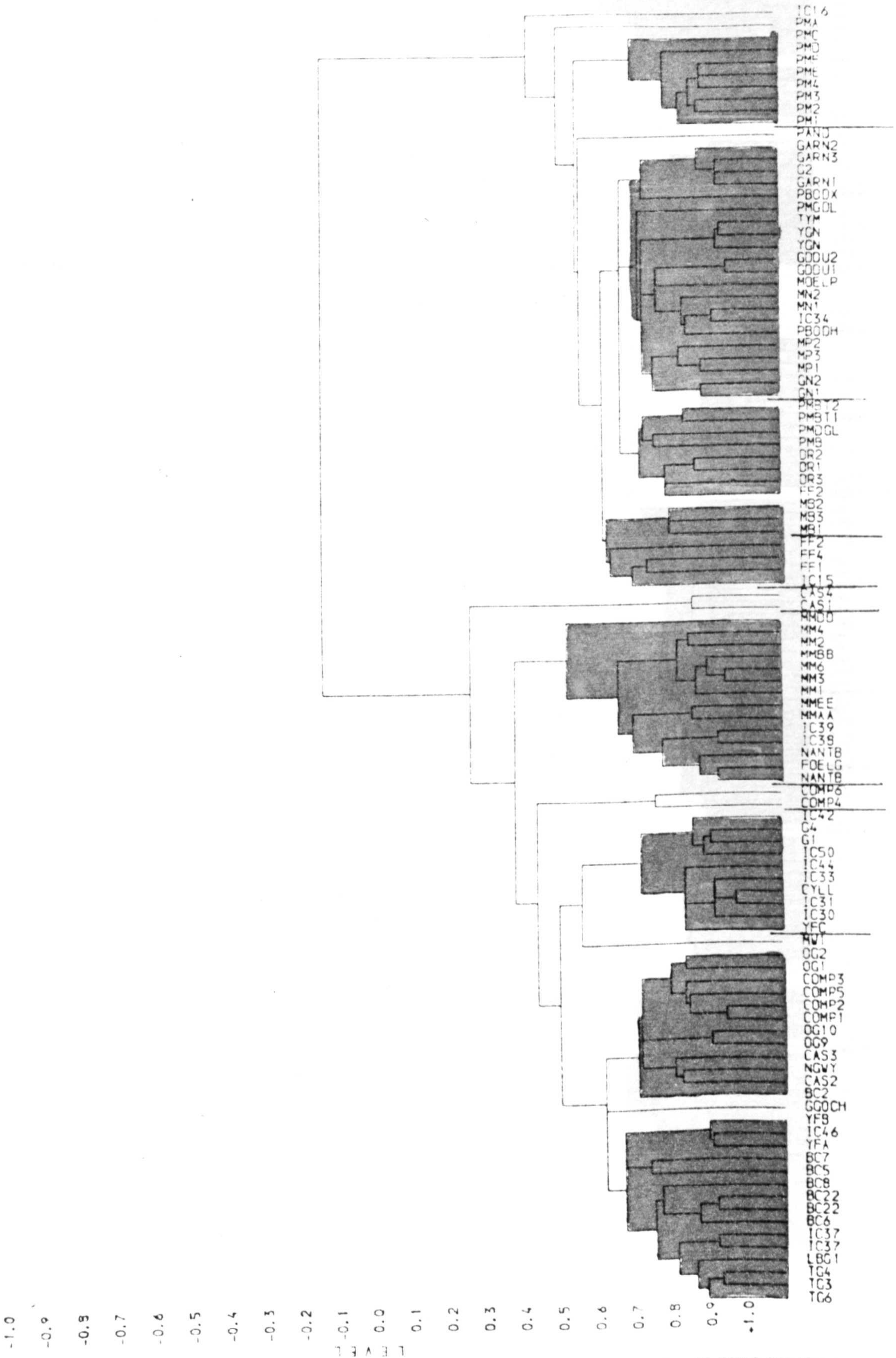
This dendrogram forms two distinct groups at a similarity level of -0.2 corresponding to the more-acid and less-acid compositions of the sample population. At a similarity coefficient of +0.65, eight groups may be seen. The groups correspond, in the more-acid supergroup, to the microgranites, granophyres and intrusive rhyolites of Snowdonia, the microgranites of Lleyn and the microgranite and granophyres of Mynydd Mawr, Nant Bodlas and Foel Gron respectively. The less-acidic supergroup forms four groups at +0.65. These correspond to the microgranodiorites, quartz-latites and microtonalites of Snowdonia and Lleyn.

b) Trace elements (figure 19, page 124)

The trace elements usedtto compute this cluster dendrogram are Y, Sr, Rb, Th, Ba, Zr, Nb, La, Ce and Nd. Two distinct groups are seen at a similarity level of 0.00. These separate the samples of Mynydd Mawr, Nant Bodlas and Foel Gron from the remaining samples. The member of this latter supergroup form six groups at a similarity coefficient of +0.65. They correspond to:-

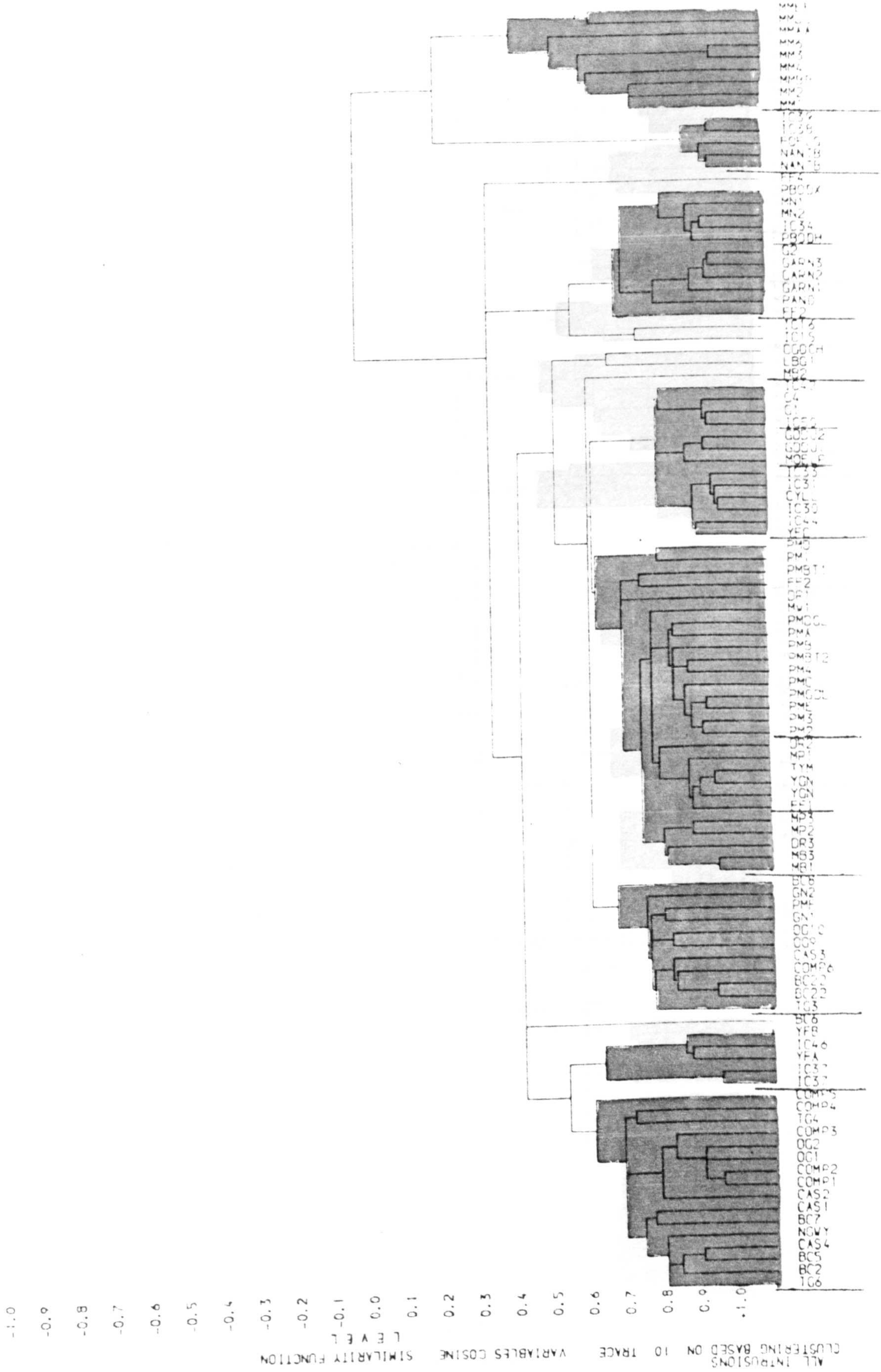
i) Snowdonian microgranites and granophyres.
ii) Yr Eifl felsites.
iii) Snowdonian microgranites and granophyres.
iv) Microgranodiorites, quartz-latites and microtonalites of Snowdonia.

Figure 18



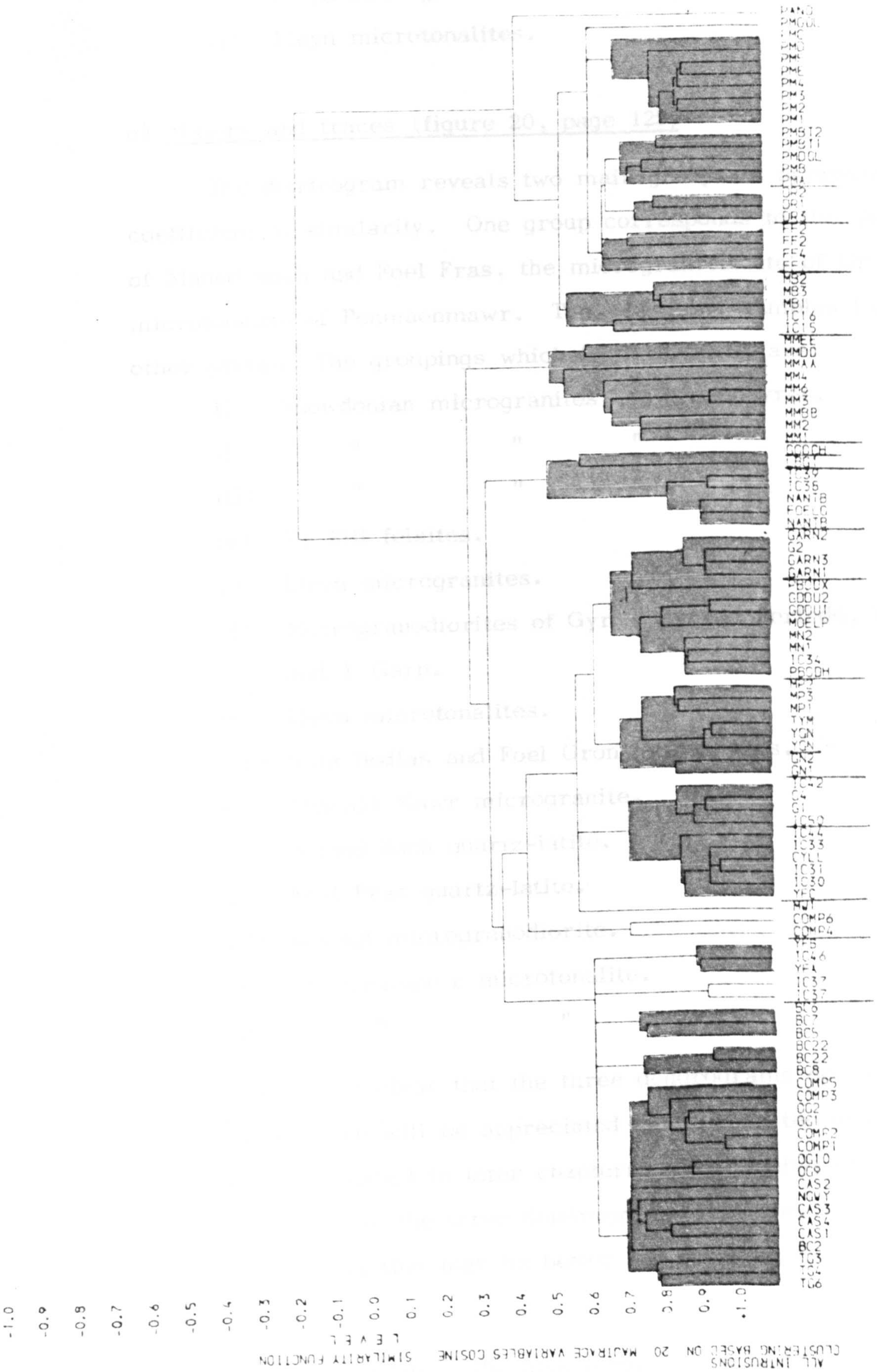
Q-Mode cluster dendrogram based on 10 major elements.

Figure 19



Q-Mode cluster dendrogram based on 10 trace elements.

Figure 20



Q-Mode cluster dendrogram based on 20 major-trace elements.

v) Lleyn microgranites.
vi) Lleyn microtonalites.

c) Majors and traces (figure 20, page 125)

The dendrogram reveals two main groups at approximately -0.2 coefficient of similarity. One group corresponds to the quartz-latites of Manod Bach and Foel Fras, the microgranodiorite of Drosgl and the microtonalite of Penmaenmawr. The remaining samples fall within the other group. The groupings which form at +0.65 are:

i) Snowdonian microgranites and granophyres.
ii) " " " "
iii) " " " "
iv) Yr Eifl felsites.
v) Lleyn microgranites.
vi) Microgranodiorites of Gyrn, Mynydd Perfedd, Tal-y-Mignedd and Y Garn.
vii) Lleyn microtonalites.
viii) Nant Bodlas and Foel Gron granophyres.
ix) Mynydd Mawr microgranite.
x) Manod Bach quartz-latite.
xi) Foel Fras quartz-latite.
xii) Drosgl microgranodiorite.
xiii) Penmaenmawr microtonalite.
xiv) " "

Thus, it is clear that the three dendrograms do supply some useful information which will be appreciated more when the geochemistry of the samples is discussed in later chapters. The number of groups and their ordering differ for the three dendrograms. In view of this it is considered that other information may be better for breaking the sample population into groups.

An examination of the geochemical data, particularly trace element abundances and ratios, shows that a number of useful discrimination relationships exists. These are Nb-SiO_2, $Na_2O + K_2O - SiO_2$, $(Ce/Y)_N - SiO_2$, $Al_2O_3 - SiO_2$ (see figures 28, p. 148 and figure 20a, page 126b). Good to reasonable separation of the granitoids into six groups is found for these discrimination diagrams. This preliminary break-down of the granitoid population is a suitable starting point for describing the salient features of their geochemistry. The sixfold classification does not, however, imply that the members of different groups are unrelated to each other.

Thus, on the basis of the Q-mode cluster dendrograms and additional information from trace elements and rare earth element patterns, the samples collected from North Wales have been divided into six groups for the purposes of describing their geochemical characteristics.

1) Snowdonian intrusions
2) Penmaenmawr, Drosgl, Manod Bach
3) Foel Fras, Gyrn, Moel Wnion (discussed separately because of REE characteristics)
4) Mynydd Mawr
5) Nant Bodlas and Foel Gron.
6) Lleyn intrusions including Moel Perfedd, Y Garn and Tal-y-Mignedd

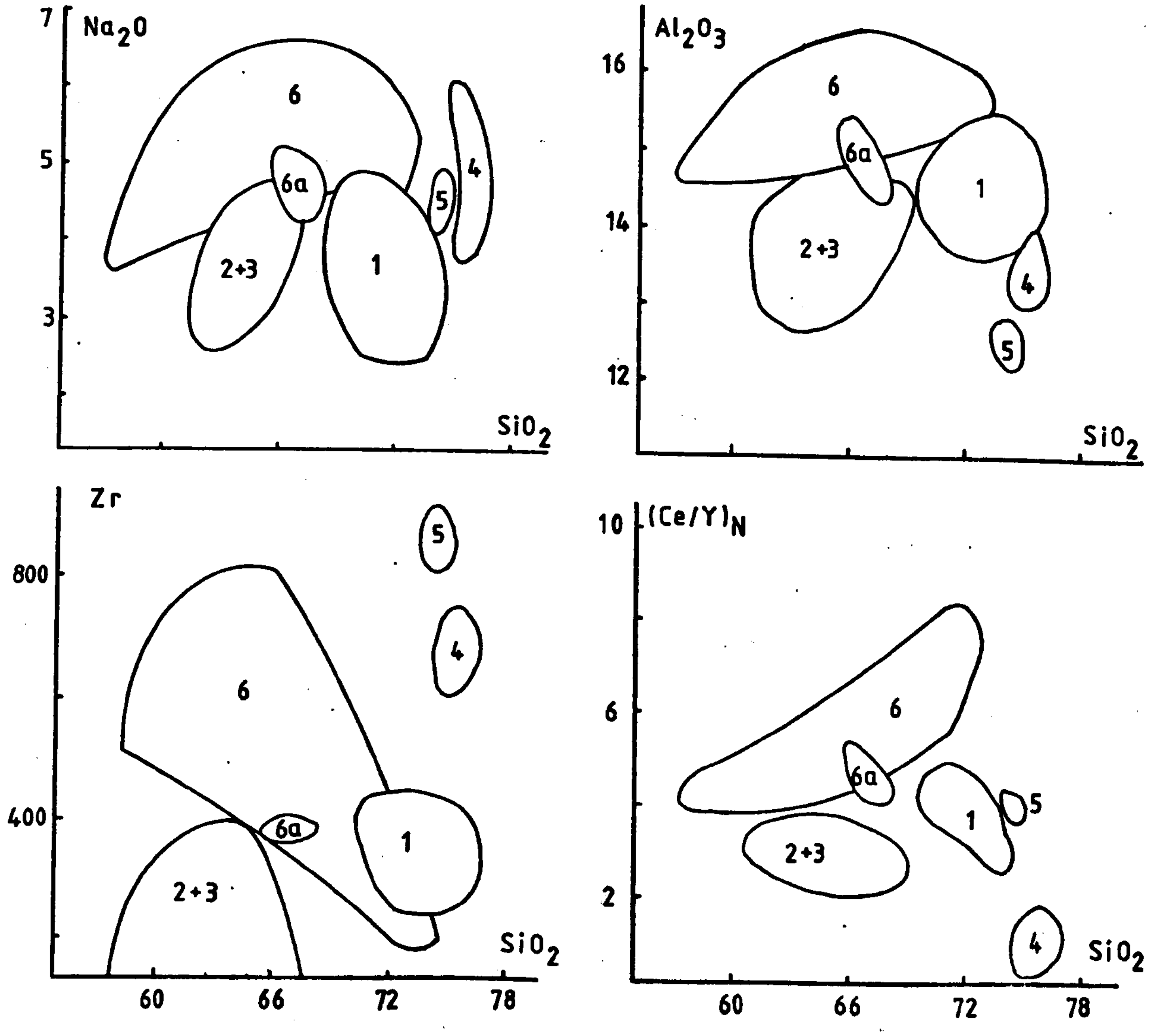
The table below provides a summary of the rare earth pattern characteristics for the six groups listed above (see also table 4, p. 99a).

	$(Ce/Yb)_N$	$(Ce/Sm)_N$	$(Tb/Yb)_N$	SiO_2 wt %
1	2 - 5	1.5 - 2.8	1.0 - 1.4	70 - 75
2	2.5	1.7	1.3	60 - 65
3	5	2.3	1.3	60 - 69
4	1.2	1.0	1.0	75
5	4.5	2.5	1.1	75
6	5.5 - 9	1.6 - 3.0	1.2 - 2.1	57 - 74*

*The smaller numbers are those for the most acidic rocks.

Rare earth patterns and their interpretation are given in a later chapter although it is expedient to present their essential features here (see fig. 20b, page 126c).

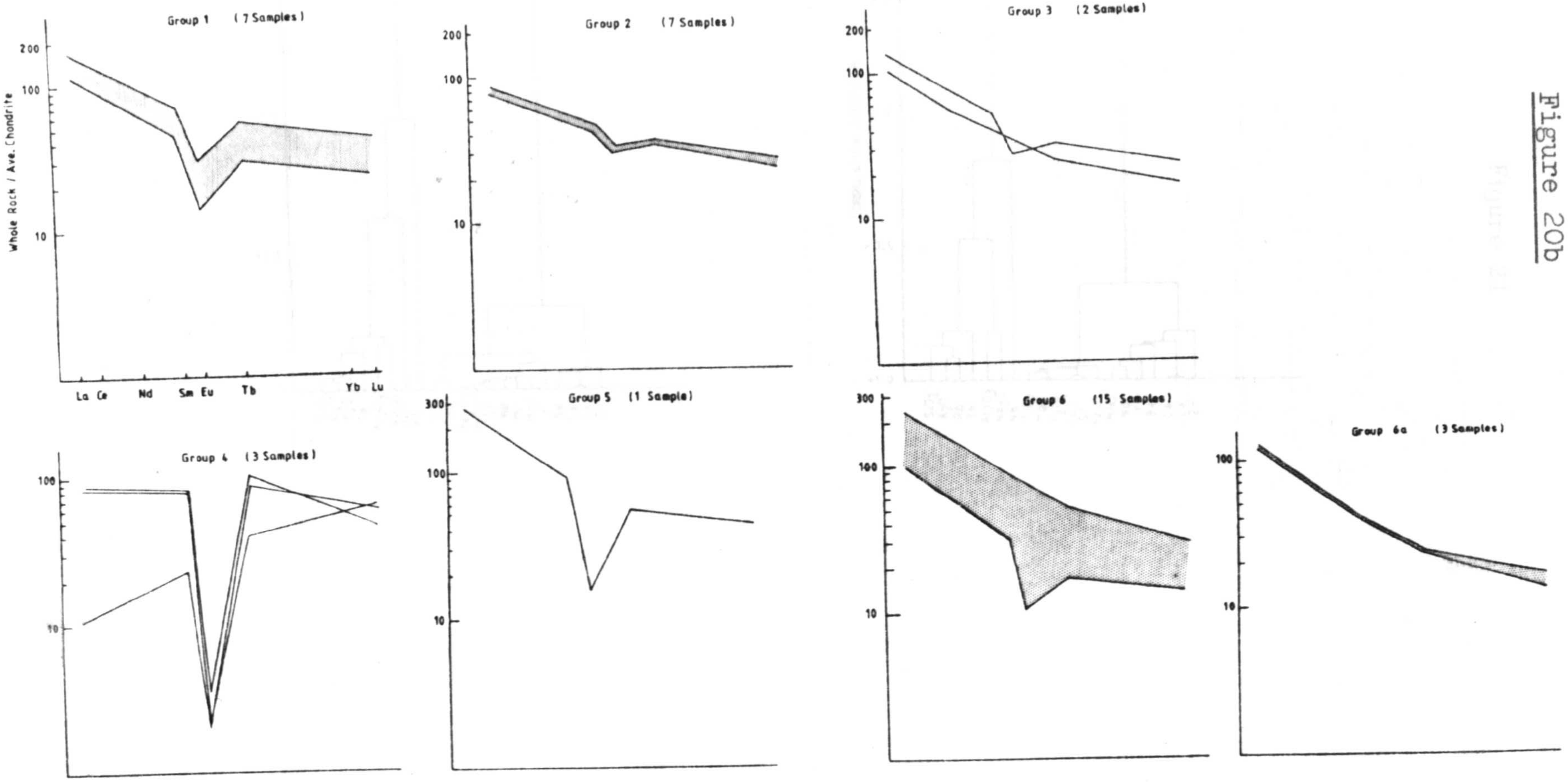
Figure 20a



1). Snowdonian granitic suite 2). Penmaenmawr, Drosgl, Manod Bach 3). Foel Fras, Gyrn 4). Mynydd Mawr 5). Nant Bodlas, Foel Gron 6). Lleyn and Garnfor suites 6a). Mynydd Perfedd, Y Garn, Mynydd Tal-y-Mignedd.

Major elements in wt.% and trace elements in p.p.m.

Figure 20b



The rare earth patterns for the various granitoid groups (chondrite normalised).

Figure 21

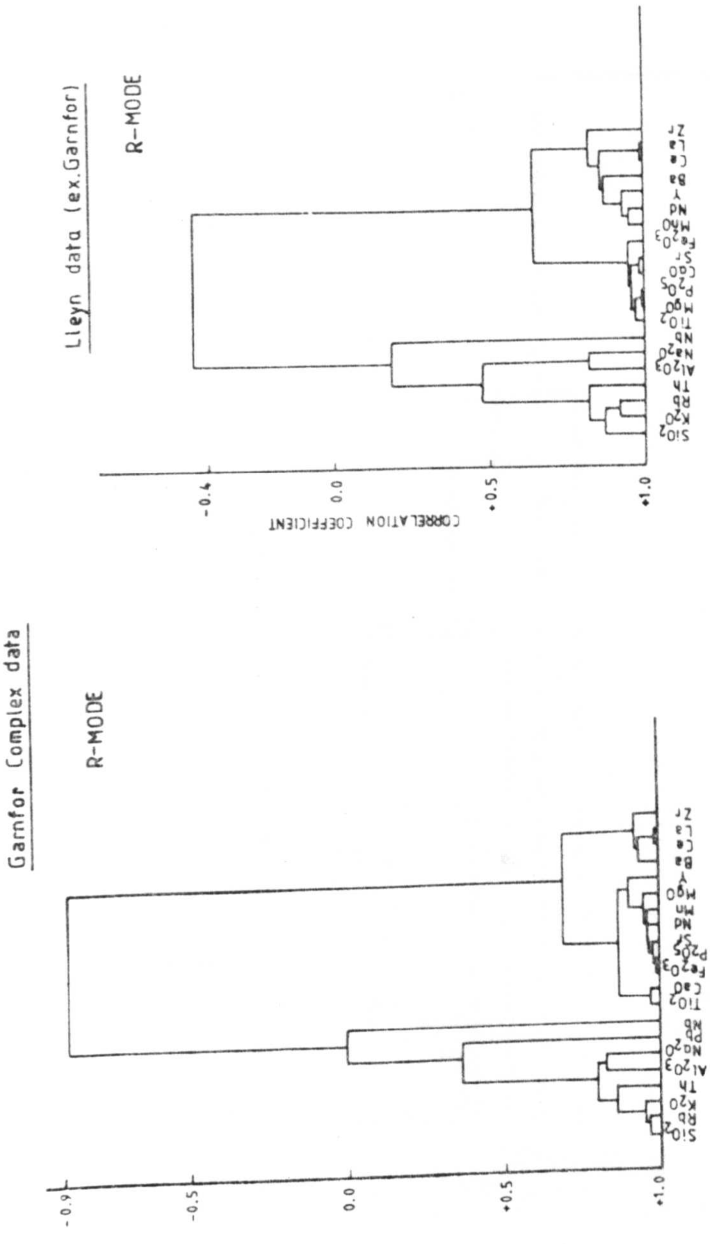

Lleyn data (ex.Garnfor)
R-MODE
Zr
La
Ce
Ba
Y
Nd
MnO
Fe_2O_3
Sr
CaO
P_2O_5
MgO
TiO_2
Nb
Na_2O
Al_2O_3
Th
Rb
K_2O
SiO_2
-0.4
0.0
+0.5
+1.0
CORRELATION COEFFICIENT
Garnfor Complex data
R-MODE
Zr
La
Ce
Ba
Y
MgO
Mn
Nd
Sr
P_2O_5
Fe_2O_3
CaO
TiO_2
Nb
Pb
Na_2O
Al_2O_3
Th
K_2O
Rb
SiO_2
-0.9
-0.5
0.0
+0.5
+1.0

Figure 22

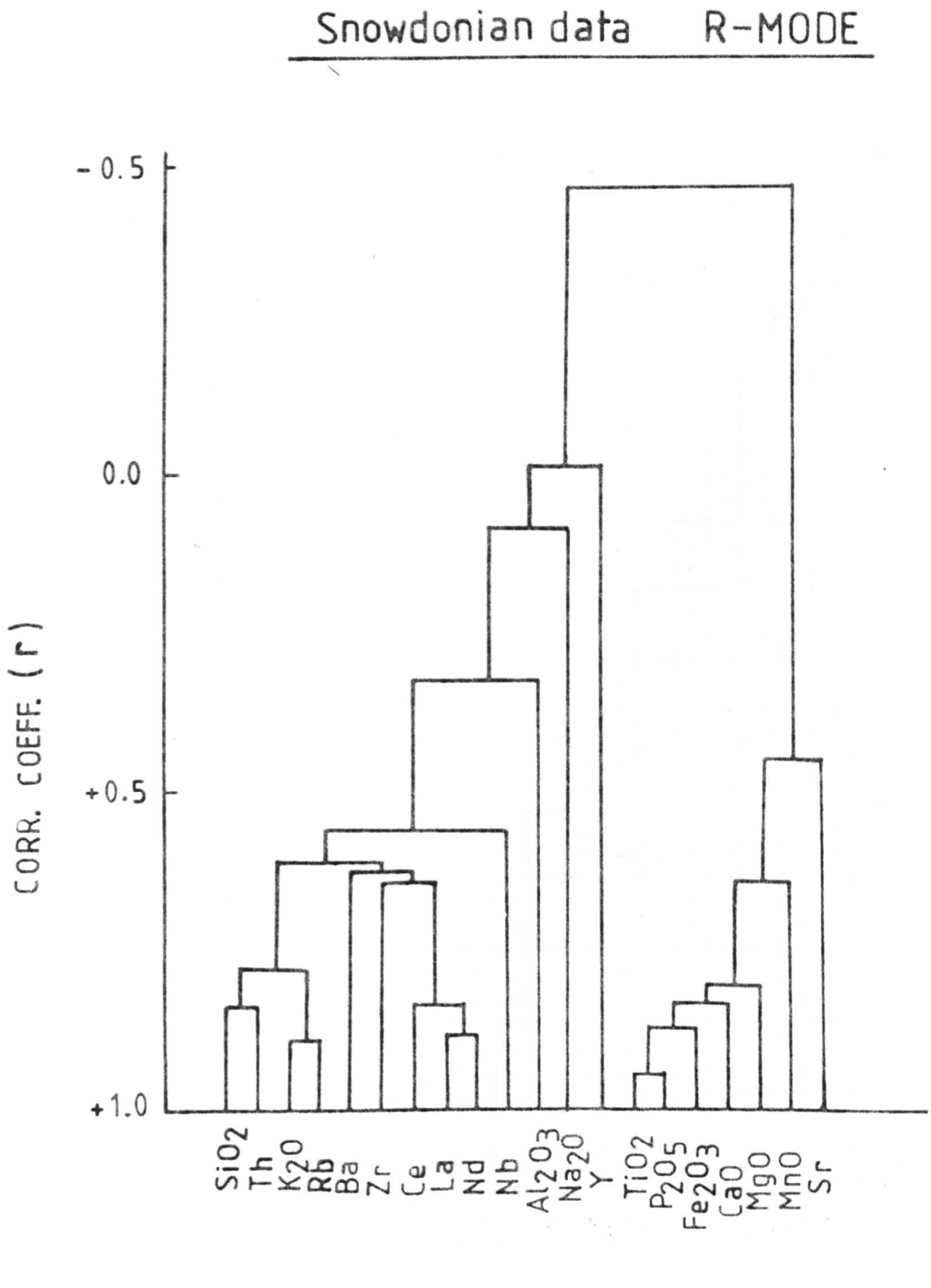

Snowdonian data R-MODE
- 0.5
0.0
+0.5
+1.0
CORR. COEFF. (r)
SiO2
Th
K20
Rb
Ba
Zr
Ce
La
Nd
Nb
Al2O3
Na2O
Y
TiO2
P2O5
Fe2O3
CaO
MgO
MnO
Sr

Figure 23

R-Mode correlation Analysis

Correlations significant at the 99% confidence level

SNOWDONIA o

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Y	Sr	Rb	Th	Ba	Zr	Nb	Ce	La
TiO_2	o −																		
Al_2O_3																			
Fe_2O_3	o −	o +																	
MnO	o −	o +		o +															
MgO	o −	o +		o +	o +														
CaO	o −	o +		o +	o +	o +													
Na_2O		o +																	
K_2O	o +	o −		o −	o −	o −	o −	o −											
P_2O_5	o −	o +		o +	o +	o +	o +	o +	o −										
Y	o +		o −			o −	o −		o +										
Sr	o −	o +		o −	o	o +	o +	o +	o −	o +	o −								
Rb	o +	o −		o −	o −	o −	o −	o −	o +	o −	o +	o −							
Th	o +	o −		o −	o −	o −	o −		o +	o −		o −	o +						
Ba	o +	o −		o −	o −	o −	o −	o −	o +	o −			o +	o +					
Zr	o +	o −		o −	o −	o −	o −		o +				o +	o +	o +				
Nb	o +	o −	o +	o −	o −	o −	o −		o +	o −			o +	o +	o +	o +			
Ce	o +	o −		o −	o −	o −	o −		o +	o −			o +	o +	o +	o +	o +		
La	o +	o −		o −	o −	o −	o −		o +	o −			o +	o +	o +	o +	o +	o +	
Nd	o +	o −		o −		o −	o −	o +			o +		o +	o +	o +	o +	o +	o +	o +

Figure 24

R- Mode correlation analysis.

Correlations significant at the 99% confidence limit.

○ Lleyn intrusions (ex. Garnfor)

● Garnfor Complex.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Y	Sr	Rb	Th	Ba	Zr	Nb	Ce	La
TiO_2	● ○ –																		
Al_2O_3	● ○ +	●																	
Fe_2O_3	● ○ –	● ○ +	● ○ –																
MnO	● ○ –	● ○ +	○ –	● ● +															
MgO	● ○ –	● ○ +	● ○ –	● ○ +	● ○ +														
CaO	● ○ –	● ○ +	● ○ –	● ○ +	● ○ +	● ○ +													
Na_2O	● ○ +	● ○ –	● ○ +	● ○ –	○ –	● ○ –	● ○ –												
K_2O	● ○ +	● ○ –		● ○ –	● ○ –	● ○ –	● ○ –	○ +											
P_2O_5	● ○ –	● ○ +	● ○ –	● ○ +	● ○ +	● ○ +	● ○ +	● ○ –	● ○ –										
Y	● ○ –	● ○ +	● ○ –	● ○ +	● ○ +	● ○ +	● ○ +	● ○ –	● ○ –	● ○ +									
Sr	● ○ –	● ○ +	● ○ –	● ○ +	● ○ +	● ○ +	● ○ +	● ○ –	● ○ –	● ○ +	● ○ +								
Rb	● ○ +	● ○ –	○ +	● ○ –	● ○ –	● ○ –	● ○ –	○ +	● ○ +	● ○ –	○ –	● ○ –							
Th	● ○ +	● ○ –	○ +	● ○ –	● ○ –	● ○ –	● ○ –	○ +	● ○ +	● ○ –	○ –	● ○ –	● ○ +						
Ba	● ○ –	●	●	● ○ +	● ○ +	● ○ +	● ○ +	○ –	● ○ –		● ○ +	● ○ +	○ –						
Zr	● ○ –			● ○ +	● ○ +	○ +	● ○ +		● ○ –	● +	● +	● ○ +	● ○ –	● –	● ○ +				
Nb								● +								○ –			
Ce	● –	○ +		● ○ +	● ○ +	○ +	○ +		● ○ –	○ +	● ○ +	● +	● ○ –	○ –	● ○ +	● ○ +	● ○ –		
La	● –	○ +		● ○ +	● ○ +	○ +	○ +		● ○ –	○ +	● ○ +	● ○ +	● ○ –	○ –	● ○ +	● ○ +	● ○ –	● ○ +	
Nd	● –	● ○ +	○ –	● ○ +	● ○ +	○ +	○ +	● –	● ○ –	● ○ +	● ○ +	● ○ +	● ○ –	● ○ –	● ○ +	● ○ +		● ○ +	● ○ +

1. Group 1 Granites

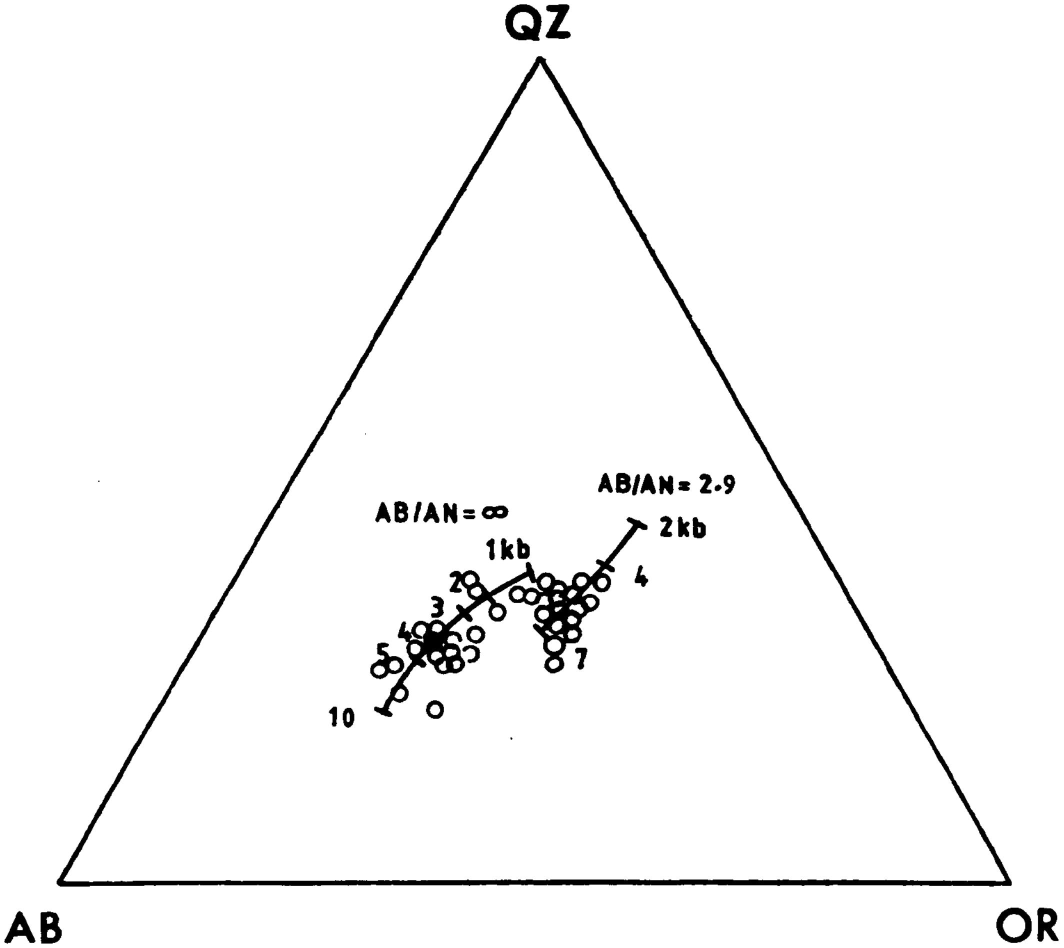
The samples that form this group are granites in the strict sense and their silica content varies between 69-75%. They are mildly peraluminous since corundum appears in their norms but it rarely exceeds 2%. The K_2O/Na_2O ratios are generally greater than one but a number of samples were collected with a ratio of less than unity. This latter observation is believed to result from late stage alterations or assimilation since both processes have operated, especially in the marginal parts of the Bwlch-y-Cywion and Tan-y-Grisiau intrusions (Bromley, 1969). Some samples from Bwlch-y-Cywion are composed almost entirely of albite (e.g. BC4) whilst others show smaller signs of potassium loss (e.g. BC3, IC7, IC6). Bromley (1969) has noted that the upper portions of some of the intrusions have had their original magmatic assemblage completely transformed by the operation of a vapour phase rich in silica and the alkalis. The metasomatic front extends into the country rocks since some hornfelses have been feldspathised and partly mobilised.

The normative quartz-albite-orthoclase and anorthite-orthoclase-albite ternary diagrams are shown in fig. 25, page 132. Although a number of samples possess a variable normative albite content, it may be seen from the Ab-Or-An diagram, using the fields of O'Connor (1965), that the samples of this group are granitic. The low temperature trough (solid line) and its error limits (broken line) are included in the plots and according to Kleeman (1965) these boundaries should delimit all granite compositions that were melts. The experimentally determined minimum melt compositions at various pressures in the system, Q-Ab-Or-An-H_2O, are shown plotted onto the Q-Or-Ab plane and the Snowdonian granites plot close to the trend line connecting the compositions derived from a source with Ab/An = 2.9. Bromley (1969) noted that the microgranites and granophyres plotted close to the low P minimum at 1 Kb pressure while the volcanic rocks, high level rhyolite plugs and metasomatically altered granites lay on the quartz side of the boundary curve. This finding is confirmed and the diagram appears to be a

Figure 25

Normative Q-Or-Ab diagrams. The figures represent a projection of the system Q-Or-Ab-An-H_2O. The loci of minimum melt compositions with varying pH_2O and Ab/An ratios are from Tuttle and Bowen (1958), Luth et al. (1964) and Winkler (1967).

SNOWDONIAN SUITE



LLEYN SUITES

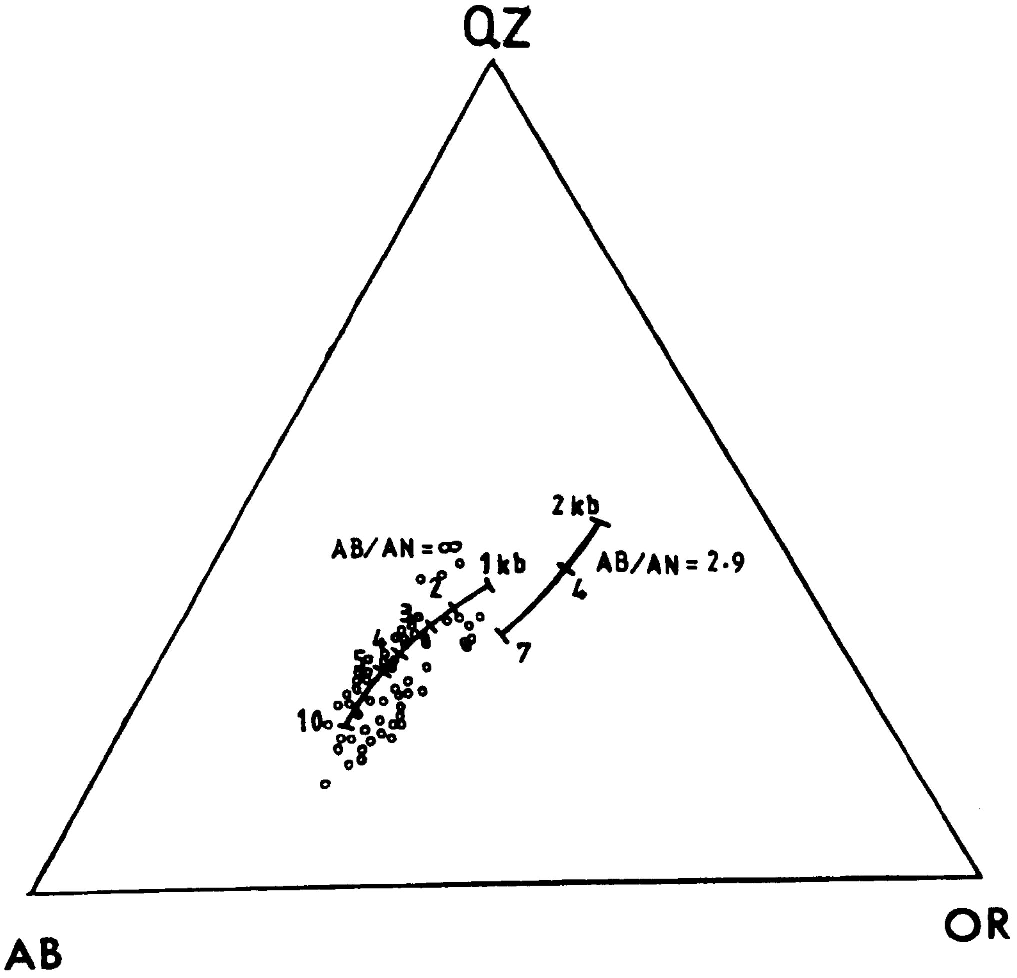
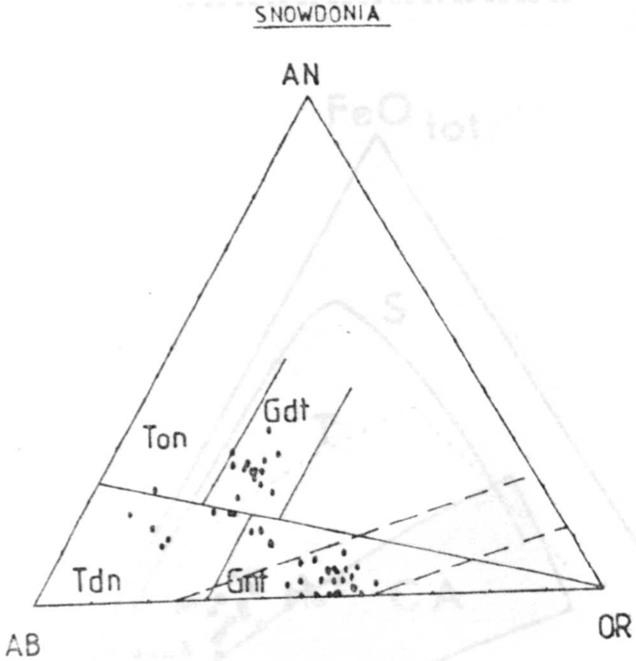
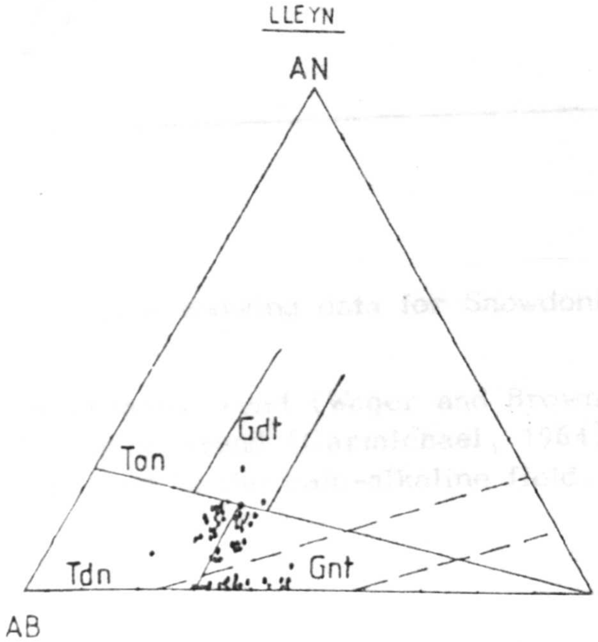


Figure 26

Normative An-Or-Q diagrams with the fields of O'Connor (1965)

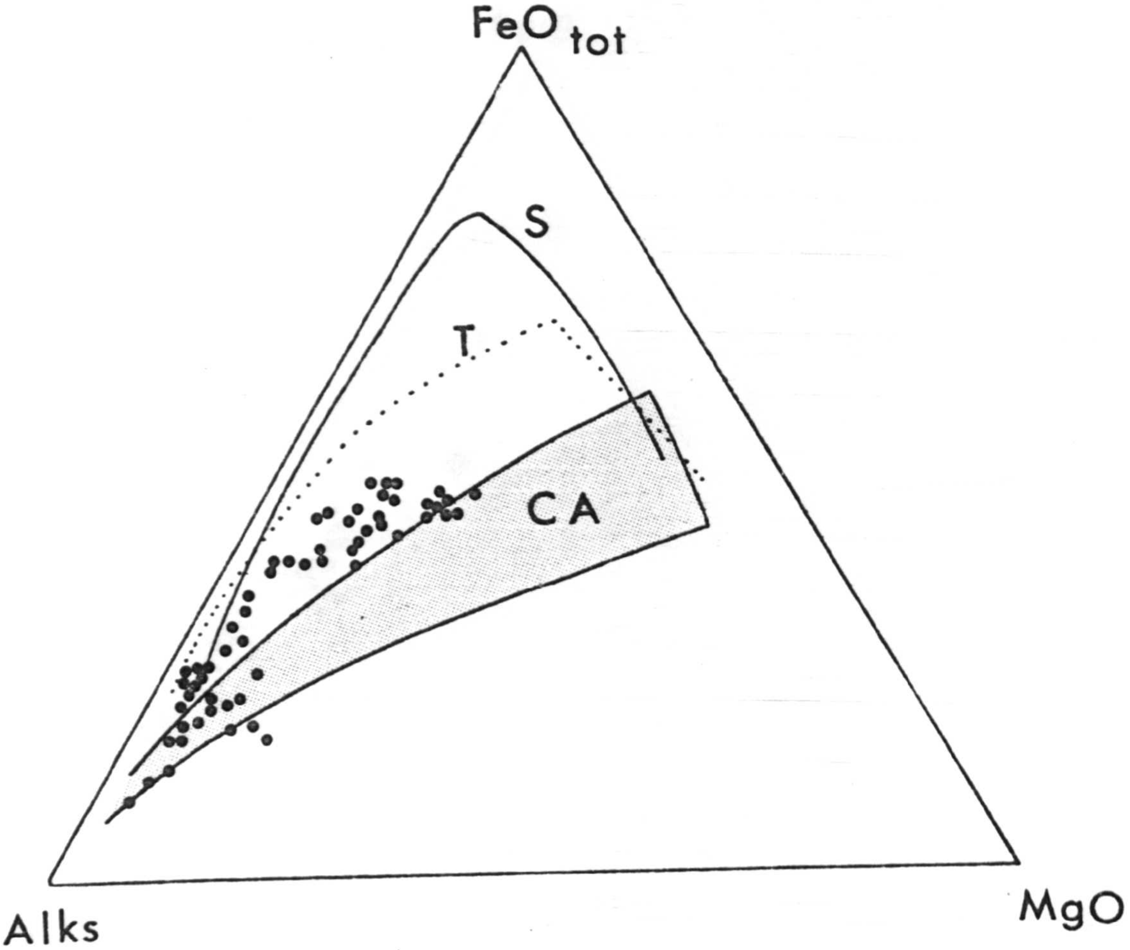




Ton - Tonalite
Gdt - Granodiorite
Tdn - Trondjhemite
Gnt - Granite

Figure 27a

SNOWDONIA

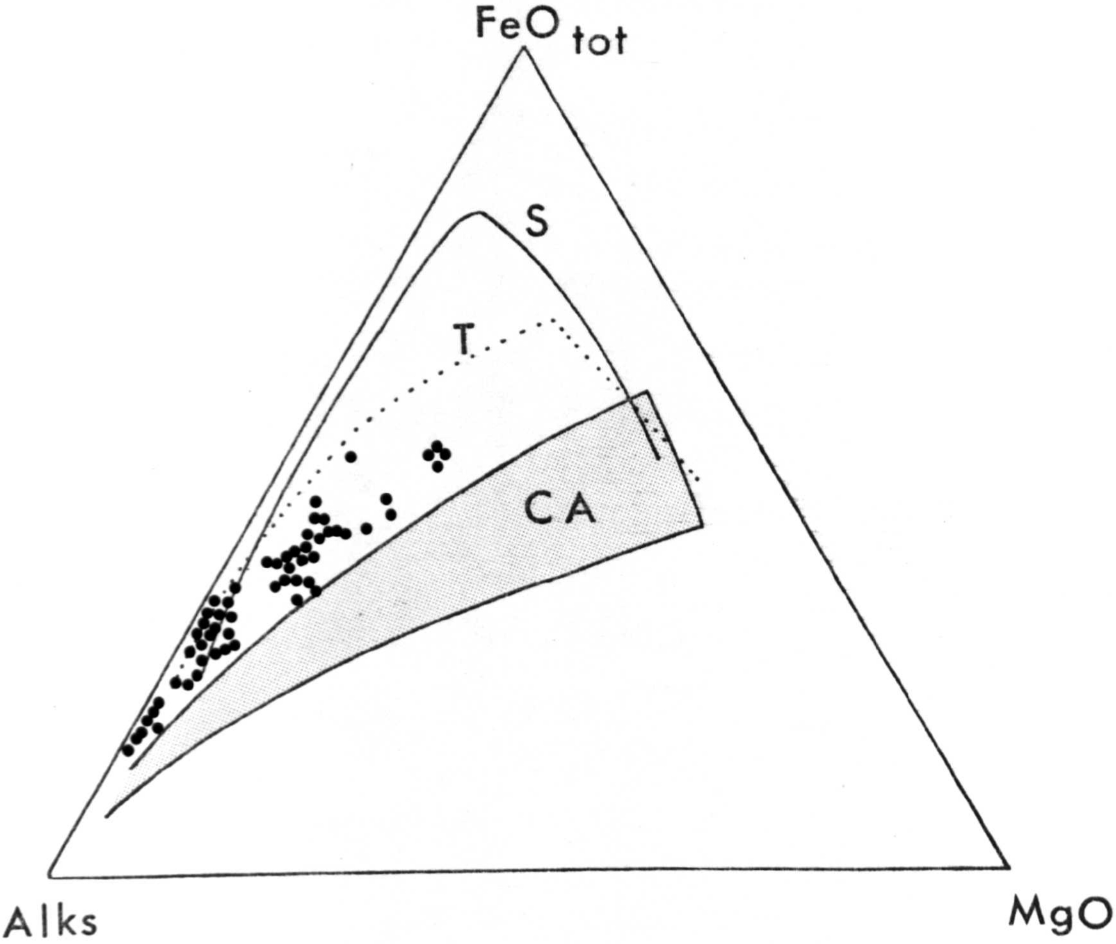


AFM diagram showing data for Snowdonian granitoids (groups 1 + 2).

S - Skaergaard trend (Wager and Brown, 1967).
T - Thingmuli trend (Carmichael, 1964).
Stippled field is the calc-alkaline field.

Figure 27b

LLEYN



AFM diagram showing the data for the Lleyn samples (groups 3 + 6).

S - Skaergaard trend (Wager and Brown, 1967).
T - Thingmuli trend (Carmichael, 1964).
Stippled field is the calc-alkaline field.

useful means of distinguishing the altered material.

The K/Rb ratios of this group vary from 180-360 and no strong correlation is seen with silica using all the data although a significant negative correlation may be obtained if samples displaying possible contamination or alterations are removed from the population. The average upper crustal K/Rb ratio is claimed to be 229 (Shaw, 1968) although considerable ranges have been reported for granitic rocks. The mean value for the Snowdonian suite is not markedly different from Shaw's average. Another alkali diagram with a descriptive use is the alkalis — SiO_2 diagram devised and delineated by Miyashiro (1978). Miyashiro considered alkalic rocks to represent an igneous rock series classification and not necessarily a petrographic class. The latter concept relied on the presence of diagnostic minerals such as the feldspathoids, alkali pyroxenes and amphiboles before a rock could be classified as alkaline. Although the diagram is commonly used and was devised for volcanic rocks it does provide a useful indicator of the affinities of the group 1 granites. Other variation diagrams are shown with the other groups included and it may be seen that some elements and ratios provide a means of identifying in which group a particular sample should be included (e.g. Nb-SiO_2, Zr/Y-SiO_2).

The rare earth element patterns for this group show close similarities to one another and they are approximately sub-parallel. The $(Ce/Yb)_N$ ratios vary from 2.1 — 5.0 although there is also a variation in the abundances of the rare earth elements, Ce_N = 90-145; Yb_N = 23-45. All patterns show a negative europium anomaly which is relatively constant (0.36 - 0.53, Eu/Eu*), light rare earth fractionation, $(Ce/Sm)_N$ = 1.5-2.9, and little fractionation of the heavy rare earth elements, $(Tb/Yb)_N$ = 0.99-1.4. It is noteworthy that yttrium closely follows the rare earths in its behaviour and it would plot very close to the heavy region of its rare earth pattern, (Y_N = Yppm/1.96). In summary the acidic intrusions of Snowdonia possess a negative europium anomaly, moderate light rare earth enrichment and fractionation and almost flat normalised heavy rare earth patterns.

The abundances of Zr, Nb and Th of this group are distinctly different from those of some of the other groups. Zr varies from 200–400 ppm, Nb from 10–20 ppm and Th from 20–35 ppm. Zirconium and niobium are both high field strength elements (i.e. high charge/radius ratio) and their behaviour in magmatic systems may provide a valuable insight into the petrogenetic processes that operated to produce the igneous rocks (Pearce and Gale, 1977). In areas of plate subduction, associated with orogenic magmatism, the abundances of Zr and Nb appear to be controlled by the operation and migration of aqueous fluids and the stability of zircon, ilmenite and rutile (Saunders et al., 1980; Wood et al., 1979). Magmas generated in within-plate areas, such as the oceanic-islands and rift zones, have different Zr, Nb and Zr/Nb values compared with volcanic arc or plate margin magmatism and these points will be discussed in a later chapter. Saunders et al. (1980) showed that Zr increased in abundance from the basaltic and intermediate rocks of the Antarctic Peninsula to a maximum at about 60–65 % SiO_2 whereupon the concentration fell slowly. This is in contrast to the continuing increase found for within-plate magmas. The relatively small changes in Zr content for the Snowdonian suite bear a close similarity to plate margin igneous activity. Pearce and Gale (1977) have shown that orogenic magmas contain relatively lower Nb abundances than anorogenic magmas and thus a reasonably clear distinction can be made between magma provinces, especially when used in conjunction with other data. On the bases of Zr and Nb concentrations in the Snowdonian suite (see page 190) their affinities appear to be with orogenic magmatism. The small ionic size and high charge of thorium prevents its ready accommodation in the main rock forming minerals. For these reasons Th tends to increase in concentration with increasing differentiation of a rock suite i.e. it possesses a very low bulk distribution coefficient. The mineral allanite is a possible host for thorium and Bromley (1964) has found accessory amounts of this mineral throughout the Tan-y-Grisiau intrusion. Owing to the high viscosity of siliceous melts it is questionable as to whether significant fractionation or crystal settling of allanite could occur which may serve to control thorium abundances.

The foregoing account suggests that the Snowdonian granitoids possess the features of calc-alkaline material and a detailed discussion of such features will be found in chapter 7.

2. Group 2 Granites

This group consists of the intrusions of Penmaenmawr, Drosgl and Manod Bach and with the exception of the last named body they outcrop in northern Snowdonia. The rocks are quartz dioritic or microtonalitic and granodioritic in composition and they have been intruded as stock-like or laccolithic bodies at relatively high crustal levels. This last point is indicated by the observations of granophyric textures and autobrecciation. The least silicic of these intrusions is found at Penmaenmawr and it has been described as a graphic microdiorite (Phillips, see Hatch, Well and Wells, p. 314, 1972), a quartz-diorite (Davies, 1968) and a microtonalite (Roberts, 1979).

These intrusions are characterised by containing measurable chromium and nickel (Ni $\gtrsim$30 ppm, Cr $\approx$50 ppm), Titania 0.7-1.2 wt %, Fe_2O_3 Total 6-7 wt % and magnesia between 1-4 wt %. The high level intrusion of Manod Bach, situated in south-eastern Snowdonia, has a fairly variable major element chemistry perhaps resulting from late stage hydrothermal alterations. Its chromium and nickel content are lower than that found for Penmaenmawr but similar to that of the Drosgl samples. The Sr abundances of Manod Bach and Penmaenmawr are subequal but lower than in the Drosgl granodiorite. A point of note concerning the Manod samples are their low abundances of alumina, $\simeq$ 13.6 wt %, compared with the other intrusions. This feature is considered to be primary since Al_2O_3 is not known to be particularly mobile during low-grade metamorphism or weathering (Hart et al., 1974).

When some of these rocks are plotted on the Q-Ab-Or triangle they lie on a trend line connecting minimum melt compositions at various pressures with $Ab/An = \infty$ (fig. 25). The samples from Manod Bach do not lie on any trend, which suggests that either they do not represent a minimum melt composition or that changes in their major element composition have occurred which do not reflect the original magmatic composition. The Ab-Or-An plot, with the fields of O'Connor (1965), show that none of the samples plots in the low temperature trough and that the normative compositions do not closely coincide with the modal compositions of the rocks; Penmaenmawr plots in the granodiorite field and Manod Bach plots in the trondjhemite field.

The K/Rb ratios are not much different from Shaw's (1968) crustal average of 229, for the Penmaenmawr and Drosgl samples (230 and 280 respectively) although the Manod Bach samples have a ratio of approximately 360. This last value may reflect metasomatic movement of the alkalis or it may be a primary feature. Miyashiro's (1978) alkalis-SiO_2 diagram shows that all samples from this group are subalkaline in character (see fig. 28 , page 148).

The rare earth data for samples of this group show a strong consistency of patterns and abundances (see fig. 38 , page 174 and table 4 page 99a). Five patterns were obtained for Penmaenmawr and one each for Drosgl and Manod Bach. The patterns for Penmaenmawr are parallel to each other except for small differences around europium, and all contain a prominent negative anomaly, $Eu/Eu^* \approx 0.8$. The light rare earth elements show a small amount of fractionation $(Ce/Sm)_N = 1.7$ which is similarly seen for the heavy rare earth elements, $(Tb/Yb)_N = 1.3$. The mean abundances of Ce and Yb are 75 times chondrite and 28 times chondrite respectively, $(Ce/Yb)_N \approx 2.7$. Yttrium, with an average concentration of 50 ppm, does not seem to behave as if it were a middle rare earth but it may act as if it had a smaller ionic radius than lutetium as claimed by Drake and Weill (1972). Variations in the predicted behaviour of certain elements may be explained by processes such as different degrees of ion hydration or complexing which may affect the effective ionic radius. The sample from Drosgl shows a very similar pattern to those found for Penmaenmawr although at higher abundances.

The europium anomaly is slightly larger Eu/Eu* = 0.74 and the light rare earths are more enriched, $Ce_N = 81$. The rare earth pattern found for the Manod Bach sample also shows a similarity to the Penmaenmawr patterns with a negative europium anomaly Eu/Eu* = 0.82, light rare earth fractionation $(Ce/Sm)_N = 1.4$, slight heavy rare earth fractionation $(Tb/Yb)_N = 1.2$ and a $(Ce/Yb)_N$ ratio of 2.7.

The high field strength elements, zirconium and niobium, show some variation between the three intrusions which may result from crystallisation of phases which could accommodate them such as zircon and ilmenite. Both of these minerals are seen in thin-sections.

	Zr	Nb	Zr/Nb
Penmaenmawr	200	10	20
Drosgl	320	16	20
Manod Bach	300	11	27

The high Zr/Nb ratios and the low abundances of Nb suggest a plate margin evolutionary environment for the magmas of this group and more detailed evidence supporting this view will be outlined in a later chapter.

The rocks of this group although more basic than those of group 1 do bear a number of similarities. These include the abundances of Zr, Nb, Y, the rare earths and the high Zr/Nb ratios. The shape of the rare earth patterns is not greatly different although the $(Ce/Sm)_N$ ratios are higher for the group 1 granites which may indicate that they represent more evolved compositions.

The alkalis and alkali earth elements show some variation between the three intrusions of group 2 and some of this may be accounted for by their high mobility during magmatic and post-magmatic processes.

	Rb	Ba	Sr	K_2O wt %	K/Rb
Penmaenmawr	100	400	120	2.7	140
Drosgl	80	700	160	2.8	280
Manod Bach	40	600	120	1.8	350

(abundances in ppm unless stated otherwise)

3. Group 3 Granites

The intrusions of Foel Fras, Gyrn and Moel Wnion form the group 3 granitoids and they outcrop about 4 km south-west of Penmaenmawr. The Foel Fras rock has been described as a quartz-latite (Evans, 1968) and it consists of altered hornblende and pyroxene set in a matrix of quartz, feldspars and chlorite. Both Gyrn and Moel Wnion are porphyritic microgranites and their mineralogy consists of hornblende, pyroxenes and plagioclase set in a groundmass of quartz, feldspars and some chlorite. The silica content of these intrusions varies from 62 - 68 % while K_2O/Na_2O ranges from 1.6-1.9.

Chromium and nickel are measurable in the samples obtained from the three intrusions and this feature is found only for group 2 and 3.

	Foel Fras	Gyrn	Moel Wnion	
Ni	15	6	5	ppm
Cr	10	6	5	Lower limits of determination = 5 ppm

In terms of the major elements these samples are similar to those of group 2 although some trace element contents and ratios suggest that the rocks of each group have not shared a similar evolutionary history. The alkalis and alkali earth elements are not greatly different in abundance between the two groups although some small differences, except for Y, may be seen for Zr, Nb and Th.

	Foel Fras	Moel Wnion	Gyrn	Group 2 (Drosgl)	
Ba	650	850	630	700	ppm
Rb	95	124	146	80	ppm
Sr	250	111	130	160	ppm
K_2O	2.8	3.6	3.7	2.8	wt %
K/Rb	260	240	211	280	ppm
Zr	370	394	278	320	ppm
Nb	10	16	18	16	ppm
Zr/Nb	25	18	12	20	
Th	10	16	18	13	ppm
Y	46	49	50	60	ppm
SiO_2	63 %	69 %	69 %	64 %	

The rare earth patterns are the most graphic means of discriminating between groups 2 and 3. The patterns for Foel Fras and Gyrn are subparallel, except for a negative europium anomaly for the Gyrn sample, and both show fractionation of the light and heavy rare earths. The Foel Fras sample does not possess a negative europium anomaly whereas that of Gyrn is sizeable, Eu/Eu* = 0.6. The table below shows the pertinent ratios which describe the rare earth characteristics and those for Drosgl are included for a comparison of groups 2 and 3.

	Foel Fras	Gyrn	Drosgl
$(Ce/Sm)_N$	2.4	2.3	1.63
$(Ce/Yb)_N$	5.22	4.8	2.89
$(Tb/Yb)_N$	1.3	1.3	1.39
Eu/Eu*	1.0	0.6	0.74
Yb_N	18	25	28

4. Group 4 Granites

The riebeckite-bearing microgranite of Mynydd Mawr possesses a very distinctive chemistry and the Q-mode cluster analysis separates them easily from the remaining samples (see figures 18,19,20, pages 123-5). The intrusion is a stock of oval plan which outcrops in central Snowdonia and its geochemical features place it securely in the realm of peralkaline granites. The samples are very siliceous with $SiO_2 \approx 75\%$, and strongly alkalic with $K_2O + Na_2O \approx 9\%$, $K_2O/Na_2O \approx 1.0$. The ternary Q-Ab-Or diagram shows that the samples lie along the trend line for minimum melts at 4-10 kb with Ab/An = ∞ and all samples lie in the low temperature trough of the Ab-Or-An diagram suggesting that the compositions represent a minimum melt or a residual melt.

The concentrations of the determined trace elements are in full accord with the known characteristics of peralkaline granites (see discussion, page 161). The alkali earths, Ba and Sr, are very low in concentration compared with subalkaline or alkaline granitic rocks which may indicate that the compositions are highly evolved and the alkalis, K and Rb are highly concentrated compared with the alkaline granites of group 1.

Sample MM1			Sample TG3 Group 1
Ba	45	ppm	897
Sr	7	ppm	30
Rb	248	ppm	164
K_2O	5.5	%	5.18 %
Na_2O	3.7	%	3.7 %
Y	150	ppm	79
Zr	655	ppm	285
Nb	114	ppm	22
Th	41	ppm	18
TiO_2	0.09	%	0.23
Al_2O_3	13.7	%	13.8 %
K/Rb	123		260

The high field strength elements, Zr and Nb, are strongly enriched relative to the group 1 samples and Y and Th are also notably concentrated.

The rare earth data for three samples are strikingly different from all other determined samples in that their heavy and light rare earths normalised abundances are similar and all samples have a very large negative europium anomaly, Eu/Eu* = 0.04. These features are not uncommon in peralkaline granites (Bowden and Whitley, 1974; Ferrara and Treuil, 1975). One sample, MM6, possesses a very unusual pattern with a positive slope (fig. 33 , page 163) and it may be seen that two other samples, which were analysed by X-ray fluorescent procedures alone (MM3, MMAA), have similar features.

	MM4	MM2	MM6	MM3	MMAA
$(Ce/Yb)_N$	1.4	1.0	0.2	-	-
$(Ce/Y)_N$	0.9	0.8	0.2	0.3	0.3
$(Ce/Sm)_N$	1.1	1.0	0.5	-	-
$(Tb/Yb)_N$	1.7	1.3	0.6	-	-
Eu/Eu^*_N	0.04	0.04	0.07	-	-
Ce_N	86	66	12	15	20
Y_N	91	90	56	55	60

5. Group 5 Granites

The leucogranites of Nant Bodlas and Foel Gron represent this group and they are peralkaline with molar Al_2O_3 less than molar $K_2O + Na_2O$. The geochemistry of these two intrusions is similar to Tremlett's (1972) analysis for the nearby Myntho riebeckite microgranite although no alkali amphiboles were recognised in the Nant Bodlas or Foel Gron samples. There are notable differences in geochemistry between the group 4 and the group 5 peralkaline granites and these may be seen clearly in the table below.

The rare earth element patterns for this group (fig. 32 , page 162) show fractionated light rare earth elements, a large negative europium anomaly and flat heavy rare earths: $(Ce/Sm)_N = 2.3$, $(Tb/Yb)_N = 1.08$, $(Ce/Yb)_N = 4.4$, $Eu/Eu^* = 0.21$. An examination of La, Ce, Nd and Y determined by X-ray fluorescence analysis indicates that the remaining samples of Nant Bodlas and Foel Gron, which were not analysed by neutron activation analysis, possess the same rare earth characteristics as those shown in fig. 32 , page 162.

Both Nant Bodlas and Foel Gron plot in the thermal valley of the normative An-Or-Ab diagram and between the $Ab/An = \infty$ and $Ab/An = 2.9$ trend lines of the Ab-Q-Or triangle. This may suggest that the compositions represent minimum melts or residual melts (figure 25, page 132).

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	Group 4 (MM4)	Group 5 (IC 38)
SiO_2	75	74
TiO_2	0.09	0.23
Al_2O_3	13.2	12.7
Fe_2O_3	2.3	3.7
MnO	0.17	0.15
MgO	0.13	0.06
CaO	0.11	0.16
Na_2O	5.33	4.08
K_2O	3.65	5.06
P_2O_5	0.01	0.02
Ba	30	15
Sr	5	19
Rb	286	206
Ce	69	178
La	29	86
Y	179	115
Zr	657	855
Nb	121	73
Th	42	26
K/Rb	125	200

6. Group 6 Granites

This group consists of the intermediate to acidic igneous rocks of the Lleyn Peninsula and the Snowdonian intrusions of Moel Perfedd, Y Garn and Mynydd Tal-y-Mignedd. Petrographically the suite consists of andesites, tonalites, granodiorites, granites and felsites. The andesitic samples do not bear a close resemblance to orogenic andesites such as those described by Taylor (1966) or Jakes and White (1971) since the former contain higher abundances of the high field strength elements Zr, Nb, phosphorus and titanium compared with reported values for orogenic andesites (table 8). The group as a whole is alkalic and all samples plot above Miyashiro's (1968) dividing line (fig. 28 , page 148). Samples with a chemistry very similar to the andesitic rocks of Lleyn have been collected from the Indian Ocean, Iceland (Thómpson et al., 1974) and Bouvet Island (Baker, 1976) and they have been termed oceanic andesites.

SiO_2	59.64	57.7
Al_2O_3	17.38	14.7
TiO_2	0.76	1.39
Fe_2O_3	5.26	9.62
MgO	3.95	2.78
K_2O	2.04	2.8
Na_2O	4.4	3.7
P_2O_5	0.28	0.74
Yb	1.9	5.12
Ce	24	107
Th	2.2	4
Zr	110	546
	(1)	(2)

(1) Jakes and White (1971)
(2) Sample PAND (this study)

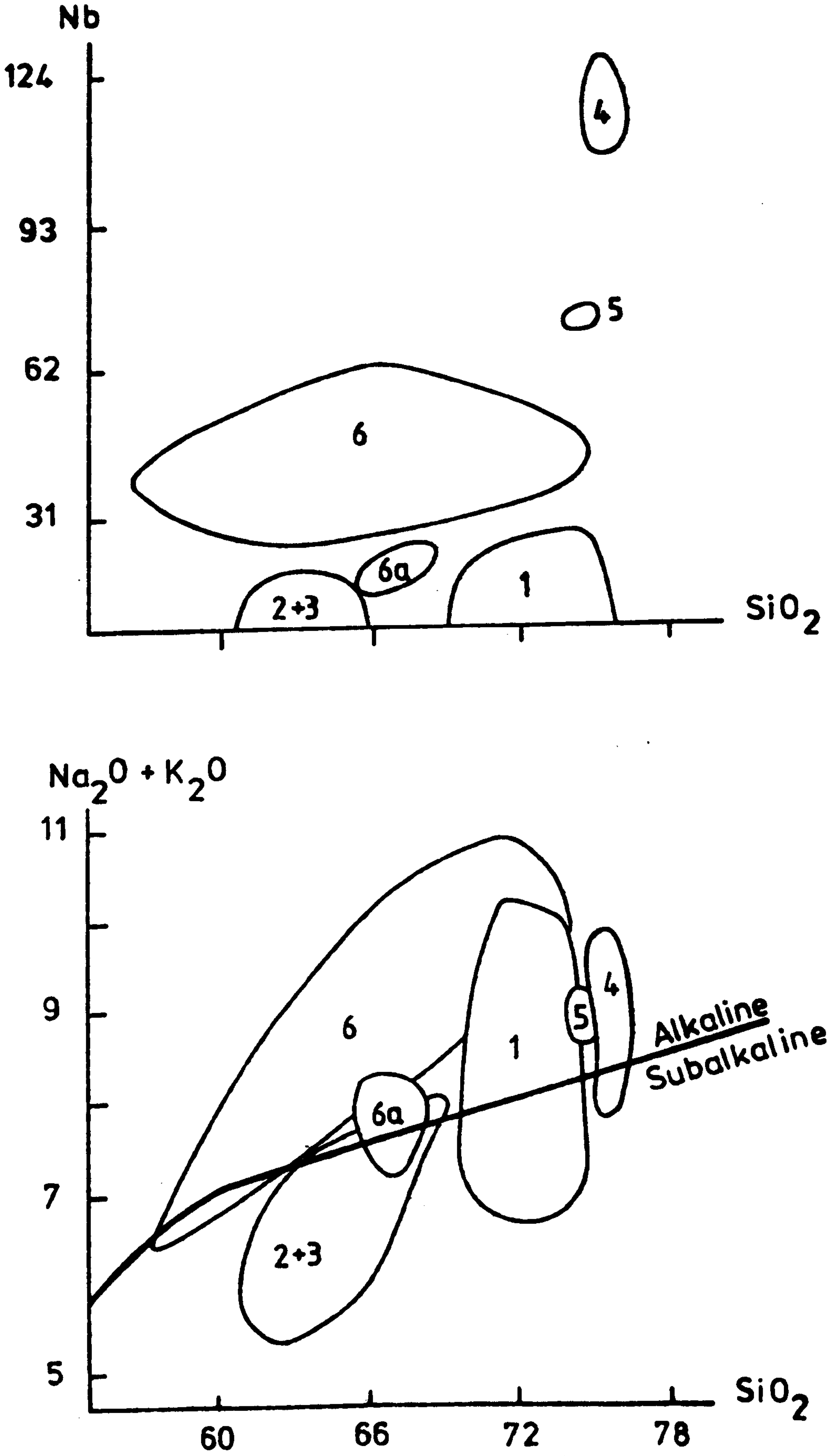
The AFM diagram (fig. 27 , page 134) shows that the samples of this group lie between the trend for Thingmuli volcano (Carmichael, 1964) and the field for calc-alkaline rocks delineated by Ringwood (1974). The rocks of this suite plot between the Ab/An = ∞ and Ab/An = 2.9 trend lines of the Q-Or-Ab ternary diagram (fig. 25) and the samples are also shown plotted on the An-Or-Ab triangle (fig. 26 , page 133).

A distinctive feature of these rocks are the concentrations of the alkali and alkaline earth elements. Soda is high (4.5-6.2 %) in most samples compared with the intermediate and acidic material of the previously discussed groups. Potash varies from 2.8-5.0 %, which is not strikingly different from the other groups. Rubidium and barium possess an abundance variation not dissimilar from the other groups although strontium covers a wider range, 20-530 ppm, which is distinctly different from the ranges of the earlier discussed suites (see variation diagrams pages 169-72). The K/Rb ratios for this group vary from 250-550 and most values are well outside Shaw's (1968) upper crustal average of 229. The andesitic material possesses the largest ratio and the granitic and felsitic samples have the lowest ratio.

The high field strength elements Zr and Nb are the most powerful means of discrimination between this group and the others. Zr varies from approximately 200 ppm in the felsic rocks to over 800 ppm in the granodioritic and tonalitic rocks. The andesitic samples from Moel-y-Penmaen contain 550 ppm Zr. Nb ranges from 30-52 ppm and this element provides the best discrimination between all groups (see fig. 28, page 148). The abundances of Zr and Nb may be useful for identifying whether acid igneous rocks were formed at a plate-margin or within-plate. Pearce and Gale (1977) consider that Nb contents of 0-10 ppm are common in calc-alkali granites while values of 50-500 ppm are not uncommon in granitic rocks from an anorogenic or within-plate environment. Zr is also characteristically enriched in within-plate magmas relative to calc-alkalic magma although considerable variations may result from the crystallisation or not of zircon.

The rare earth element abundances and patterns are distinctive compared with most of the other groups and they display some variations which are shown in Fig. 48 (page 230). The granodioritic rocks generally possess light and heavy rare earth fractionation with a small or no Eu anomaly. The andesitic sample has a subparallel pattern to those of the granodiorites although at higher abundances. The felsic rocks such as the Yr Eifl microgranite, Carreg-y-Llam microgranite and the Yr Eifl felsite generally have lower abundances of the rare earths than the intermediate rocks and have small to large negative Eu anomalies. A negative correlation between rare earth abundance and SiO_2 and a positive correlation between SiO_2 and the size of the Eu anomaly exist (fig. 48 ,

Figure 28



1). Snowdonian granitic suite 2). Penmaenmawr,Drosgl,Manod Bach 3). Foel Fras,Gyrn 4). Mynydd Mawr 5). Nant Bodlas,Foel Gron 6).Lleyn and Garnfor suites 6a). Mynydd Perfedd,Y Garn, Mynydd Tal-y-Mignedd.

Alkaline-subalkaline dividing line from Miyashiro (1978).

page 230). The latter feature is not uncommon in igneous suites (Emmerman et al., 1975) although the former point appears to be less common. Arth et al. (1978), however, have reported a similar occurrence in a trondjhemitic suite from S.W. Finland and the variations are interpreted as resulting from the fractional crystallisation of hornblende from an originally gabbroic magma. Hornblende possesses distribution coefficients for the rare earth elements that are greater than unity in acidic melts and its removal from a magma will produce successive residual liquids which are poorer in the rare earths than some of the earlier liquids. Thus, similar behaviour in the Lleyn rocks may point to the involvement of a mineral(s) with a bulk distribution coefficient greater than unity. The essential rare earth ratios which describe the pattern characteristics for the Lleyn samples are shown below.

	$(Ce/Yb)_N$	$(Ce/Sm)_N$	$(Tb/Yb)_N$	Eu/Eu*
Yr Eifl Felsite	5.7	2.9	1.2	0.44
Garnfor (IC50)	7.2	2.6	1.4	0.64
" (G1)	6.9	2.1	2.0	0.99
" (G3)	6.8	2.2	1.9	1.02
PAND	5.5	1.6	2.1	1.02
Yr Eifl microgranites	7.4	2.8	1.5	0.86
Mynydd Nefyn	7.1	2.3	1.6	0.85
Penrhyn Bodelias	6.9	2.2	1.8	0.95
Carreg-y-Llam	7.6	3.1	1.4	0.88
Llanbedrog	7.5	2.6	1.6	0.23

A point of some importance concerning this group of rocks is the very low abundance of the two transition elements, Cr and Ni. These elements fall below the determination limit for the X-ray Fluorescence procedure used (see Appendix II) and no amounts were measured in the andesitic samples. These observations are considered to be of considerable importance for the petrogenetic evolution of this group and they will be discussed in chapter 8 .

An examination of the variation diagrams for this group (fig. 43 , page 212) and the Q-mode cluster dendrograms (fig. 18 , page 123) show that members of this suite possess geochemical differences. The most significant of these are shown by the SiO_2 versus Y, Zr, Nb, La, Ce and Nd diagrams. These demonstrate that the rocks of the Garnfor Complex (see fig. 43 , page 212), which range in SiO_2 from 62–69 %, have different abundances of these elements compared with the remaining samples. Similarly, it may be seen that a smoothly changing trend emerges if the andesitic samples are considered as one end-member and the Yr Eifl felsites as the other. Most element pairs are strongly correlated if the sample population consists of the andesites, Garnfor complex and the felsites (see fig. 43 , page 212). The R-mode cluster dendrogram shows that the light rare earths, Y, Ba and Zr cluster with the mafic constituents which is not commonly found in igneous suites since the rare earths, Ba and Zr are normally found to behave incompatibly and they would cluster with the felsic constituents.

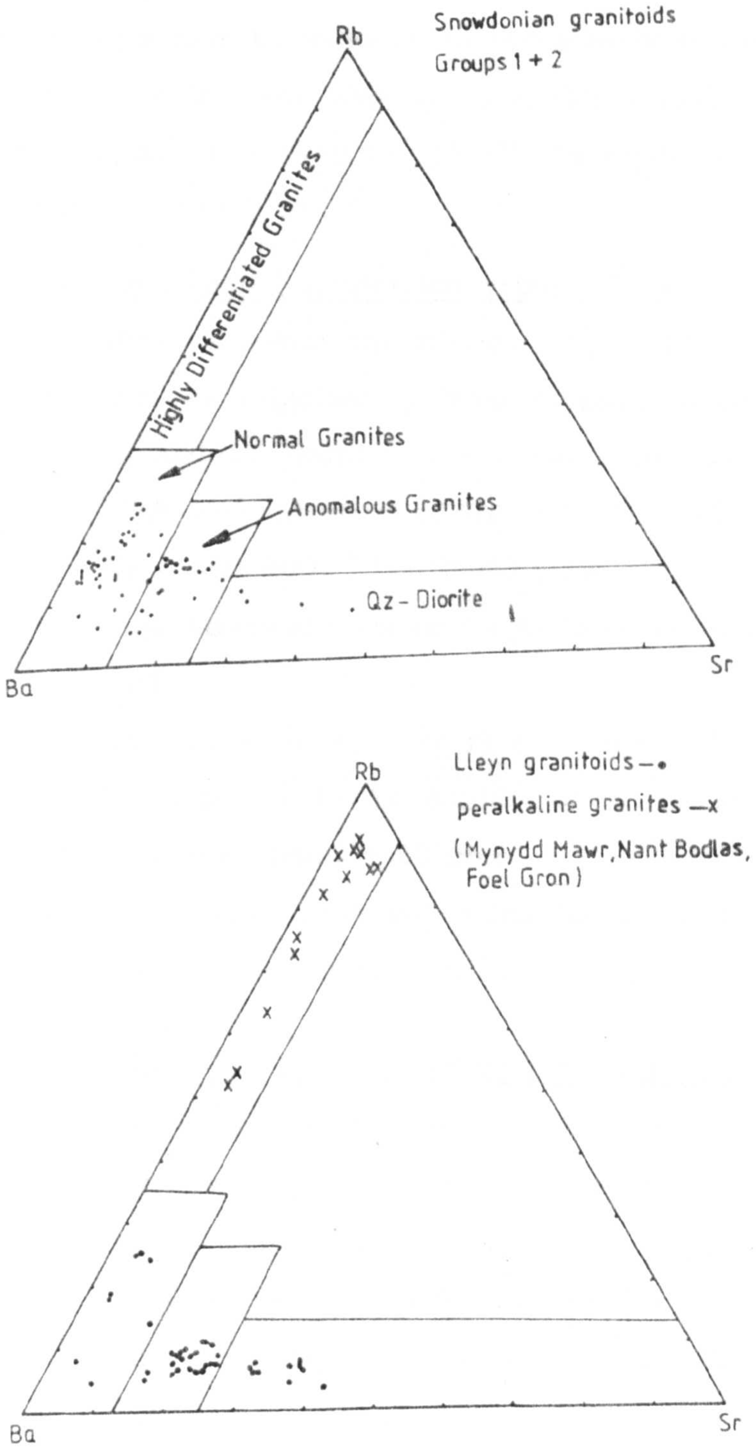
Good linear correlations are found with the remaining data if the Garnfor suite is excluded and a similar behaviour of the elements is noted (see fig. 43, page 212). Strong linear correlations are observed if Llanbedrog and Penrhyn Bodelias are considered as the end-members. However, if the andesitic samples are used as the basic end-member strong correlations remain although Y, Zr and Nb versus SiO_2 produce more or less curved trends. Zr, for example, increases from 550 ppm (PAND) to 780 ppm (PBodH) followed by a rapid decrease to 200 ppm (LBG). Since zircons are found in thin-sections of all samples but the andesites the variation may be explained readily by crystallisation of zircon when the zirconium content of the magma reached a sufficiently high value. Alternatively if partial melting were considered to be the petrogenetic mechanism, zircon in the source undergoing fusion would be required to disappear after the extent of melting that produced PBodH and the decline in concentration to PAND would result from the diluting effect of further melting.

Further examination of the data suggests that there are differences in element abundances for the intrusions of Gurn Ddu, Moel Penllechog and Gurn Goch. The rare earths, particularly the heavy members, Th and Rb are more enriched in these intrusions than in the Garnfor or Lleyn suites and Zr and Nb appear to be poorer in concentration. On the basis of the close geochemical similarities between the members of this group it would seem reasonable to assume that they shared a similar evolutionary history but that their differences resulted from minor variations in petrological processes (see later discussion).

The Snowdonian intrusions of Moel Perfedd, Y Garn and Mynydd Tal-y-Mignedd possess many of the features of the group 6 samples although there are differences in detail. Zr and Nb abundances, which are distinctive in the Lleyn samples are not so high in the three Snowdonian intrusions and the rare earth element contents are also lower. The rare earth patterns bear a close similarity to those of the Garnfor complex and the abundances of Th, Ba, Sr and Rb are not dissimilar.

				GARNFOR	
	YGN	TYM	MP3	IC50	Garn1
$(Ce/Yb)_N$	6.3	6.4	5.3	7.2	6.8
$(Ce/Sm)_N$	2.4	2.6	2.4	2.6	2.1
$(Tb/Yb)_N$	1.5	1.5	1.3	1.4	2.0
Eu/Eu*	0.95	0.87	0.99	0.64	0.99
Ba	804	794	924	643	620
Rb	80	85	94	98	72
Sr	266	263	180	204	363
Th	9	10	11	13	8

Figure 29



The Rb-Ba-Sr ternary diagram for the granitoids of North Wales. The four fields are those of El Bouseily et al. (1975). The diagram seems to have a limited genetic use.

Conclusions

The preceding account has shown that it is possible to break the sample population of Lower Paleozoic granitoids into six groups. On the basis of the rare earth patterns especially it seems that the number of these groups may be reduced to three main groups as listed below. It will be shown in later chapters that this threefold group does have genetic significance even though all the members of each group are not necessarily comagmatic.

1. Alkaline Group (comprising groups 3 + 6)
    - i) Wide chemical variations, $SiO_2 = 57 - 74\%$
    - ii) Inverse relationship between rare earths and SiO_2 and Th
    - iii) Ni and Cr contents below determination limit (< 5 ppm)
    - iv) High concentration of Zr and Nb in all but the acidic members; Zr = 500-800, Nb = 30-60 ppm
    - v) High concentration of Na_2O (5-6 %) in the intermediate - acid rocks
    - vi) No europium anomaly in the intermediate samples but a sizeable one in the acidic rocks (0.2-0.4)
    - vii) Th varies from 4-20 ppm
    - viii) Some heavy rare earth fractionation especially in the intermediate samples, $(Tb/Yb)_N \approx 2$.

2. Peralkaline Group (comprising groups 4 + 5)
    - i) High concentrations of the heavy rare earth elements with flat chondrite normalised heavy rare earth abundances ($\approx$ 50 x chondrite)
    - ii) Large negative europium anomalies (≈ 0.18)
    - iii) High concentrations of Zr, Nb, Th, Rb and Y
    - iv) Low concentrations of Ba and Sr (< 100 ppm and < 20 ppm respectively)
    - v) Silica content $\approx 74\%$

3. Sub-alkaline and Alkaline Group (groups 1 + 2)

   i) Wide range in SiO_2 level (60-74 %)

   ii) Generally a positive relationship between rare earth content and SiO_2

   iii) Ni and Cr contents measurable in the intermediate rocks, (Ni $\approx$ 30 ppm; Cr $\approx$ 60 ppm)

   iv) Zr and Nb abundances are $\lesssim$ 400 ppm and $<$ 20 ppm respectively

   v) Th contents vary from 7-33 ppm

   vi) All members contain a negative Eu anomaly (0.36-0.87)

   vii) There is no marked fractionation of the heavy rare earths, $(Tb/Yb)_N \approx 1.2$

   viii) There is moderate enrichment of the light rare earths over the heavy rare earths, $(Ce/Yb)_N = 2\text{-}5$

As a general statement it appears that the abundances of Zr, Nb and the rare earth elements are the most diagnostic for assigning an intrusion to one of the three main groups of North Wales granitic rocks (sensuo lato) while other elements, such as Na_2O, Al_2O_3, Th, Rb, Sr and Y, may be useful for placing the rocks into the subgroups.

Chapter 7

THE INTERMEDIATE AND ACID INTRUSIVE ROCKS OF CENTRAL AND NORTHERN SNOWDONIA

The silicic intrusive igneous rocks of this area consist of sills, laccoliths and boss-like bodies which range from quartz-diorite through granodiorite to alkali granite. Texturally they vary from fine-grained porphyritic varieties (quartz-latite) to porphyritic microgranites, granophyres and intrusive rhyolites. These bodies have received attention from Harker (1889), Shackleton (1959), Rast (1969), Bromley (1963, 1969), Davies (1968) and Evans (1969) who considered that the intrusives represented the sub-surface equivalents of the voluminous deposits of intermediate to acid volcanic material. Rast and Bromley believed that the acid material formed through the melting of crustal rocks by an ascending body of basic magma although their conclusions were based largely on structural and stratigraphic evidence. Hendry (1968) supported their view of crustal melting for the origin of the volcanic rocks basing his evidence on the geochemistry of the Pitt's Head Tuffs.

The present study has concerned itself with a geochemical investigation of the acidic intrusions and a considerable body of new chemical data has been obtained. On a chemical basis it is possible to separate the sample population into three main groups.

Group 1	Foel Fras, Gyrn, Moel Wnion, Tal-y-Mignedd, Y Garn, Mynydd Perfedd
Group 2	Mynydd Mawr, Nant Bodlas, Foel Gron
Group 3	Bwlch-y-Cywion, Tan-y-Grisiau, Ogwen, Nant Gwynant, Castell, Croesor composites, Penmaenmawr, Drosgl and Manod Bach

The strongest criteria for separating the groups are the rare-earth element abundances and patterns but other features are also diagnostic and they will be described in more detail during the discussions.

GROUP 1 GRANITOIDS

Foel Fras, Gyrn, Moel Wnion, TYM, YGN and MP

These intrusions have been described by Shackleton (1959), Evans (1969) and Davies (1968). Evans and Davies studied the intrusions of the northern Carneddau and they included some major and trace element chemical analyses. Their results consist largely of descriptions and interpretations of the structures, petrography and stratigraphic relations of the bodies. Shackleton (1959) described the intrusions of Tal-y-Mignedd and Y Garn as 'porphyrites' and they were briefly included as part of a more extensive study of the Moel Hebog area.

The rare earth element patterns of these intrusions are subparallel to one another and it is this feature which indicates that the rocks are closely related. All the samples show fractionated patterns with light rare earth enrichment, $(Ce/Sm)_N \simeq 5$, heavy rare earth fractionation $(Tb/Yb)_N \simeq 1.4$, and the sample from the Gyrn intrusion has a sizeable negative Eu anomaly, $Eu/Eu^* = 0.59$. No sample from Moel Wnion was analysed for the REE, other than La, Ce and Nd, but from a consideration of its trace and major element chemistry to that of Gyrn it can be predicted that its REE pattern would be very similar.

The various rare earth element ratios (table 4 , p. 99a) for this group are similar to those of the intermediate and acid rocks from Lleyn, discussed in pages 145-151. The Q-mode statistical analysis (page 126) of all the samples from North Wales shows that Mynydd Perfedd, Y Garn, Taly Mignedd, Gyrn and Moel Wnion cluster with the Lleyn group although Foel Fras does not. The chemical differences observed between this group and the Lleyn suites are not great enough to preclude a similar origin and variations in the proportions of crystallising phases and some physicochemical parameters (P, T, fO_2) may account for the differences. A list of some of the more important geochemical ratios, especially those elements which are not particularly mobile during low grade metamorphism or weathering, are presented below for the Lleyn suite and this group of intrusions. Perhaps the most important difference

Figure 30

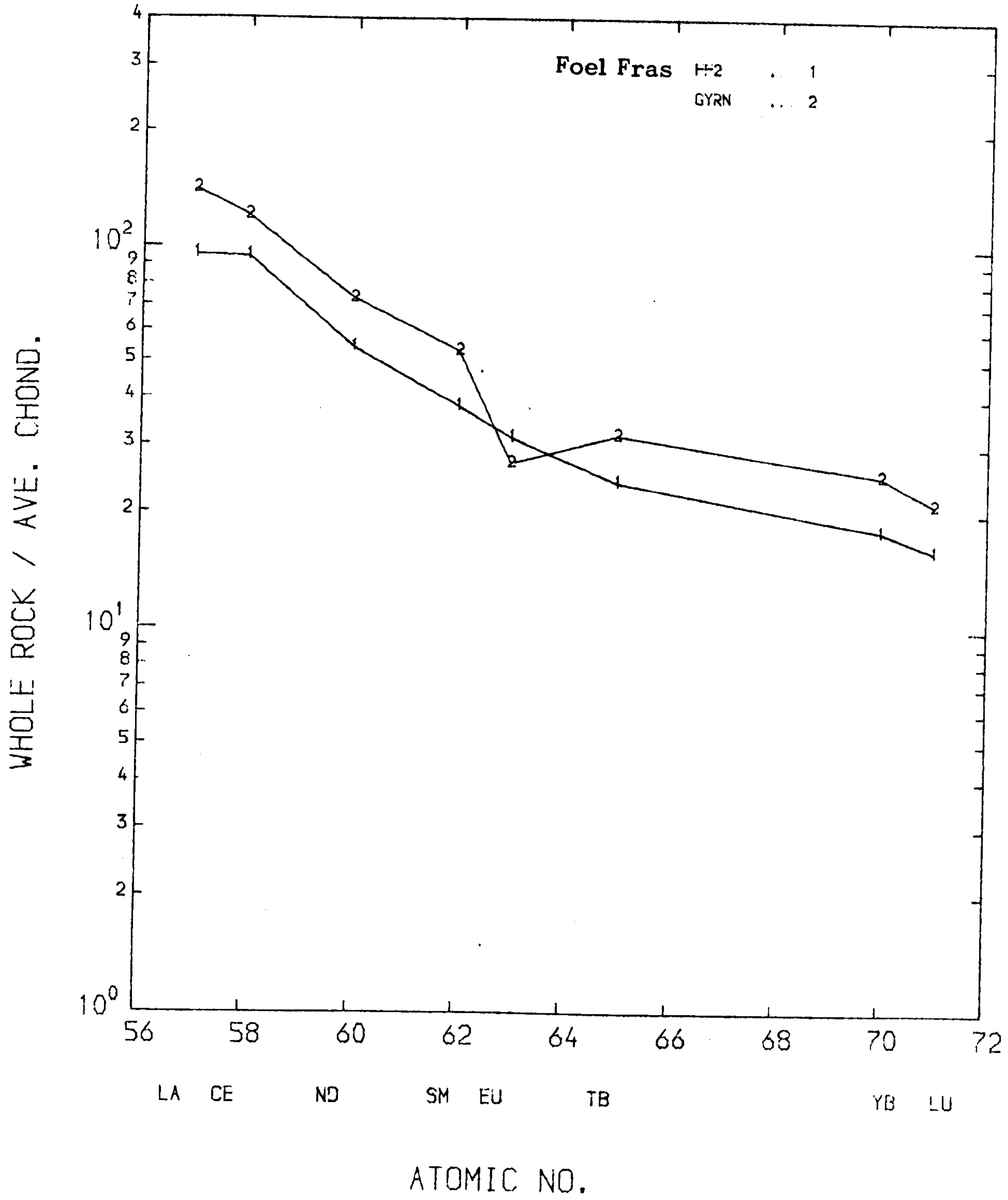
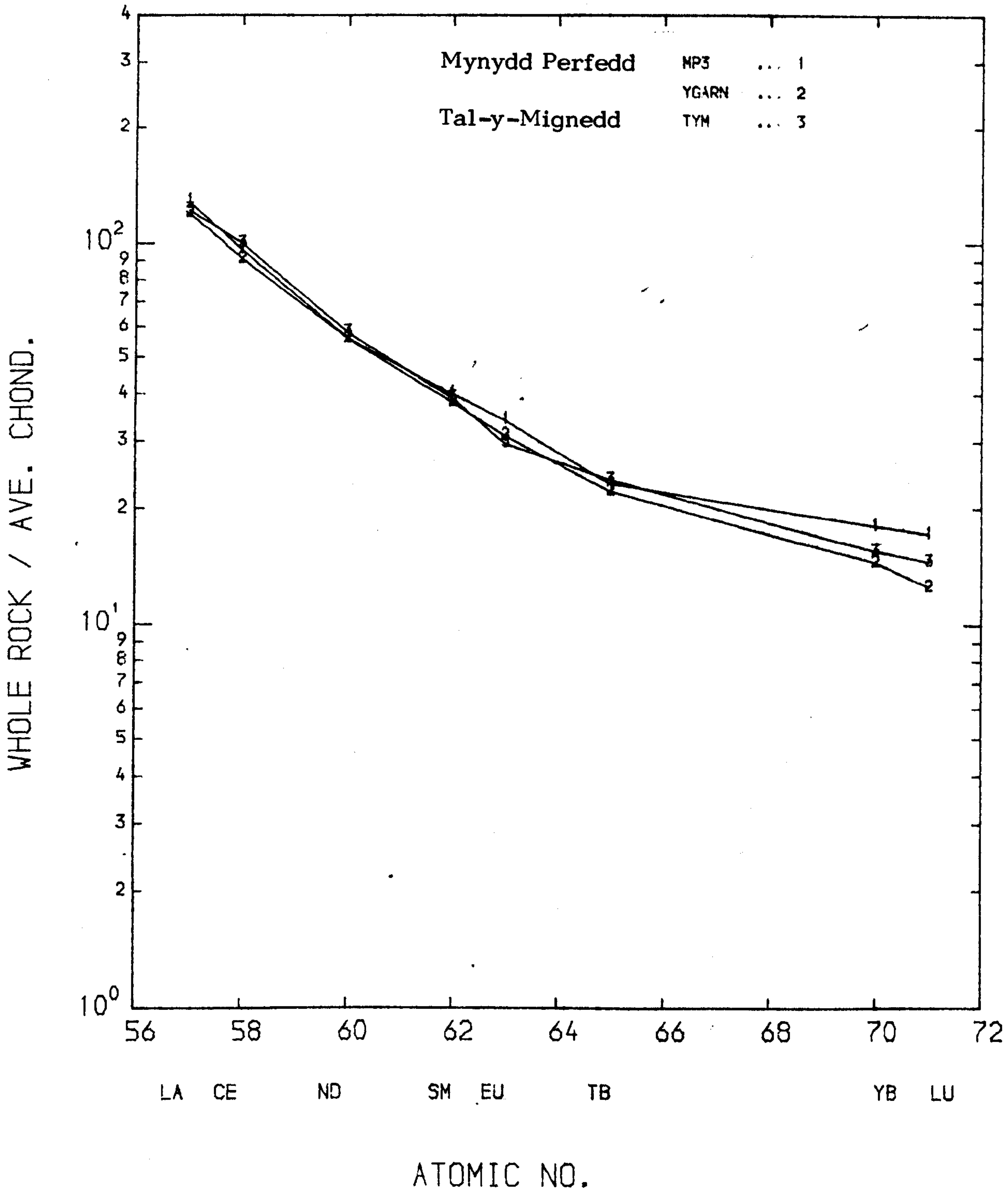

Foel Fras
H-2 . 1
GYRN .. 2
4
3
2
10²
9
8
7
6
5
4
3
2
10¹
9
8
7
6
5
4
3
2
10⁰
WHOLE ROCK / AVE. CHOND.
56
58
60
62
64
66
68
70
72
LA
CE
ND
SM
EU
TB
YB
LU
ATOMIC NO.

Figure 31


Mynydd Perfedd
MP3 ... 1
YGARN ... 2
Tal-y-Mignedd
TYM ... 3
WHOLE ROCK / AVE. CHOND.
ATOMIC NO.
10^0
10^1
10^2
2
3
4
5
6
7
8
9
56
58
60
62
64
66
68
70
72
LA
CE
ND
SM
EU
TB
YB
LU

is the higher Zr/Nb ratio found for the northern and central Snowdonian group.

	Lleyn intrusions	Foel Fras, Gyrn, Moel Wnion etc.
SiO_2	60 - 70 %	60 - 70 %
Zr/Nb	6 - 18	12 - 25
Zr/Y	6 - 16	5 - 10
$(Ce/Y)_N$	4 - 6	4 - 5
K/Na	0.6 - 0.9	0.4 - 1.0
Th	7 - 17 p.p.m.	9 - 18 p.p.m.

Weaver (1977) and Ferrara and Treuil (1975) have demonstrated that fractional crystallisation does not cause Zr/Nb ratios to change if these elements are behaving incompatibly and the magnitude of this ratio is generally low (<10) for suites derived from tholeiitic and continental alkali basalts. High Zr/Nb ratios are a feature of magmas generated above a subduction zone (calc-alkaline or island-arc associations) and they result largely from the retention of niobium in titanium-rich residual phases during hydrous partial melting (Wood et al., 1980; Tarney, Windley, 1979). Ilmenite is such a phase and it is a phenocryst phase in the samples of this group. Its crystallisation and removal from a magma may bring about a reduction in the Nb content and therefore, if Zr is not removed at the same time, in zircon for example, the Zr/Nb ratio will rise. Recent experimental determinations of partition coefficients for Nb have shown that it may be appreciably accommodated by ilmenite, ortho- and clinopyroxenes, hornblende and magnetite (Pearce and Norry, 1979). McCallum et al. (1978) state that ilmenite is capable of fractionating Nb from Zr since $D^{Nb} \simeq 3 \times D^{Zr}$ in ilmenite. The K^{Nb} for ilmenite appears to be temperature dependent.

The criteria used to distinguish between partial melting and fractional crystallisation for the Lleyn intrusions are the abundances of Cr and Ni and the relationship between Rb and Th. An examination of these geochemical features shows that Cr and Ni abundances are about 18 ppm and 10 ppm respectively and the Rb/Th ratio is about 8 for the most undifferentiated samples (Foel Fras). The concentrations of Cr and Ni fall sharply with increasing silica content and this feature is better explained by fractional crystallisation than by partial melting (Allegre et al., 1977). The Rb/Th ratio varies from 7-9 for the range of compositions sampled, which is within the observed range for the Lleyn suites, and on this basis a fractional crystallisation origin is favoured (see pages 222-226 for a fuller discussion of Rb/Th ratios). The existence of a negative Eu anomaly in the Gyrn sample (and possibly Moel Wnion) and a less marked anomaly in the Tal-y-Mignedd sample is consistent with fractionation of plagioclase. The petrographic features found for many of the Lleyn samples, such as glomeroporphyritic clusters of plagioclase and clots of pyroxenes and feldspars, are also observed in thin-sections of samples from Foel Fras, Y Garn and Tal-y-Mignedd. It is clear that the Snowdonian samples have been affected by the greenschist metamorphism and possibly other processes because the mafic minerals and plagioclase are partially converted to chlorite and epidote. Apatite appears to have been an important mineral phase in the Lleyn suites and its fractionation seems to have had a profound effect on the abundances of the rare earth elements and strontium. The involvement of apatite in this group is likely, although the correlation of P_2O_5 with the rare earths and yttrium is not so strong as that found for the Garnfor and Lleyn suites. If the evolutionary history of this group is similar to the Lleyn groups then it is necessary to explain the relatively low REE contents compared with the andesitic samples from Lleyn. Apatite is an observable phase in the samples of this group and it is considered to be the most likely mineral to produce the required control on REE abundances.

On the basis of geochemical similarities and an original mineral assemblage like that of the Lleyn intrusions it is considered that this Snowdonian group of intrusions is possibly derived by fractional crystallisation of a tholeiitic basaltic magma. Owing to the geographical separation of some of the intrusions of this group it is likely that a number of magma chambers existed and that differences in P, T, pH_2O and fO_2 may have controlled the proportion of mineral phases that crystallised. Plagioclase, for example, seems to have been more important for the evolution of the N. Snowdonia members of this group than for the Central Snowdonian members (Y Garn, Mynydd Perfedd etc.).

GROUP 2 GRANITOIDS

Mynydd Mawr, Nant Bodlas and Foel Gron

The intrusions of Nant Bodlas and Foel Gron outcrop on the Lleyn Peninsula but owing to their geochemical similarities to Mynydd Mawr it is expedient to discuss their origins together. The geology of Mynydd Mawr has been described by Harker (1889) and Cattermole and Jones (1970). The boss penetrates Llanvirnian sediments and refraction of the regional cleavage along with deformed metamorphic spots led Cattermole and Jones (1970) to conclude that the intrusion was pre-cleavage and post Llanvirnian. An Ordovician age, possibly Caradocian, is suggested. Tremlett (1972) investigated the intrusions of Lleyn and he assigned the intrusions of Nant Bodlas and Foel Gron to the Ordovician although his evidence was based on chemical affinities to other intrusions which he believed had an Ordovician age.

The intrusions of this group are all peralkaline with an excess of the alkalies over alumina (agpaitic index $\simeq$ 1.04) although texturally and mineralogically there are differences between the intrusions. Mynydd Mawr contains the distinctive amphibole riebeckite, which is commonly replaced by chlorite, and a fine-grained quartz-feldspar mosaic. The intrusions from Lleyn are coarser-grained microgranophyres and some samples have been described as containing riebeckite although none was found in this study. Tremlett (1972) has presented three analyses of riebeckite-bearing microgranites from Myntho Common and their chemistry is very similar to that of the samples from Nant Bodlas and Foel Gron (table 5, page 166).

The trace element geochemistry of oversaturated peralkaline rocks is very distinctive and details may be found in various papers in Bulletin

Figure 32

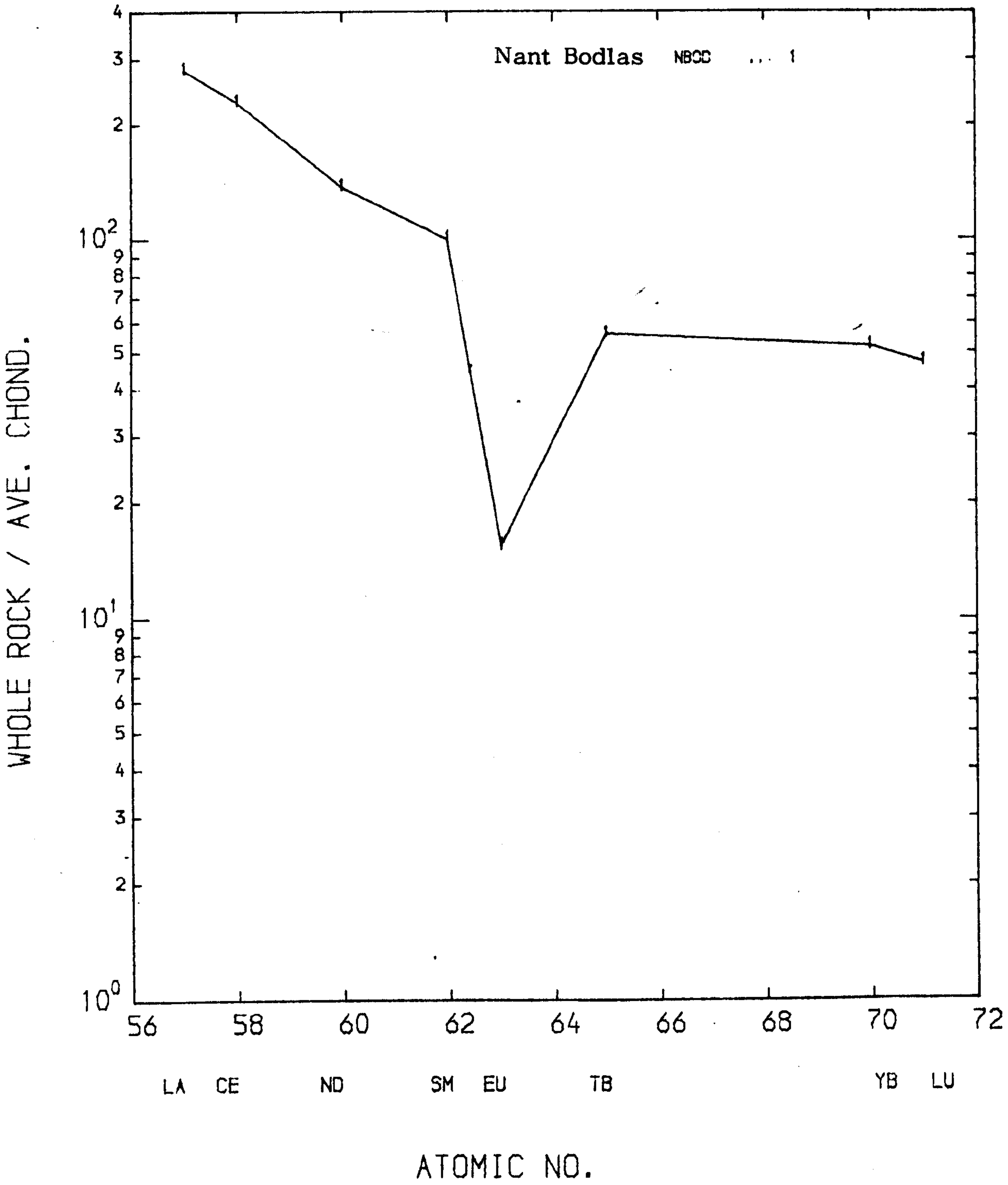
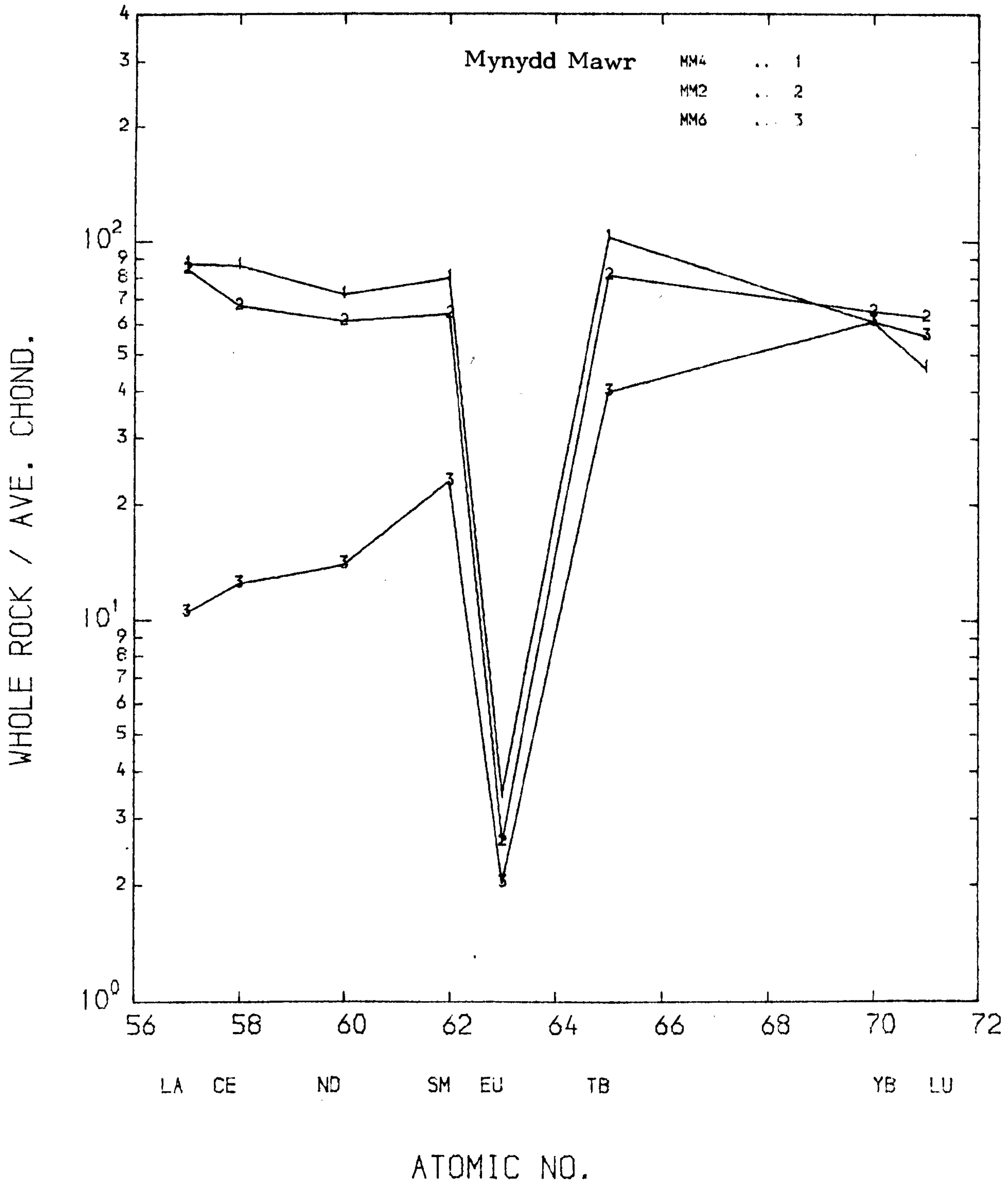

Nant Bodlas NBCC ... 1
WHOLE ROCK / AVE. CHOND.
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
9
8
7
6
5
4
3
2
10^0
56
58
60
62
64
66
68
70
72
LA
CE
ND
SM
EU
TB
YB
LU
ATOMIC NO.

Figure 33


Mynydd Mawr
MM4 .. 1
MM2 .. 2
MM6 .. 3
WHOLE ROCK / AVE. CHOND.
10^0
10^1
10^2
2
3
4
5
6
7
8
9
56
58
60
62
64
66
68
70
72
LA
CE
ND
SM
EU
TB
YB
LU
ATOMIC NO.

Volcanologique (Vol. 38, 1975) where oversaturated peralkaline volcanic rocks are considered in detail. Briefly, the geochemistry of such rocks shows that some elements are greatly enriched and some are greatly impoverished relative to alkaline or subalkaline igneous rocks.

1) The rare earths, Y, Rb, Th, U, Zr, Nb, Hf, Ta, Mo, Zn, F, Cl are strongly enriched.
2) The alkali earths (Ba, Sr), Eu, Sc, Cr, Ni, Co, Cu, V are strongly impoverished.

The origin of oversaturated peralkaline rocks has received considerable attention in recent years and experimental and chemical data have been collected which provide an insight into possible evolutionary mechanisms (White et al., 1979; Baker , 1977; Weaver, 1977; Bowden et al., 1974, 1979). The consensus view for the evolution of peralkaline rocks is that of crystal fractionation from a mafic magma with plagioclase or orthoclase as important fractionating phases (White et al., 1979; Weaver, 1977). Feldspar fractionation can adequately account for the observed impoverishment of Eu, Sr and Ba found in most oversaturated peralkaline rocks and the importance of "the plagioclase effect" was stated by Bowen (1945) while Bailey and Schairer (1964) suggested an "orthoclase effect" to account for the generation of such rocks. The "plagioclase effect" would tend to produce potassic or potassi-sodic peralkaline rocks whereas the operation of the "orthoclase effect" would produce sodic peralkaline rocks. The operation of a "feldspar effect" demands that the amount of anorthite precipitated in plagioclase must exceed the normative anorthite content of the parental magma. Virtually all basaltic magmas satisfy this requirement but not all basalts are associated with peralkaline felsic magmas. Bailey (1975) claims that oversaturated tholeiites are not found with oversaturated peralkaline rocks and he argues that the "plagioclase effect" can only succeed in mafic rocks which have initially high alkali contents, such as transitional and alkali basalts.

There is a controversy concerning open- or closed-system mechanisms for peralkaline suites and the literature reflects the uncertainties associated with either concept owing to the poor understanding of element behaviour in supercritical aqueous liquids or volatile phases. Bailey (1977) argues that the consistently low H_2O in natural peralkaline glasses contradicts a closed-system evolutionary mechanism. The intrinsic H_2O content of such material is often found to be lower than that of the proposed parental basalts, which is contrary to that predicted by a closed-system process. Baker (1977) considers that the behaviour of the incompatible or hygromagmatophile elements would be very different for a solid-melt than for a melt-aqueous (gas) phase. The ratios of the incompatible elements (e.g. Zr/Hf, Ta/Nb, Th/U) are not appreciably affected by closed-system differentiation processes in alkalic suites but Baker suggests that there is some evidence to show that the ratios may vary by an order of magnitude during open-system processes such as fenitisation. His explanation for this behaviour is that ionic mass may be the controlling factor where a fluid or gas phase is present rather than ionic radius and charge.

The trace element characteristics of the peralkaline rocks of North Wales are in full accord with the generalised features stated by Ferrara and Treuil (1975) noted on page 164. The abundances of Ba, Sr and Eu are very low compared with other oversaturated igneous rocks and their magnitude may be explained by the crystallisation differentiation of plagioclase, orthoclase or anorthoclase all of which can appreciably accommodate the alkali earth elements and Eu. The abundances of Cr, Ni, TiO_2, MgO, CaO, P_2O_5 are low compared with alkaline granites, and their REE, Y, Zr, Nb, Rb and Th are high (table 5 , page 166). All of these chemical features are consistent with either a derivation by extensive crystal fractionation or very small degrees of partial melting of a mafic source. In view of the great difficulty in separating a small volume of melt from a residue (partial melting) and because crystal fractionation from a basaltic magma has already been shown to provide a plausible explanation for the Lleyn suites, it is considered likely that Mynydd Mawr, Nant Bodlas and Foel Gron have evolved via crystal fractionation. Buma et al. (1971) have described the geochemistry of some New England granites and subalkaline, alkaline and peralkaline varieties were found. The chemistry of the Quincy granite is closely similar to that of Nant Bodlas (see table below) and it has been claimed by those workers to be derived from a basic magma by extensive crystal fractionation.

Table 5

	Nant Bodlas	Foel Gron	Quincy(1)	Myntho Common(2)
SiO_2	74.02	74.6	74.86	75.02
TiO_2	0.25	0.24	0.2	0.24
Al_2O_3	12.4	12.2	11.61	11.43
Fe_2O_3	0.91	1.84	2.29	0.79
FeO	2.68	1.84	1.25	2.89
MnO	0.21	0.21	0.02	0.07
MgO	0.11	0.10	0.05	0.47
CaO	0.26	0.39	0.41	0.87
Na_2O	4.51	4.68	4.30	3.73
K_2O	4.00	4.06	4.64	4.08
P_2O_5	0.02	0.01	trace	trace
Ba	17	51	n.d.	trace
Rb	140	155	n.d.	182
Sr	8	7	n.d.	15
Th	26	27	14	n.d.
Zr	850	833	936	990
Nb	73	74	n.d.	115
Y	115	114	n.d.	114
La	91	84	89	200
Ce	183	166	212	255
Sm	18.55	n.d.	20	n.d.
Eu	1.06	n.d.	0.81	n.d.
Tb	2.62	n.d.	2.2	n.d.
Yb	10.8	n.d.	8.9	n.d.
Lu	1.64	n.d.	1.4	n.d.

(1) Buma et al. (1971)

(2) Tremlett (1972), trace elements
Fitch (1967), major elements

n.d. not determined

The rare earth element data for Mynydd Mawr show some marked differences from the sample analysed from Nant Bodlas. An examination of La, Ce, Nd and Y abundances for Foel Gron and Tremlett's (1972) analysis of the Myntho Common riebeckite microgranite suggest that their rare earth abundances would be similar to that found for Nant Bodlas (table 5, page 166). The $(Ce/Yb)_N$ and $(Ce/Sm)_N$ ratios of Mynydd Mawr are approximately unity, whereas Nant Bodlas has a $(Ce/Yb)_N$ ratio of 4.4 and a $(Ce/Sm)_N$ ratio of 2.3. Furthermore, europium anomalies are larger for Mynydd Mawr ($Eu/Eu^* = 0.04$) than for Nant Bodlas ($Eu/Eu^* = 0.23$). It is not clear whether the unusual rare earth parameter for Mynydd Mawr reflect the parent or whether they have been imposed by secondary processes. Similar patterns to those of Mynydd Mawr have been found in riebeckitic granites from the U.S.S.R. and the sample which displays the $(Ce/Yb)_N$ ratio of 0.2 (MM6) also has an analogue with an albitised riebeckitic granite from the U.S.S.R. (Mineyev, 1963). Similar REE patterns have also been found in alkalic and peralkalic granites from Nigeria and the operation of a hydrothermal fluid has been proposed to explain those patterns (Bowden et al., 1974, 1979). Such a process does not seem unlikely for the Mynydd Mawr Microgranite especially in view of the $(Ce/Sm)_N$ ratios of less than unity for MM3, MM6, MMA.

GROUP 3 GRANITOIDS

The Snowdonian Suite - Tan-y-Grisiau, Bwlch-y-Cywion, Ogwen, Nant Gwynant, Castell, Croesor acid composites, Drosgl, Penmaenmawr and Manod Bach

The intrusions of this group outcrop in northern and central Snowdonia and they have been emplaced as stocks, laccoliths or sills in sedimentary and volcanic rocks of Cambrian to Ordovician age. The bodies, which rarely have an outcrop area exceeding 2 km^2, consist of porphyritic microgranites and granophyres, quartz-latites, Figures 34 - 37

Harker Diagrams for the intermediate-acid rocks of the Snowdonian suite:

Penmaenmawr	(+)
Drosgl	(.)
Manod Bach	(.)
Bwlch-y-Cywion	(o)
Tan-y-Grisiau	
Ogwen	
Castell	
Nant Gwynant	
Croesor composites	

Figure 34

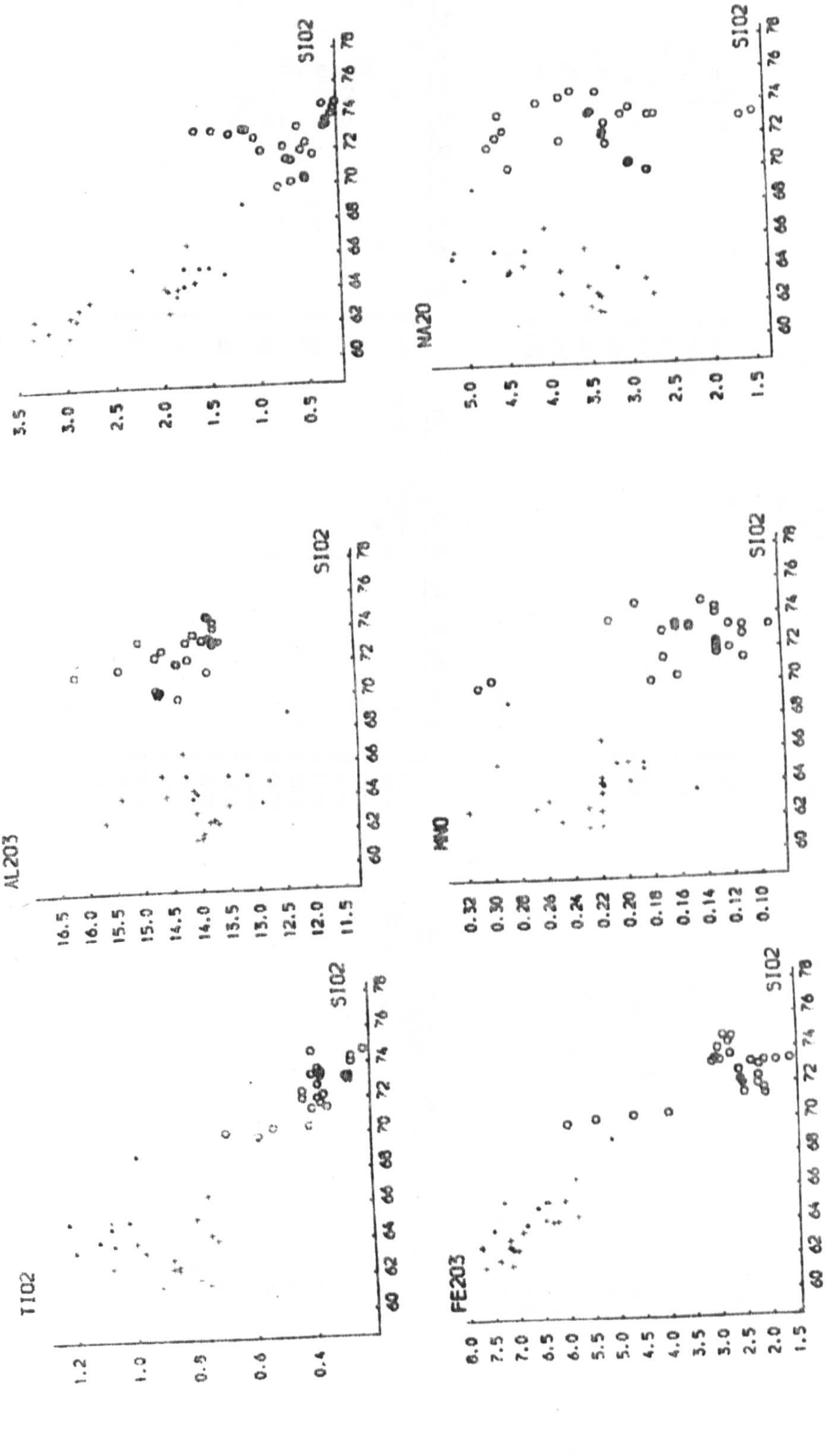

TIO2
1.2
1.0
0.8
0.6
0.4
AL2O3
16.5
16.0
15.5
15.0
14.5
14.0
13.5
13.0
12.5
12.0
11.5
MGO
3.5
3.0
2.5
2.0
1.5
1.0
0.5
FE2O3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
MNO
0.32
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
NA2O
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
SIO2
60
62
64
66
68
70
72
74
76
78

Figure 35

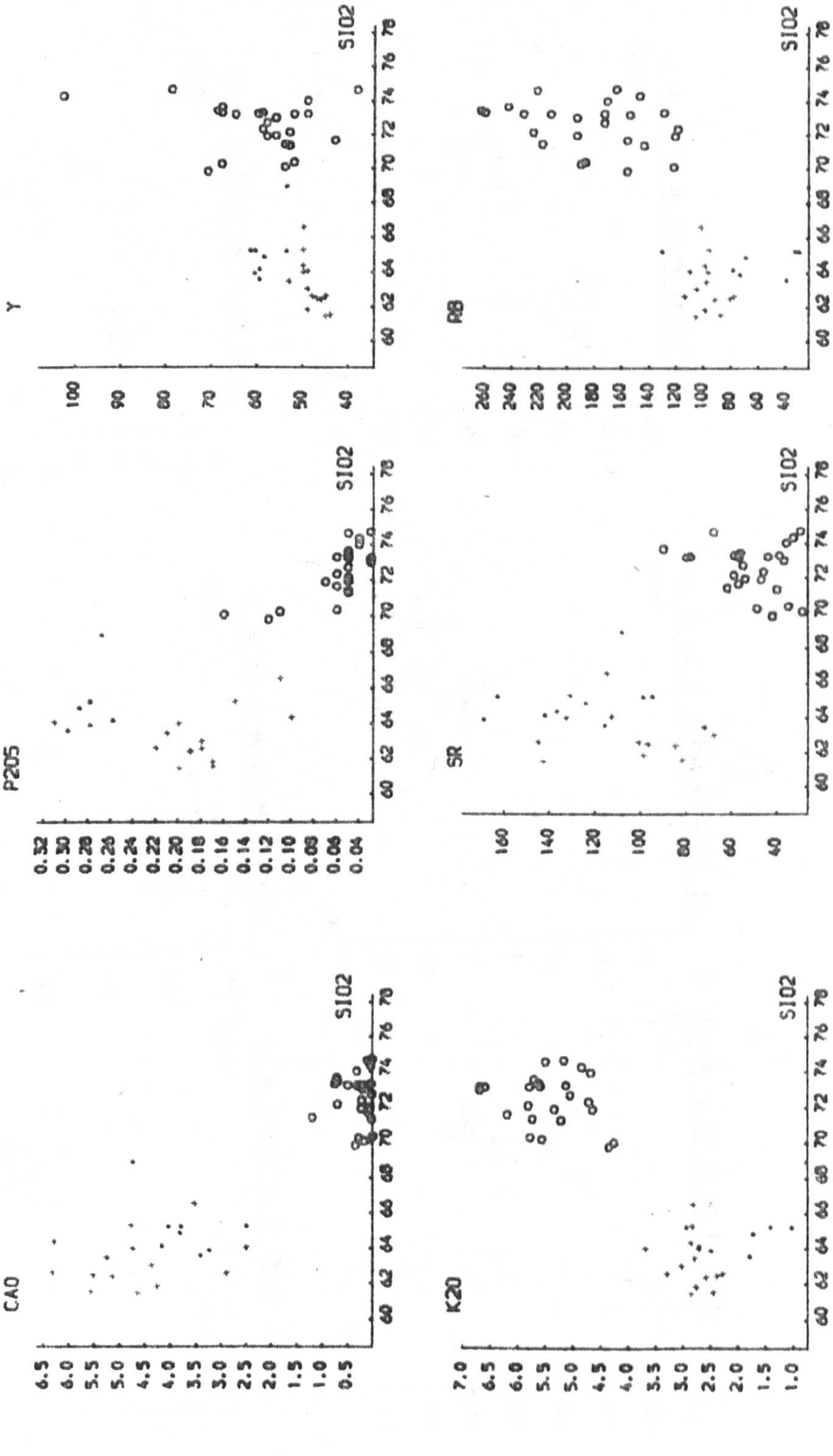

CAO
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
P2O5
0.32
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
Y
100
90
80
70
60
50
40
K2O
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
SR
160
140
120
100
80
60
40
RB
260
240
220
200
180
160
140
120
100
80
60
40
60
62
64
66
68
70
72
74
76
78
SIO2

Figure 36

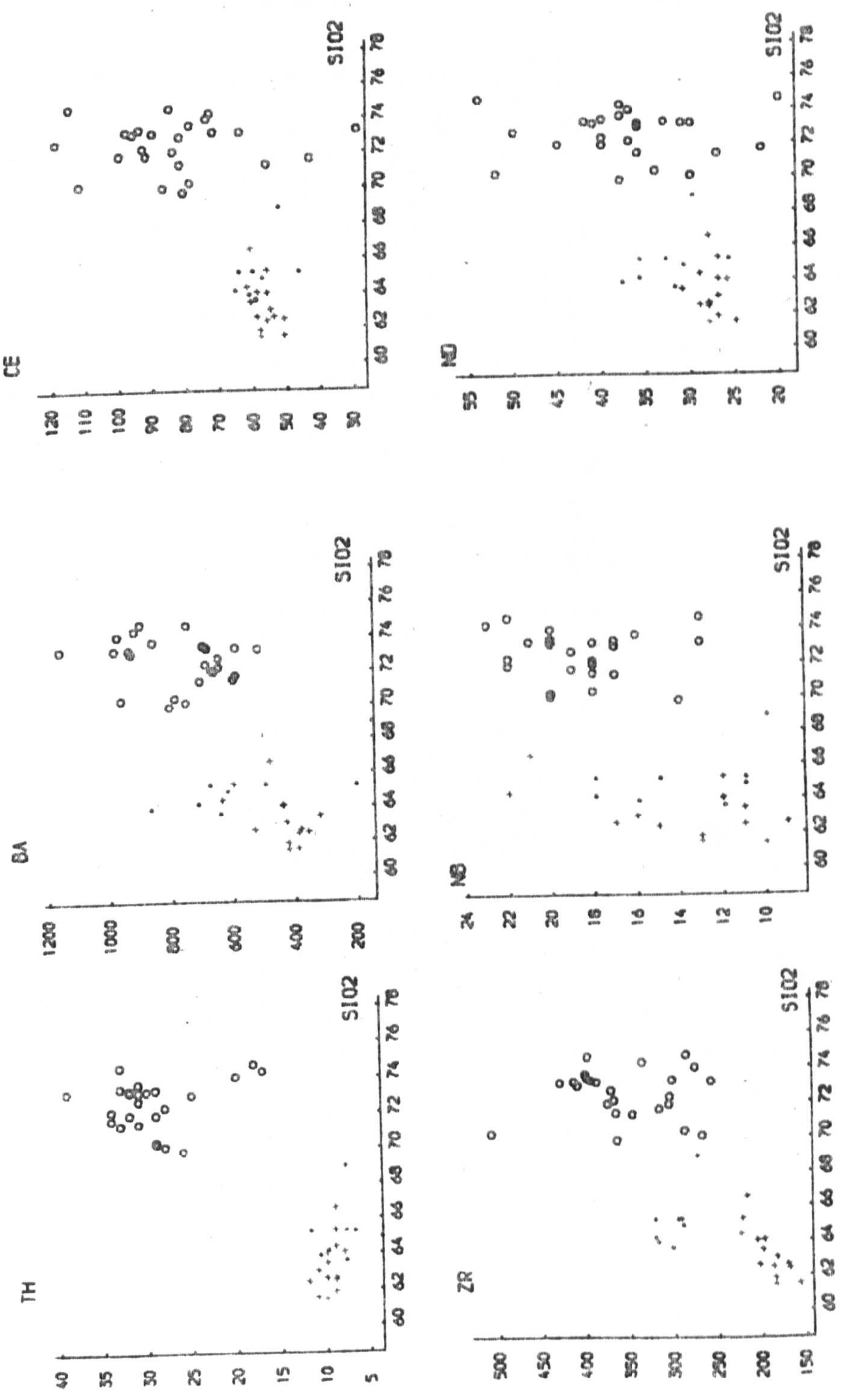
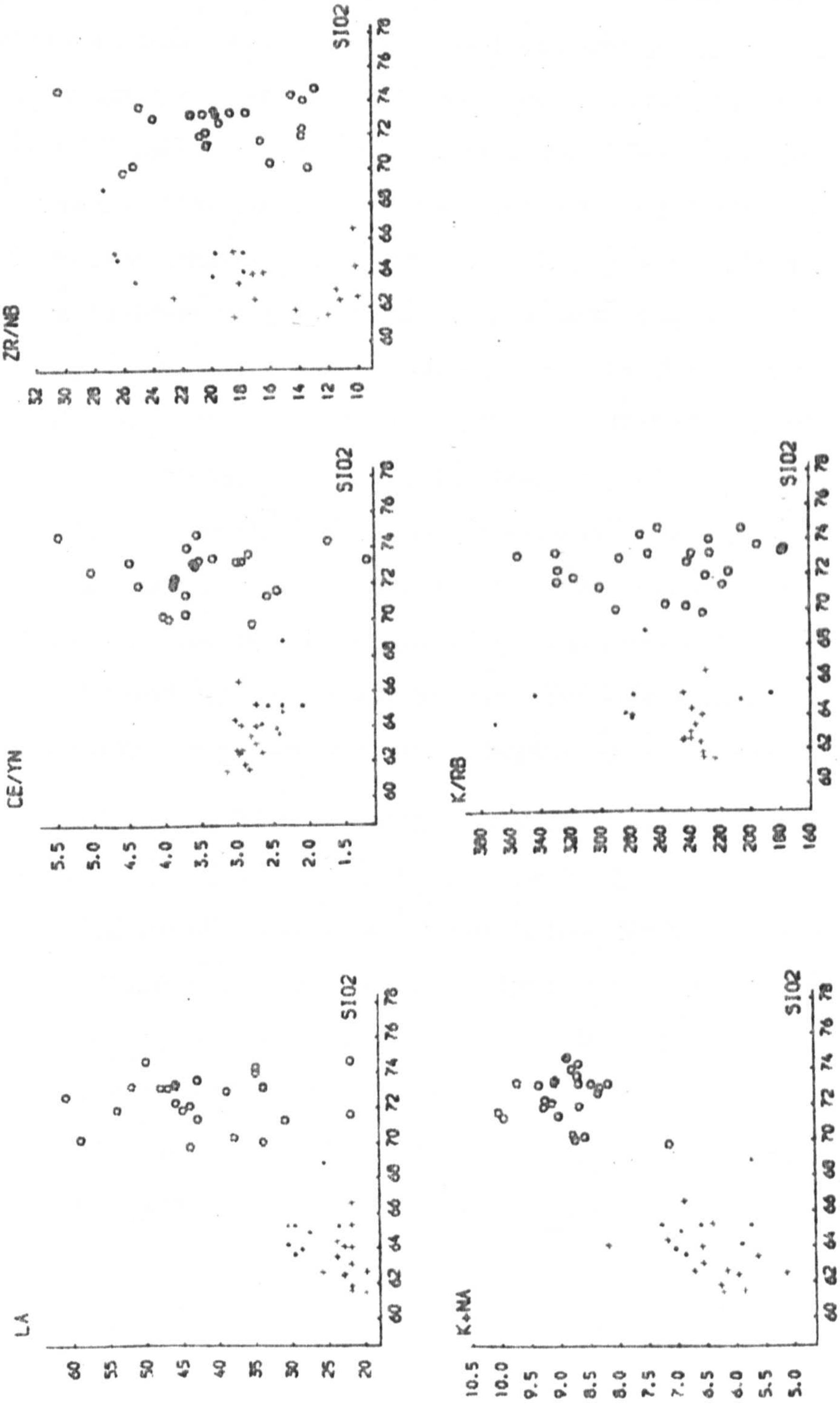

CE
120
110
100
90
80
70
60
50
40
30
SIO2
60
62
64
66
68
70
72
74
76
78
ND
55
50
45
40
35
30
25
20
BA
1200
1000
800
600
400
200
NB
24
22
20
18
16
14
12
10
TH
40
35
30
25
20
15
10
5
ZR
500
450
400
350
300
250
200
150

Figure 37


LA
60
55
50
45
40
35
30
25
20
CE/YN
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ZR/NB
32
30
28
26
24
22
20
18
16
14
12
10
K+NA
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
K/RB
380
360
340
320
300
280
260
240
220
200
180
160
SIO2
60
62
64
66
68
70
72
74
76
78

microgranodiorites, rhyolites and microtonalites. Previous investigations of the petrography, structural relationships and chemistry of the intrusions have included studies by Williams (1930), Bromley (1963, 1969), Davies (1968), Evans (1969) and Olver (1979). The Q-mode statistical analysis of the chemical data has shown that the acidic members of this group cluster together, generally in isolation from the other groups. The intermediate-acid members, which outcrop in northern Snowdonia, however, cluster along with members of some other groups (fig. 18 , page 123) although their rare earth patterns are distinctly different from those of this group. There are a considerable number of significant interelement correlations for this group (fig. 23 , page 129) although the data show greater scatter than that found for the Lleyn groups. The R-mode cluster dendrograms (fig. 22 , page 128) show that the REE, Y, Zr, Nb and Ba correlate positively with the felsic constituents in this Snowdonian group whereas the reverse is found for the Lleyn suites. The explanation for the latter observation is that precipitation of apatite removes the REE and Y whereas Zr and Nb are removed from the crystallising melt by zircon, magnetite and the pyroxenes (see chapter 8 for a discussion).

There are sufficient geochemical similarities between the members of this group to suggest a coherent relationship. These may be generated by the operation of particular evolutionary processes although not necessarily at the same time (see page 20 for a discussion of timing). A number of processes are considered which may explain the evolution of this suite of intrusions.

1) Vapour or liquid phase transfer
2) Fractional crystallisation or partial melting of mafic material
3) Partial melting of the Upper Mantle
4) Partial melting of crustal material:-
    a) Lower Crust
    b) Crustal Contamination
    c) Sediments
    d) Igneous material

Figure 38

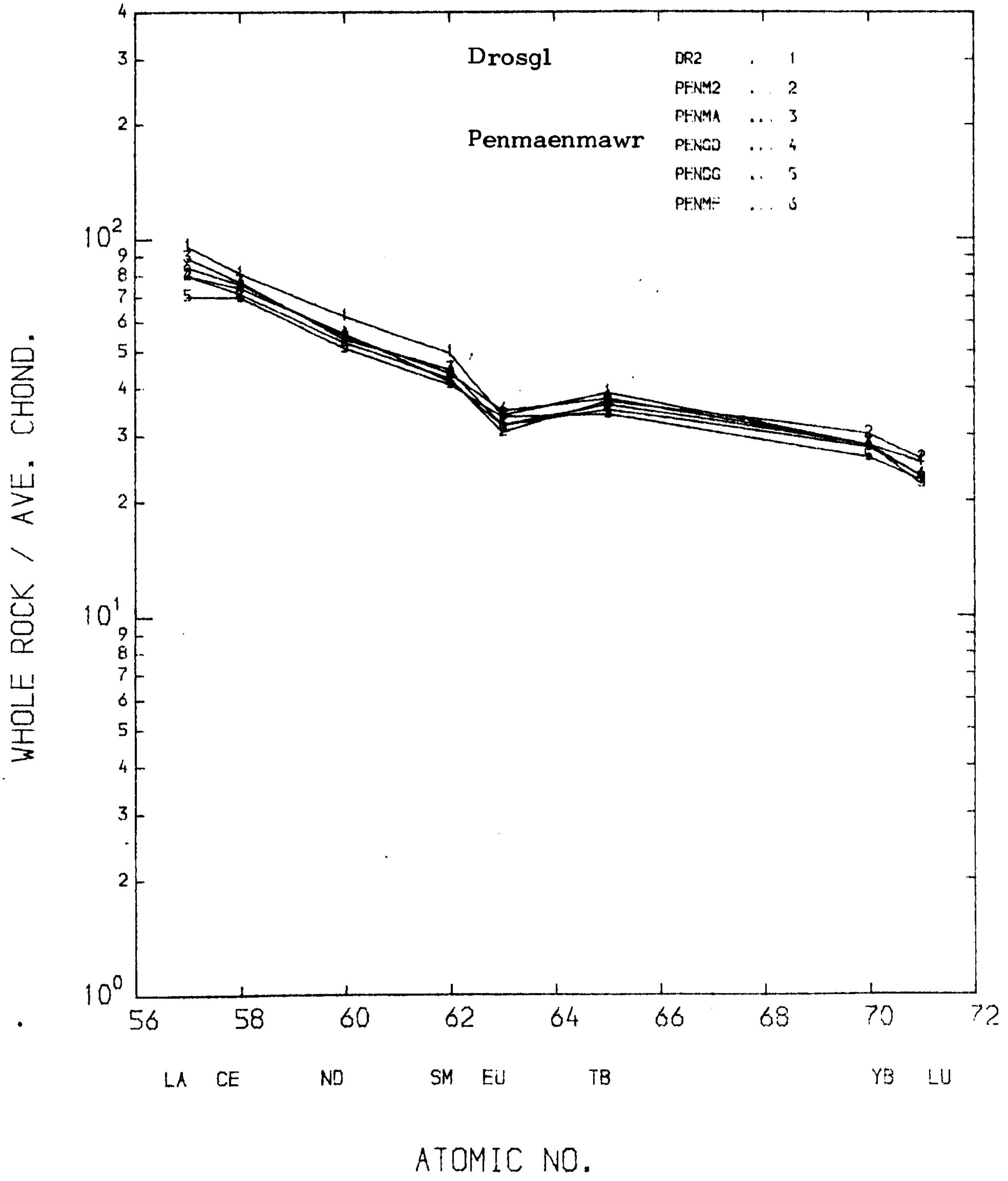

Drosgl
Penmaenmawr
DR2 . 1
PENM2 . . 2
PENMA ... 3
PENGD ... 4
PENGG .. 5
PENMF ... 6
WHOLE ROCK / AVE. CHOND.
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
9
8
7
6
5
4
3
2
10^0
56
58
60
62
64
66
68
70
72
LA
CE
ND
SM
EU
TB
YB
LU
ATOMIC NO.

Figure 39

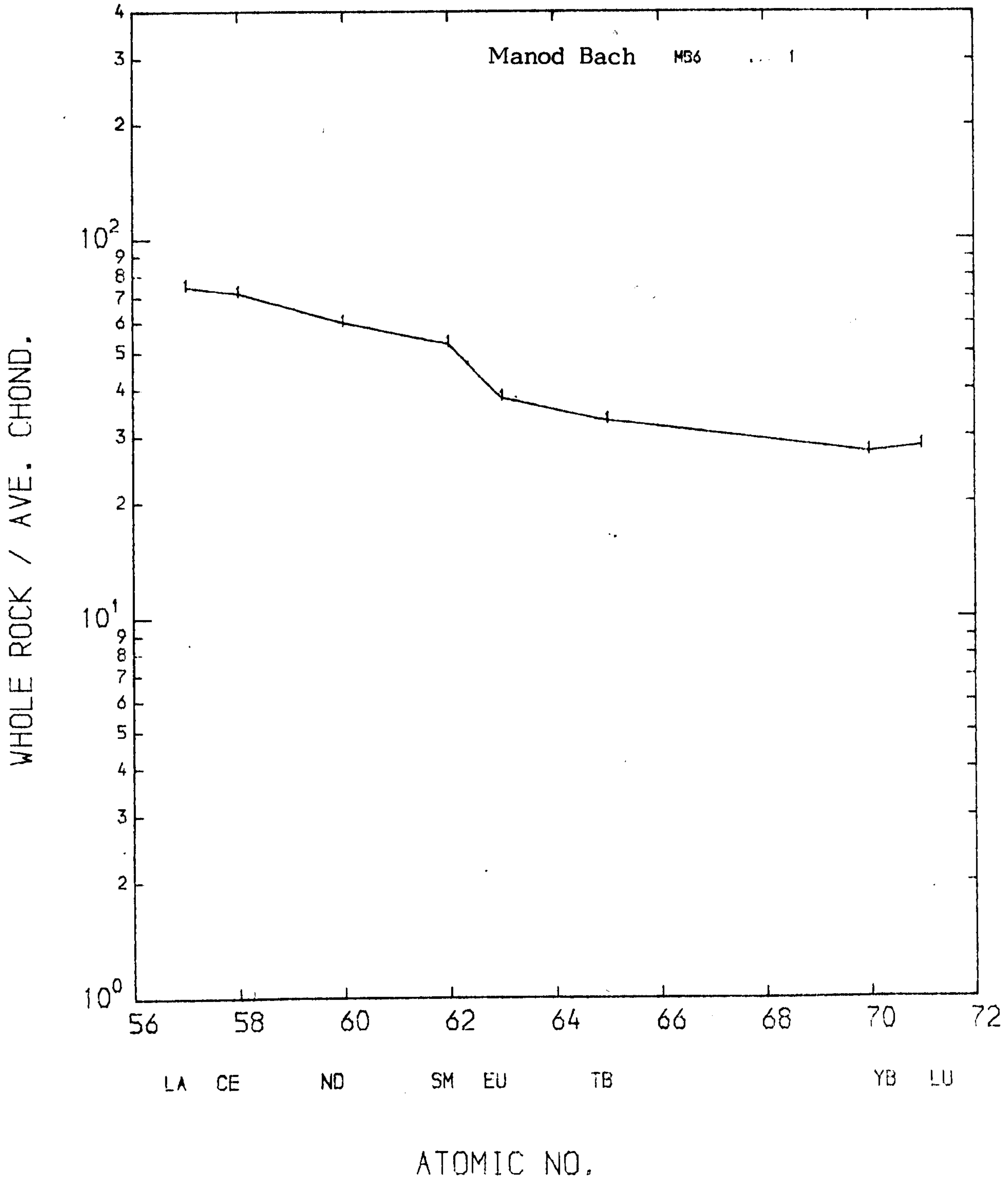
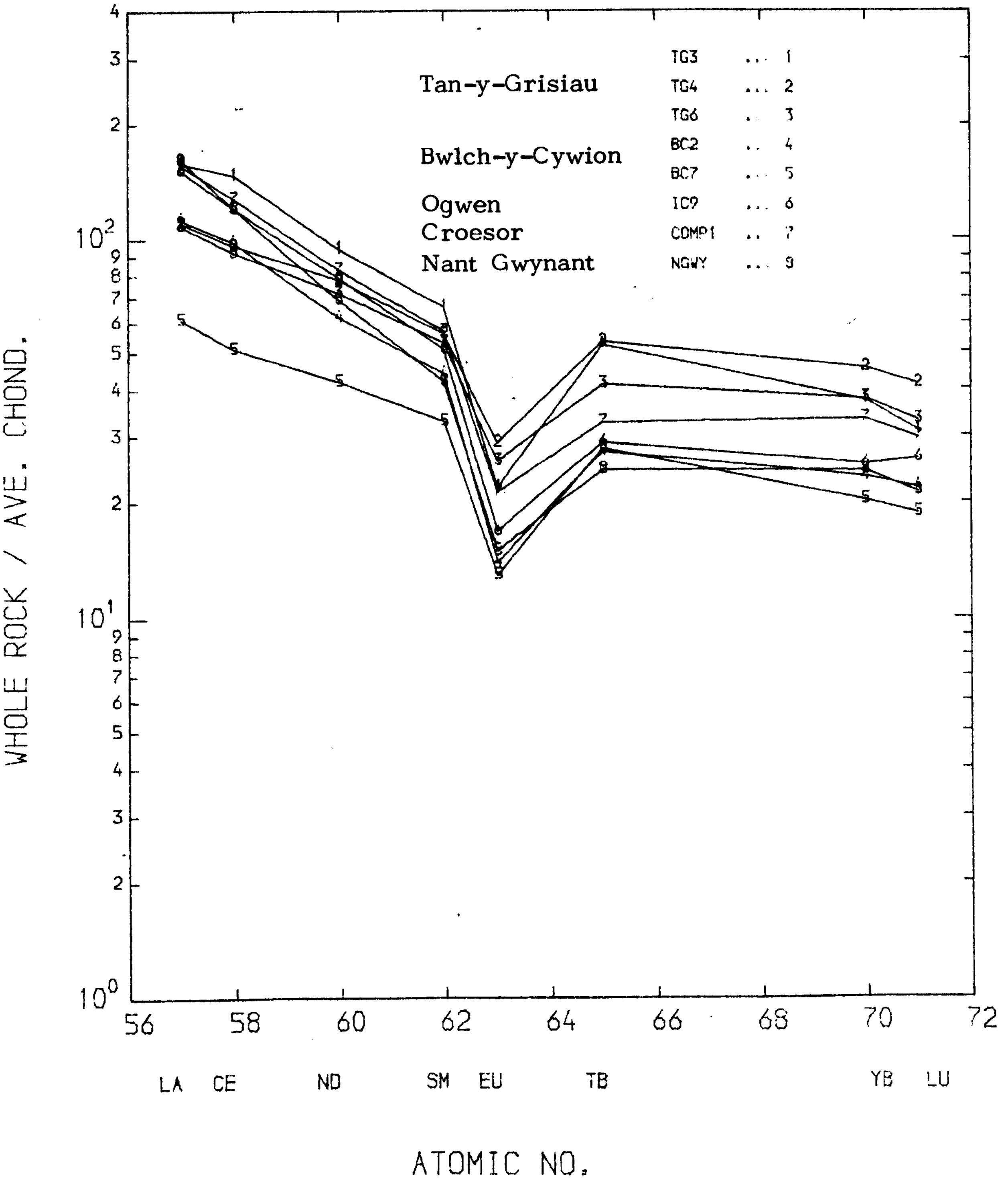

Manod Bach MB6 ... 1
WHOLE ROCK / AVE. CHOND.
10^2
10^1
10^0
56
58
60
62
64
66
68
70
72
LA
CE
ND
SM
EU
TB
YB
LU
ATOMIC NO.

Figure 40


Tan-y-Grisiau
TG3 ... 1
TG4 ... 2
TG6 .. 3
Bwlch-y-Cywion
BC2 .. 4
BC7 ... 5
Ogwen
IC9 ... 6
Croesor
COMP1 .. 7
Nant Gwynant
NGWY ... 8
WHOLE ROCK / AVE. CHOND.
10^{0}
10^{1}
10^{2}
2
3
4
5
6
7
8
9
56
58
60
62
64
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LA
CE
ND
SM
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TB
YB
LU
ATOMIC NO.

1. Vapour or Fluid Phase Transfer of the Rare Earth Elements

Owing to the extensive use of the rare earth elements in petrogenetic modelling it is appropriate to consider the extent to which such elements may be mobilised during weathering, metasomatism or hydrothermal action. At present it is only possible to consider the effects of fluid or gas transfer in a qualitative way since little is known about the magnitude of their distribution coefficients between melt-gas, melt-aqueous phase, solid-gas or solid-aqueous liquid. Such distribution coefficients would likely depend on variables such as pressure, temperature, oxygen fugacity and the nature of possible complexing agents.

In recent years the behaviour of the rare earth elements during weathering and hydrothermal processes has been examined mainly for basaltic material. Generally, the results of such studies have shown that the heavy rare earth elements are not affected by seawater-basalt interactions but that the light rare earths may be appreciably enriched relative to the HREE (Coish et al., 1977; Hart et al., 1974; Humphris et al., 1978). Wood et al. (1976) found that the HREE and Y are not mobilised during low grade regional metamorphism but that the LREE are. The effects of spilitisation on tholeiitic rare earth abundances were investigated by Hellman and Henderson (1977) who found that the abundances and the La/Sm and La/Yb ratios increased as a result of the alteration. The rare earths do not appear to undergo any changes during epidotisation but carbonisation and chloritisation do mobilise the LREE (Condie et al., 1977). Humphris et al. (1978) claim that the degree of mobility or immobility of the REE cannot be related to metamorphic grade and that the observed mobility in basaltic rocks is due to the amount of interstitial glass present, which contains relatively high REE abundances.

Martin et al. (1978) studied the REE abundances in samples from the Loch Borrolan alkaline complex of N.W. Scotland. They found that all rare earths were transported, via an aqueous fluid, from the alkaline igneous complex into originally pure country quartzites. McLennan and Taylor (1979) have found extensive rare earth mobility associated with uranium mineralisation in a Proterozoic sedimentary sequence from Australia. Their results show that the La/Yb ratio of the rocks decreases with increasing uranium content and they noted that Th did not follow U in its behaviour. This and other facts led them to the conclusion that carbonate complexing was important for fluxing the mobile elements and that such movement occurred at low temperatures ($\simeq 100^{o}C$) and under alkaline conditions. The behaviour of Eu was not seen to be different from the other REE and this led them to consider that the initial source rocks possessed all Eu in the Eu(III) form. Bowden et al. (1979) believe that hydrothermal processes may be very important for controlling the distribution of the trivalent rare earth elements and the extent of such action can be estimated from the size of the europium anomaly. They found that the granitic and syenitic rocks of Nigeria often show signs of subsolidus recrystallisation of felsic and mafic minerals and that this feature is associated with a dispersed U-Nb mineralisation and a later, vein-controlled Zn-Sn mineralisation. They consider it likely that the rare earth patterns of many of the igneous rocks were set during the dispersed mineralisation event and enhanced by the later replacement vein-mineralisation. The behaviour of Eu, however, was claimed to be fixed by the original magmatic crystallisation processes and the hydrothermal actions caused an increase in the abundances of the trivalent rare earths and consequently an increase in the size of the Eu anomaly.

The importance of late-stage fluids on granitic rocks has been stated for many years by Russian geochemists (Mineyev, 1963) but western researchers have been sceptical about their effects on lanthanide distributions. Experimental evidence (Cullers et al., 1970, 1973) suggests that the rare earths are strongly partitioned into silicate phases (Kd $\simeq$ 10) and are very strongly partitioned into a melt phase (Kd $\simeq$ 100) relative to a supercritical aqueous phase. The introduction of fluoride as a complexing agent did not cause a measurable change in their measured partition coefficients.

The view that the rare earth elements are immobile during weathering, or hydrothermal and metasomatic processes does not appear to be supported, particularly for basaltic rocks. There is some evidence to suggest that mobilisation of the rare earth group of elements may occur during hydrothermal processes although such observational data have been obtained from alkalic suites (Bowden et al., 1979; Martin et al., 1978; Mineyev, 1963) or sedimentary successions (McLennan and Taylor, 1979). It is known that salic alkalic rocks commonly contain high abundances of the REE, Y, Zr, Nb and non-metallic elements such as fluorine and chlorine (Bailey, 1977; Baker, 1977) compared with less-alkaline salic rocks. If complex formation for the REE is important then they are more likely to be transported in alkaline rocks, with their high halogen contents, than in less-alkaline igneous rocks.

Humphris et al. (1978) have presented evidence which shows that REE mobility in basalts may be dependent on their mineralogy and their amount of interstitial glass. Since the REE (along with Zr, Nb, Th etc.) do not readily enter the crystallising phases in alkalic magmas they may ultimately reside in late-formed salic or mafic minerals, accessory minerals or quench phases. If this is true then the operation of a gas or fluid phase would possibly break down some accessory minerals, and almost certainly glassy phases, more readily than the main magmatic assemblage. The REE, Zr, Nb etc. (hygromagmatophile elements) would be therefore released and mobilised. Sub-solidus recrystallisation may afford release of such elements, although the extent is uncertain and the presence of CO_2 and the halogens may be required. However, the likelihood of REE transfer in less-alkalic rocks would be smaller.

In a geochemical investigation of a rock suite it is clearly important to assess the extent to which the samples have been affected by secondary processes before an attempt is made to determine which primary processes have operated. The effects caused by weathering are not normally important since samples should be chosen such that weathering is insignificant or the weathered portions may be removed prior to the analysis.

Possible vapour/fluid phase transfer in the Snowdonian suite

The rocks of North Wales have been affected by a regional metamorphism of low grade (greenschist facies) which occurred some time during the Caledonian cycle and by hydrothermal and mineralisation events of various ages (Fitch et al., 1969). The importance of these events, concerning possible influences on the geochemistry of the samples of this study, requires some consideration.

Bromley (1969) has shown that the Tan-y-Grisiau, Bwlch-y-Cywion and Mynydd Mawr intrusions display sizeable metamorphic aureoles where the country rocks originally converted to hornblende hornfels, have suffered almost complete retrogression to albite-epidote facies. The other intrusions of Snowdonia do not possess an aureole of any great extent and slight baking and spotting is all that is developed. Close to the roof of the Tan-y-Grisiau and Bwlch-y-Cywion intrusions, there is evidence that the hornfelses have been feldspathised. This feature, along with the retrogression, led Bromley to the idea that a volatile phase, rich in silica, water and the alkalis, had concentrated at the upper parts of the intrusion and caused retrogression of the minerals in the granites and the country rocks. The occurrence and distribution of the rare earth-bearing mineral, allanite, is thought to be related to a hydrothermal process that operated during the cooling of the Tan-y-Grisiau intrusion (Bromley, 1964, 1969). The mineral occurs as small euhedral crystals up to 1 mm in length throughout the intrusion, commonly enclosed in chlorite, and as large irregular interstitial masses up to 4 mm across; the latter form has been found to replace the K-feldspar component of microperthite crystals. Allanite also lines small veins and cavities, both within and outside the intrusion, especially around the northern margin which represents the upper part of the body.

The three samples from the Tan-y-Grisiau intrusion which were analysed for the rare earth elements do not show any petrographic indications of having suffered the effects of hydrothermal or metasomatic action. The grain-size of the samples is variable, the feldspars are not sericitised, and unaltered biotite and hornblende are present. These features argue against any marked alteration by fluids operating at sub-magmatic temperatures. Bromley (1969) showed that many of the volcanic rocks of Snowdonia and some of the intrusions which had been affected by late-stage fluids plotted on the quartz-side of the eutectic on the normative Q_z-Ab-Or ternary diagram (after Tuttle and Bowen, 1958). Five samples from the northern edge of the intrusion, which do show petrographic signs of alteration, plot above the eutectic but the three samples analysed for the rare earths (TG6, TG4 and TG3) plot near the eutectic (see Fig. 25 , page 132). The abundances of Rb, Sr and Ba do not suggest that a volatile phase has operated since these elements, along with Na_2O and K_2O, are readily mobilised during alteration processes. On the foregoing bases the three samples from Tan-y-Grisiau are considered to be largely unaffected by secondary effects.

Fifteen samples were collected from the Bwlch-y-Cywion intrusion which is composed of three textural types, viz. a microgranite, a fine-microgranite and an intrusive rhyolite (Williams, 1930). Petrographic and chemical evidence suggests that a number of these samples may have been subject to subsolidus recrystallisation and loss of some elements, particularly the alkalies. All mafic minerals are converted to chlorite and quartz and the feldspars have a more uniform and smaller grain-size compared with their unaltered counterparts. Nine of the fifteen samples collected from Bwlch-y-Cywion appear to be altered and for this reason they are excluded from the petrogenetic discussions. They are seen to lie below the eutectic and often plot close to the albite apex of the ternary plot of Q-Or-Ab (fig. 25 , page 132). Sample BC6 shows a lower normalised cerium content than does neodymium and the resulting negative cerium anomaly may well indicate the operation of an oxidising hydrous phase. Sample BC7 was analysed for the rare earth elements and the LREE are less concentrated than in sample BC2. Both of these samples were collected from the coarse microgranite intrusion but BC7 has higher Na_2O and lower K_2O, Ba and Rb compared with BC2. In view of the alteration found for sample BC7 it has been excluded from any petrogenetic discussion.

The samples collected from the intrusions of Ogwen, Nant Gwynant, the Yr Arddu composite minor sill, Penmaenmawr and Drosgl are largely unaffected by secondary processes. One sample (COMP7) from a composite sill, however, shows possible alteration. Its rare earth pattern is unusual with La_N being lower than Ce_N and its major element chemistry shows substantial differences from the analyses of other composite material. For these reasons this sample is excluded from any petrogenetic discussions.

The presence of primary phenocrysts, zoned plagioclase, unaltered primary augite and hornblende and perthitic feldspars in many of the Snowdonian samples suggests that they have not been affected by extensive deuteric, hydrothermal or metasomatic action. Although there is evidence that metasomatic action and greenschist facies metamorphism has affected the intrusive rocks of North Wales to a greater or lesser extent, material displaying these effects has been removed from the sample population prior to petrogenetic considerations.

2. Fractional Crystallisation or Partial Melting of Mafic Material

The basaltic rocks of North Wales are tholeiitic with mildly alkaline tendencies (Fitton and Hughes, 1970). Two dolerite samples, one from central Snowdonia and the other from Cader Idris, were collected and analysed for major and trace elements and one of them was analysed for the rare earth elements. On the basis of this very limited sample population the data are not inconsistent with those for transitional tholeiitic basalts (Wood et al., 1980; Saunders et al., 1980).

Researchers in North Wales have not favoured the idea that the acidic rocks originated from basaltic magma, mainly because of the great volume of silicic volcanics. Rast (1969) estimated that acid extrusives represented 30-45 per cent of the total volume of exposed extrusive rocks of North Wales although these figures could have been reduced if account had been taken of the intrusive material (e.g. dolerites). The temporal and geochemical relationships of these dolerites have, however, yet to be determined. The volume problem is not insurmountable, however, since Weaver (1977) has argued that if the upper, silicic fraction of a stratified magma chamber were preferentially sampled by a volcano then the ratio of acid/basic volcanic material would be unrepresentative of the true ratio.

The formation of silicic magma from a basaltic magma at crustal depths requires the removal of such phases as olivine, orthopyroxene and clinopyroxene. Owing to the present knowledge of the distribution coefficients of the rare earth elements in such minerals it is often possible to identify their involvement. Olivine does not possess markedly different distribution coefficients for any REE and if it had been a precipitating phase it would not cause any notable fractionation of those elements. The pyroxenes, however, possess lower distribution coefficients for the light rare earths than for the middle or heavy members of the series and their removal would produce an increase in the $(Ce/Sm)_N$ and $(Ce/Yb)_N$ ratios of successive melts (see table 1 , page 48 for Kd's). Assuming that the original basaltic magma possessed a $(Ce/Yb)_N$ of 1-2 and that at least 80 % fractionation had occurred [both assumptions are reasonable since transitional tholeiites generally have $(Ce/Yb)_N \simeq 1$ (Wood et al., 1980; Saunders et al., 1980) and silicic differentiates from basaltic magma are estimated to represent about 10 per cent or less of the original volume of magma (O'Nions, Gronvold, 1973)] which involved significant pyroxene removal, the resulting silicic magmas would be likely to possess $(Ce/Yb)_N$ ratios of considerably greater than unity. The values are largely dependent on the proportions of extracted minerals, the extent of crystallisation and on the distribution coefficient data. The later discussion concerning the petrogenetic evolution of the Lleyn group, for which a fractional crystallisation origin from a tholeiitic magma is suggested, has shown that the intermediate rocks from Moel-y-Penmaen possess a $(Ce/Yb)_N$ ratio of 5.5 compared with the proposed parental value of about two. The development of more silicic liquids would result in larger $(Ce/Yb)_N$ ratios if pyroxenes continue to be removed and the Llanbedrog granophyre from Lleyn possesses a ratio of 7.5. Thompson et al. (1974) concluded that oceanic andesites from the Indian Ocean are derived from transitional tholeiitic basalts via crystal fractionation and their intermediate rocks bear a striking similarity to the intermediate samples from Moel-y-Penmaen. The $(Ce/Yb)_N$ ratios of their samples vary from 2.2 for the basalts to 4.6 for the andesitic material. The lavas of Deception Island range in composition from basalt to rhyodacite and Weaver et al. (1979) have demonstrated the strong possibility that their compositions are related through fractional crystallisation. It is notable that their $(Ce/Yb)_N$ ratios do not show a very marked change from basalt to rhyodacite (1.9-2.9) and this may reflect the increased importance of olivine removal relative to the pyroxenes.

The rare earth element patterns for the Snowdonian suite (figs 38,40, page 174) do not show any marked differences in form although their abundances do vary from the intermediate to the acid material. The $(Ce/Yb)_N$ ratios are 2.3-2.8 for the intermediate samples and 2.13-5.0 for the acidic samples. This rather limited range of values does not favour a crystal fractionation origin from basaltic magma of a transitional nature unless olivine was the principal mafic phase that crystallised. The abundance of Ni (20 ppm) in the Penmaenmawr microtonalite argues against this possibility since olivine with its high distribution coefficients for Ni would rapidly deplete the melt in that element and it is unlikely that a significant amount would remain in melts of intermediate - acid composition. The involvement of a hydrous mafic mineral like hornblende would not improve the position since hornblende possesses rare earth element distribution coefficients which are equivalent or larger than those for clinopyroxenes in basic and acidic melts respectively.

	Snowdonia	Garnfor	Deception(1)	Azores(2)	Emuruangogolak(3)
Zr	200-406	219-546	140-675	-	318-1300
Nb	7-20	40-52	2-17	-	95- 350
Th	8-34	4-19	2-7	10-18	7-39
Rb	75-260	40-179	20-32	82-103	62-218
La	20-60	52-66	25-30	62-113	65-205
Ce	50-120	99-167	61-68	157-255	105-355
Zr/Nb	10-30	5-12	35-39	-	5
SiO$_2$ wt %	60-74	57-74	62-68	62-68	62-65

(1) Weaver et al. (1979)
(2) White et al. (1979)
(3) Weaver (1977)

The origin of particular igneous suites via crystal fractionation of a basaltic magma has been frequently proposed and it has become clear that the incompatible elements may concentrate to a considerable extent in the more silicic members of the suite (White et al., 1979; Weaver et al., 1979; Weaver, 1977; Baker, 1977; Thompson et al., 1974). These elements include Zr, Nb, Th, Rb, La and Ce and their ranges and some useful ratios are presented in table , page 185 along with those for the Snowdonian suite. It is clear that there are considerable differences between the Snowdonian data and those for other areas, and on the basis of this and the earlier discussion, a fractional crystallisation origin is rejected.

Partial melting of basaltic material is unlikely to produce any clear differences in trace element chemistry from crystal fractionation as far as low bulk distribution coefficient elements are concerned. The two processes may only be clearly identified if the abundances of elements with large bulk distribution coefficients are considered. Cr and Ni would satisfy this criterion but the wide range of observed values (0-20 ppm Ni) is not consistent with a partial melting origin since the abundances of elements with large D are considered to vary in a small way during partial melting (see fig. 8 , page 47).

3. Partial Melting of Upper Mantle Material

In recent years there has been an increasing popularity for the generation of silicic magmas of calc-alkaline nature from the upper mantle wedge (Best, 1975; Mysen , 1978; Hawkesworth et al., 1977; Saunders et al., 1980) rather than by partial melting of the subducted oceanic crust which was thought to be of amphibolite or eclogite composition depending on the depth (Ringwood, 1974). Apart from Archean orogenic rocks, the $(Ce/Yb)_N$ ratios of most orogenic suites are too low for melts to have been in equilibrium with garnet and this provides strong evidence against an eclogite melting model (Tarney and Windley, 1977).

The investigation of the geochemistry of volcanic and plutonic rocks from such key areas of active subduction as the Andes and the Western Pacific has provided a large body of major trace and isotopic element data (e.g. Thorpe et al., 1976; Dostal et al., 1977; Lopez-Escobar, 1977). The isotopic data from various parts of the Andes have shown that contamination of the mantle-derived magmas by sediments or crustal material has occurred but only in minor amounts, $\leqslant 5\%$ (Francis et al., 1977). The behaviour of certain major and trace elements in magmas produced above subduction zones appears to be distinctly different from those produced in other areas and these facts may prove to be very useful for determining whether a particular suite is likely to have formed at a destructive plate margin. The incompatible trace elements of non-orogenic associations, such as the Kenya rift (Weaver, 1977) or oceanic islands (White et al., 1979) include the so-called LIL elements (K, Rb, Th, U, Ba, Sr, Rb), the high field strength elements (Zr, Nb, Ta, Nb, Y, REE, P) and the rare earths, and they consequently increase in concentration as the magmas become more silicic. In calc-alkalic magmas, or those produced above subduction zones, the HFS elements behave differently from the LIL elements and such magmas are characterised by having high LIL/HFS ratios (Saunders et al., 1980). This feature is observed for the most primitive island-arc tholeiitic basalts, andesites and the most evolved shoshonites. The explanation for the behaviour of these two groups of elements lies in their different respective mobilities during the postulated dewatering of the subducted slab. The large ion lithophile elements, which are highly mobile under low grade metamorphic conditions and hydrothermal action, are readily transported during the dehydration of the slab into the overlying mantle wedge. The HFS elements, however, are not readily mobilised during low-temperature processes, unless suitable complexing agents are present, and they are retained in the slab. Wood et al. (1980) and Tarney and Saunders (1979) consider that the HFS elements are mainly accommodated in minor mineral phases such as rutile, ilmenite, apatite, sphene and zircon in the slab and these minerals are probably stabilised by the high pH_2O and fO_2 of the dewatering process. The fluids released from the slab, enriched in SiO_2, alkalies and LIL elements relative to the HFS elements, are thought to permeate and vein the upper mantle wedge resulting in a lowering of the mantle solidus. Partial melting of the mantle assemblage could then occur and magmas with a high LIL/HFS would be produced. Some other features of calc-alkaline suites are:

1) Low to moderate iron enrichment relative to magnesia and the alkalies.
2) Rapid silica increase with evolution of magmas.
3) High abundances of K_2O, Rb, Ba, Sr, Th and U.
4) Low K/Rb and Na_2O/K_2O ratios.
5) Moderately low $(Ce/Yb)_N$ ratios (2-10).
6) High proportion of intermediate-silicic rocks relative to basic rocks.
7) Constant or decreasing abundances of the HFS elements.
8) Cr and Ni abundances are generally lower in calc-alkaline suites compared with Andesitic or alkaline series, < 90 and <50 ppm respectively.
9) Eu anomalies are usually developed in the more silicic magmas.

Several geochemical studies of calc-alkaline provinces have been conducted in recent years in which trace element determinations have played an important part. Saunders et al. (1980) studied the rocks of the Antarctic peninsula, which range in composition from gabbro to alkali granite, and they concluded that the suite was produced by partial melting of the upper mantle wedge and that most of the geochemical variations resulted from partial melting and not fractional crystallisation processes. The reasons given for this are the generally small proportion of possible basic or intermediate parents relative to the large proportion of granitic material, the unlikely mechanism of crystal settling in viscous acid magmas and the small proportion of cumulates. Thorpe et al. (1976, 1976 , 1979) have studied the chemistry of volcanic rocks from the Andes and they consider that the high-Al basalt-andesite-dacite groups, which form the bulk of volcanic material,are derived by partial melting of the upper mantle wedge which they consider to have been enriched in the LIL elements. A considerable volume of dacite-ignimbrite volcanics are developed in the Central Andes and Thorpe et al. (1979) consider that they formed via plagioclase-dominated fractionation from andesitic magma. Atherton et al. (1979) have described the geochemistry of some of the segmented coastal batholith of Peru and some associated volcanic material and they claim that the chemical variations observed in the volcanic sequences and the batholith are explicable by high level crystal fractionation from mantle-derived magmas.

The generation of calc-alkaline magmas does not appear to be a single-stage process for it may incorporate partial melting, fractional crystallisation, magma mixing and crustal contamination mechanisms to varying degrees and at various pH_2O, fO_2, P, T etc. The considerable scatter of many element-element plots may be partly explained if multi-stage processes have operated and it is clear that considerable caution must be applied to any attempts at quantitative or semi-quantitative petrogenetic modelling.

Comparisons of the chemical data of the Snowdonian suite with those from other suites of calc-alkaline character show that there are

TABLE 6

	A	B	C	D	E	F	G	H
SIO2	69.9	74.0	66.6	71.1	64.3	66.8	66.6	74.0
TIO2	0.44	0.13	0.68	0.40	0.68	0.23	0.76	0.27
AL2O3	14.59	13.57	15.76	15.06	16.45	18.24	14.30	13.70
FE2O3	3.56	1.61	4.70	2.40	5.05	2.30	5.88	3.01
MNO	0.07	0.03	0.10	0.07	0.10	0.06	0.22	0.13
MGO	1.18	0.15	1.27	0.64	1.83	1.50	1.74	0.22
CAO	2.68	0.34	3.33	1.83	4.49	3.17	3.53	0.32
NA2O	3.62	3.67	4.28	3.82	3.77	4.97	4.07	4.12
K2O	3.50	4.83	3.16	4.58	3.11	1.92	2.83	4.69
P2O5	0.12	0.04	0.17	0.11	0.23	0.09	0.11	0.04
BA	741	647	460	1330	776	520	482	971
SR	245	64	259	339	353	460	115	36
RB	132	186	105	163	95	45	102	171
ZR	217	152	271	248	177	100	218	275
NB	13	13	6	18	21	-	21	20
LA	24	28	31	77	23	14	22	35
CE	65	55	59	174	52	19	61	74
Y	28	33	47	29	28	-	50	49
K/RB	220	216	257	233	272	380	230	228
RB/SR	0.5	2.9	0.4	0.48	0.27	0.10	0.90	4.80
CE/YN	4.8	3.4	3.1	14.7	4.56	3.4	3.0	3.7
CR	5	3	3	4	16	13	25	<5
NI	<1	<1	1	5	12	5	15	<5

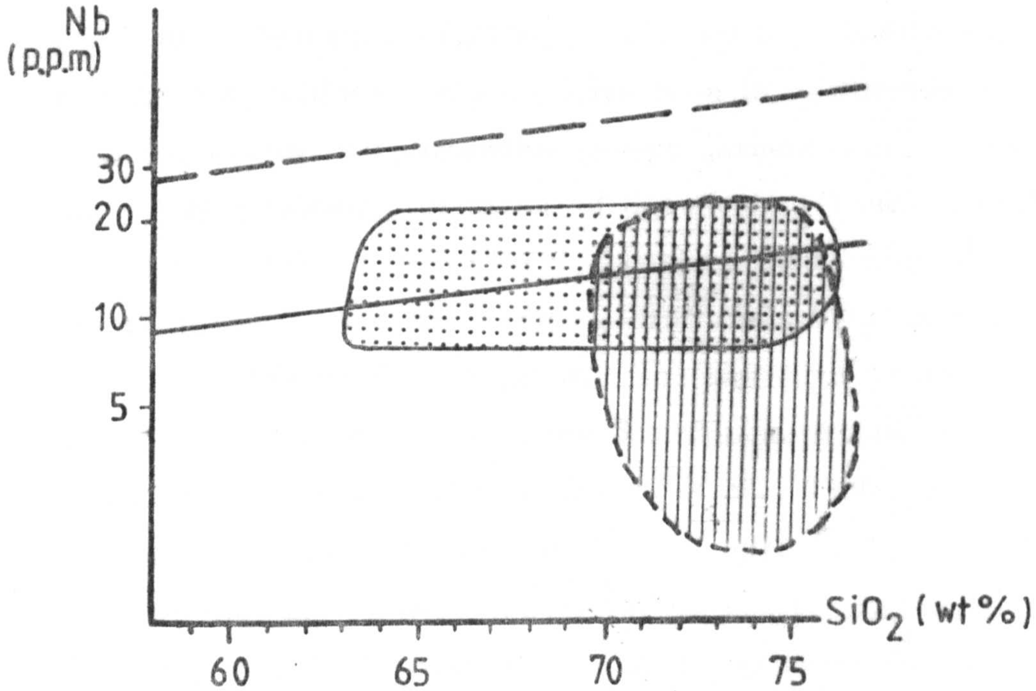
CE/YN IS (CE/Y)N, I.E. CHONDRITE NORMALISED CE/Y RATIO

A,B ANTARCTIC PENINSULAR..... SAUNDERS ET AL., 1980
C INDONESIAN VOLCANIC ARC)
D WESTERN U.S.A.) EWART,1979
E MEDITERRANEAN)
F DACITE.... JAKES AND WHITE, 1971
G PENMAENMAWR.....THIS STUDY
H TAN-Y-GRISIAU.....THIS STUDY

MAJOR ELEMENTS IN WT. %

TRACE ELEMENTS IN P.P.M.

many similarities. Table 6 (page 189) gives some data for the Antarctic peninsular group for compositions between 60-76 % SiO_2 and some selected data from the Snowdonian suite are included for comparison. An important feature of this latter suite, and indeed for all calc-alkaline rocks, are the low abundances of the high field strength elements Zr and Nb. Zr varies from 150-400 ppm, Nb from 8-22 ppm and the ratios Th/Nb are high and comparable with data from the Antarctic calc-alkaline suite. For most data plotted against SiO_2, there appears to be a continuum from the microtonalitic rocks of Penmaenmawr to the felsic samples of Tan-y-Grisiau and Bwlch-y-Cywion (see figs 34-37, pages 169-72). Pearce and Gale (1977) have recently compiled data from various sources and they consider that plots involving Nb are particularly useful for discriminating between volcanic-arc magmas and those generated within-plates. Their SiO_2-Nb diagram with its field limits is shown below.



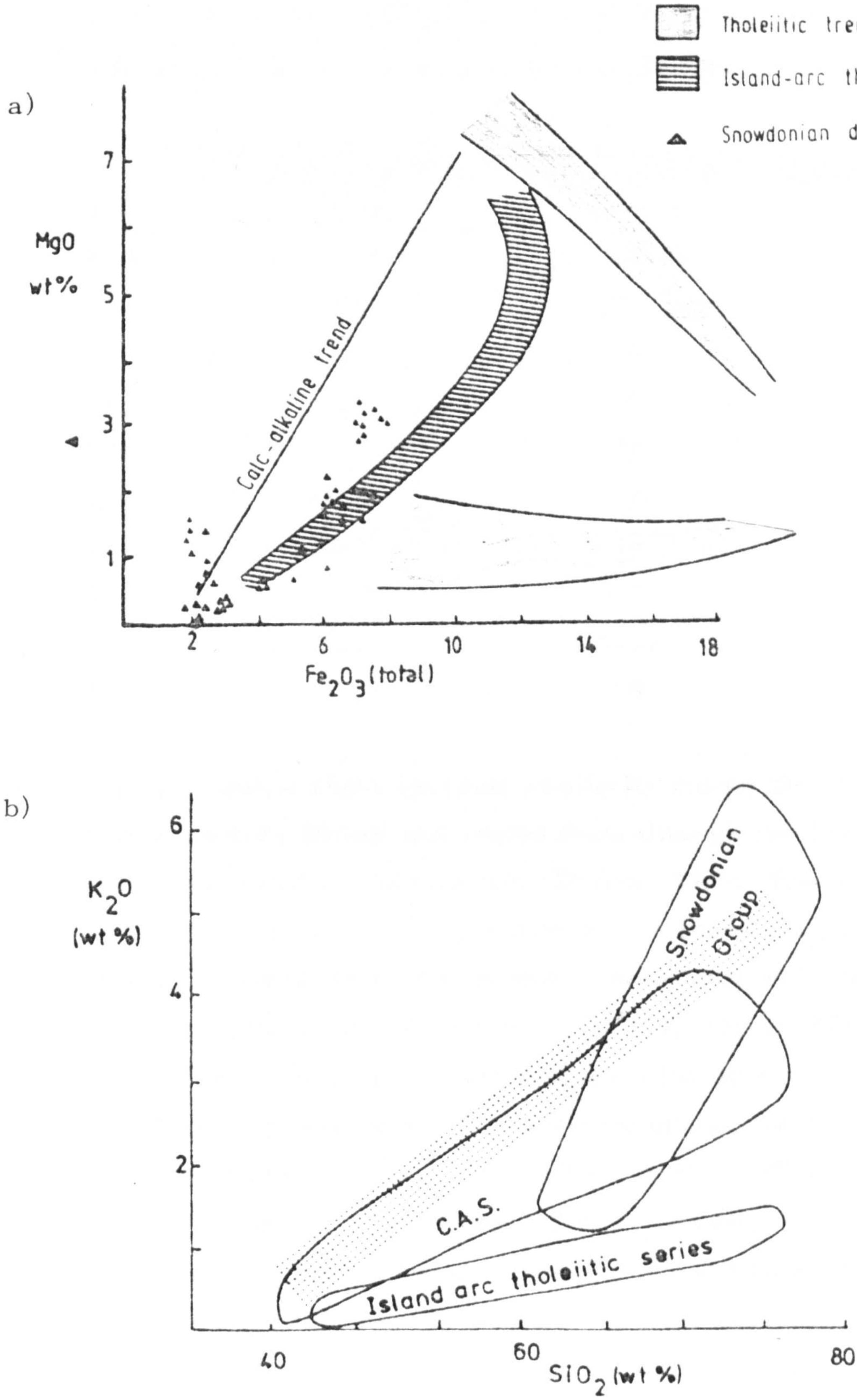
The vertically ruled region represents the field for crustal melts.
The stippled region represents the field for the Snowdonian intrusions.
The single line is the lower limit for within-plate magmas and the broken line is the upper limit for volcanic arc magmas.

The overlap of the two magma provinces can be partly eliminated by considering the K_2O and Rb contents of the samples, for acid within-plate magmas range from about 100 ppm Rb (at 15 ppm Nb) to 300 ppm Rb (at 500 ppm Nb) whereas acid volcanic-arc magmas range from about 50 ppm (at 5 ppm Nb) to greater than 200 ppm (at $\simeq$ 20 ppm Nb). On the basis of these criteria the intrusions of the Snowdonian suite belong to those magmas produced in a volcanic-arc or destructive plate margin environment.

The rare earth element patterns of this group show a small variation with the $(Ce/Yb)_N$ ratios varying from 2-5 and europium anomalies (Eu/Eu*) lying in the range 0.36-0.87. The intermediate rocks possess the smaller europium anomaly (0.8) and low $(Ce/Yb)_N$ ratios (2.7), while the acidic rocks have europium anomalies from 0.36-0.53 and a $(Ce/Yb)_N$ ratio from 2-5. None of the samples analysed for the rare earth elements shows any marked fractionation of the heavy rare earth elements, $(Tb/Yb)_N \simeq 1.5$, and this feature suggests that the magma compositions could not have been in equilibrium with garnet. It is noteworthy that almandine-pyrope garnets occur in rocks of the Capel Curig volcanic formation of Snowdonia (Francis and Howells, 1973; Williams, 1930). Olver (1979) considers these minerals to be phenocrysts, although from low La/Y ratios he finds it unlikely that any fractionation of this phase took place. The high abundances of the light and heavy rare earth elements in the Snowdonian group, compared with the Antarctic peninsular rocks (Saunders et al., 1980) or with some Andean intermediate-acid rocks (Thorpe et al., 1976, 1979), is important, for it shows that the parental magma(s) or source rock(s) possessed a low $(Ce/Yb)_N$ ratio. In view of the continuous chemical trends between the intermediate-acid rocks and their similar rare earth element patterns it seems reasonable to assume that members of this suite are related in some way and that the rocks have evolved from considerably more basic material than the microtonalite of Penmaenmawr.

An interesting discovery is that a close comparison exists between some Japanese andesites belonging to the island-arc tholeiitic series and

Figure 41



a) The fields of this diagram are from Dixon and Batiza (1979).

b) The calc-alkaline field and the island-arc tholeiite fields are from Jakes and Gill (1970). The stippled field is for the low pressure fractionates of transitional tholeiitic magma.

the Manod Bach quartz-latite. A complete set of data is not available for the augite-bearing andesite from Japan (sample H14; Masuda et al., 1975) although the abundances of SiO_2, K_2O, Cr and the rare earths are almost identical to the data for sample MB3 from Manod Bach.

	H14 Japanese andesite	MB3 Manod Bach	Penmaenmawr (P.ENDG)
SiO_2	63.45	63.6 %	65.3
K_2O	1.34	1.84 %	2.84
Cr	5.5	3 ppm	40
La	21	25	21
Ce	58	57	55
Nd	-	34	29
Sm	9.4	9.8	7.6
Eu	2.57	2.6	2.3
Tb	1.54	1.55	1.6
Yb	5.5	5.64	5.4
Th	6	9	9

There is also a close chemical similarity among the intrusions of Penmaenmawr, Drosgl and Manod Bach although the first two intrusions have a proposed Caradocian age (Davies, 1968; Evans, 1969) while the last is claimed to be Upper Llanvirnian - Lower Caradocian (Bromley, 1965). Although there are problems associated with comparing data from one area to another the low $(Ce/Yb)_N$ ratios, high $(Yb)_N$ and the high LIL/HFS ratios of the intermediate (and acid) compositions from Snowdonia compare well with the characteristics of evolved island-arc magmas (Masuda et al., 1975; Dixon et al., 1979). Intermediate-acid calc-alkaline material described by Saunders et al. (1980), Tarney and Saunders (1979), Thorpe et al. (1979) and Lopez-Escobar et al. (1979) possess moderately low $(Ce/Yb)_N$ ratios although $(Yb)_N$ is also commonly less than 25 units. This feature may indicate that the Snowdonian suite evolved via partial melting of the upper mantle wedge and that crystal fractionation from a mafic-intermediate calc-alkali magma occurred whereby the middle - heavy rare earths could concentrate in successive liquids. This mechanism would preclude any significant removal of amphibole, which is often invoked for the production of calc-alkaline magmas (e.g. Garcia et al., 1979) since these minerals possess large distribution coefficients for the middle - heavy rare earths.

Thus there are some similarities between the Snowdonian suite and calc-alkaline rocks from Japan which are related to the island-arc tholeiite series. It is also likely that the magmas that formed the Snowdonian suite represent evolved compositions and this feature may have resulted from fractional crystallisation.

4. Partial Melting of Crustal Material

a) The Lower Crust

A review of the geochemistry and possible petrology of lower crustal rocks has been presented by Tarney and Windley (1977) and they present a model for its evolution based on the geochemistry of a number of Precambrian granulite provinces. The evidence which throws light on the nature of the lower continental crust includes fragments of deeper crust and mantle found in explosive volcanic pipes, tectonic slices of deep crustal material exposed within rocks of a lower temperature and pressure metamorphic facies, and seismic evidence. An overall intermediate composition for the lower crust is compatible with the seismic evidence and such rocks appear to form the greater proportion of granulite terrains.

Perhaps the most popular model for the evolution of the lower crust was developed by S.R. Taylor and co-workers (Taylor and White, 1966; Nance and Taylor, 1976) and it involves the lateral accretion of andesitic island-arcs. Taylor's model involves a multistage evolution of the continental crust with the upper crust becoming progressively enriched in SiO_2, K_2O, Na_2O, Rb, Th, U, Ba and the light rare earth elements relative to island-arc andesites. Tarney and Windley (1977) have raised objections to the island-arc accretion model based largely on the abundances of the rare earth elements in granulitic rocks.

They consider it more likely that the continental crust has evolved through the accretion of Cordilleran-type igneous material, such as that found along the western coast of South America, which are largely of tonalitic and granodioritic compositions. Tarney and Windley (1977) were able to estimate the rare earth element composition of the lower crust based on the simple equation: island arc = upper crust + lower crust. The upper crustal rare earth pattern is fairly well known and may be approximated to the post-Archean average sediment (Nance and Taylor, 1976) but an average composition for an island-arc is less well known. This latter point is a contentious issue and the choice of an average pattern may have a dramatic effect on the calculated rare earth pattern of the lower crust. Another important component of the above equation is the fraction of upper crust : lower crust and Tarney and Windley produced two estimated lanthanide patterns for the lower crust based on a ratio of 1:1 and 1:2 using an andesite with a $(Ce/Yb)_N$ ratio of 2.5 and no Eu anomaly. The patterns that resulted show a lower crust with considerable depletion of the light rare earth elements and moderately large positive Eu anomalies. Taylor and McLennan (1979), in a discussion article, have criticised the andesitic rare earth pattern chosen by Tarney and Windley (1977) and they have proposed an "average andesite" with a $(Ce/Yb)_N$ ratio of 4.5 and a Eu/Eu* of 0.67. The use of such an andesite results in a lower crust with a small positive Eu anomaly and moderate light rare earth enrichment (Ce/Yb - 2.3). Tarney et al. (1979) point out that recent investigations of Western Pacific island arcs show that the bulk of such arcs are composed of basalts and basaltic andesites with $(Ce/Yb)_N$ ratios of 0.9-2.0 and that andesitic material is a minor component. Taylor and McLennan's andesitic rare earth pattern, with its relatively large $(Ce/Yb)_N$, is therefore questioned.

The rare earth abundances of supposed lower crustal granulites from Norway and Greenland show light rare earth enrichment and positive and negative Eu anomalies. A large number of Lewisian amphibolite and granulite facies gneisses show that they also possess light rare earth enriched patterns and for the more silicic granulites this could be appreciable, $(Ce/Y)_N \simeq 100$. The chemical characteristics of granulitic rocks may be summarised as follows:-

1) Ultramafic and mafic granulites have flat to moderately fractionated REE patterns, $(Ce/Yb)_N \simeq 2$, with or without a small negative Eu anomaly.
2) Intermediate gneisses have fractionated REE patterns, $(Ce/Yb)_N = 4$-25, with a small positive Eu anomaly.
3) Acid gneisses have highly fractionated REE patterns, $(Ce/Yb)_N = 18$-300, and they generally have a marked positive Eu anomaly.
4) K and Rb may be low, with a K/Rb ratio up to 1000.
5) Cs, Th and U may be low in abundance but this feature along with those of (4) are thought to be secondary, resulting from the action of metasomatic fluids and the development of mineral phases which cannot appreciably contain these elements.

Thus, assuming that Precambrian granulites may be taken as representative of the lower crust (Tarney and Windley, 1977, 1979; Windley, 1977), the geochemical data obtained from such terrains appear to conflict with a simple overall andesitic composition for the continental crust. A model involving generation of calc-alkaline plutonic rocks of trondhjemitic, tonalitic and granodioritic compositions to produce the continental crust is not inconsistent with rare earth, Ba/Sr and isotopic data.

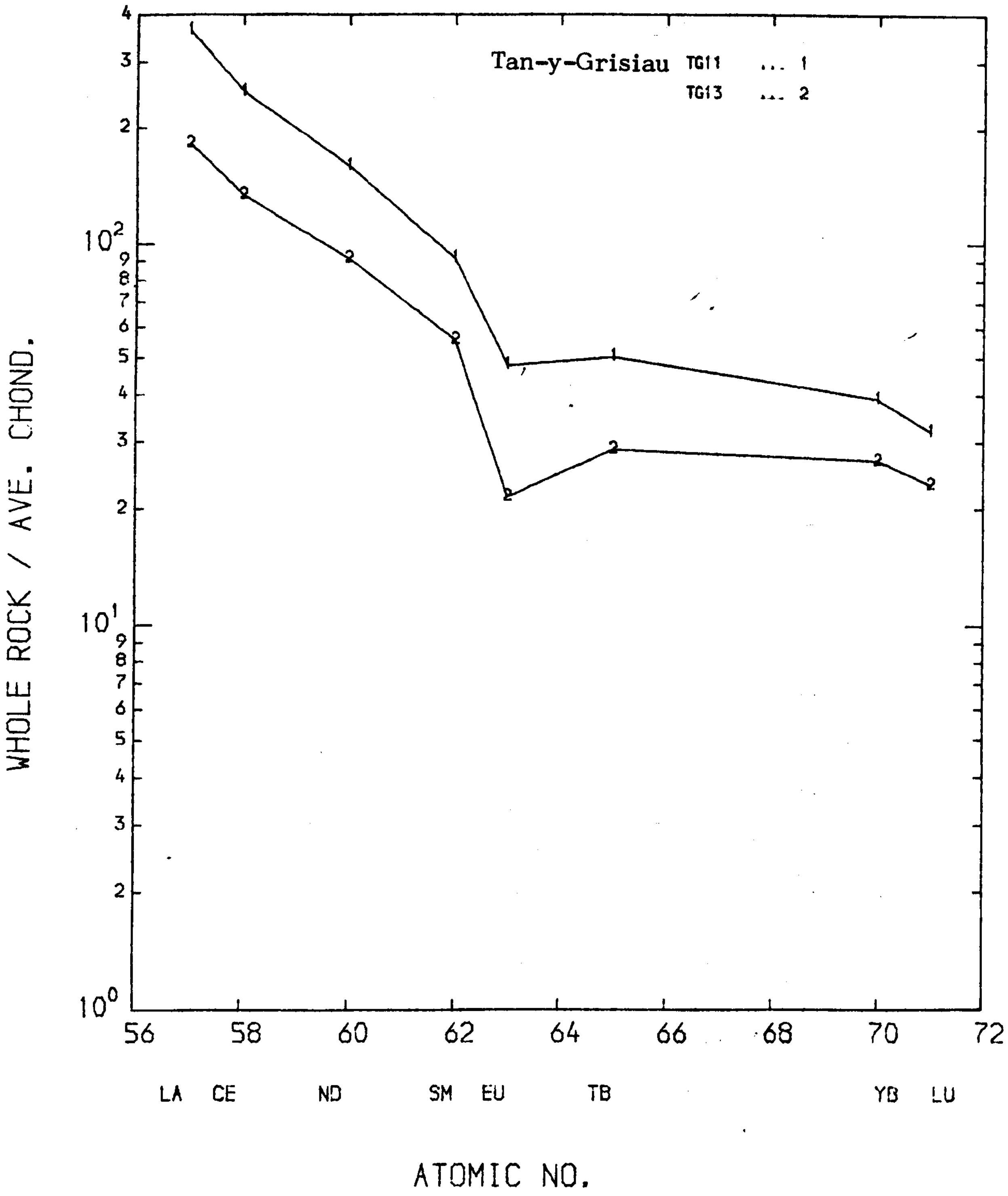
There is evidence that North Wales has been an area of plate subduction during the Precambrian — Devonian (Thorpe, 1970; Wood, 1974). Precambrian rocks of variable metamorphic grade are exposed on Anglesey and along the Lleyn Peninsula and recent geophysical evidence indicates that the continental crust beneath the North Wales area is about 36-39 km deep (Bamford et al., 1976). More recent but unpublished work using the LISPB-delta seismic data from Bamford et al. shows that there is a significant change in seismic velocity which corresponds to 13 km depth. This region could represent the upper crust - lower crust boundary (Nunn, 1979; personal communication) in which case the lower crust is possibly twice as thick as the upper continental crust in North Wales. In view of the earlier discussion of the possible nature and evolution of the crust it is clearly appropriate to consider whether the granitic (sensuo lato) rocks of Snowdonia could have formed by anatexis of the lower crust. The rare earth element data for the Snowdonian suite ,with their low $(Ce/Yb)_N$ ratios,do not accord with partial melting of lower crustal compositions as we know them at present. Ultramafic and mafic granulites are the only known material to possess low $(Ce/Yb)_N$ ratios although it is very unlikely that partial melting of such rocks would occur without melting of more silicic material. Since there are no granitic rocks in the area with highly fractionated rare earth patterns, like those of acid gneisses (point 3, above), a model involving partial melting of lower crustal rocks can be rejected.

b) Crustal Contamination

The assimilation of country rock has often been suggested as a mechanism for the chemical variation of igneous suites or individual bodies (e.g. Tremlett, 1962). Evidence has accumulated over the last twenty years or so to indicate that this mechanism may not be of great importance. Chappel (1978) found that there was little incorporation of country rocks in the New England Batholith and that it was restricted to a few metres from the contact. Pitcher (1979), in an extensive discussion of granite magmas, stated that, apart from roof and wall zones, granite plutons are volumetrically poor in true xenolithic material. The chemical zonation of some plutonic bodies has been shown to be a result of accretionary crystallisation rather than the progressive assimilation of xenoliths (Taylor, 1976).

The Tan-y-Grisiau microgranite possesses a well-displayed xenolithic zone along its northern margin. Here xenoliths, in various stages of digestion, are seen below its discordant contact with Tremadocian hornfelses. Clots of chloritic material, further away from the contact, are claimed to be the residues from extensively digested xenoliths. Three samples (TG11, TG13, TG14) were collected from the northern edge of the

Figure 42


Tan-y-Grisiau TG11 ... 1
TG13 ... 2
WHOLE ROCK / AVE. CHOND.
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
9
8
7
6
5
4
3
2
10^0
56
58
60
62
64
66
68
70
72
LA
CE
ND
SM
EU
TB
YB
LU
ATOMIC NO.

intrusion and their petrography and chemistry is different from those samples from the central parts. Petrographically the former rocks are equigranular, ferromagnesian minerals are chloritised and feldspars are converted to albite and sericite while chemically they are richer in Al_2O_3, MgO, CaO, Na_2O, Sr and the light rare earth elements. It is unclear whether these differences are a result of xenolithic incorporation and digestion and/or other effects such as hydrothermal alterations. Two rare earth analyses show clearly the more-enriched and fractionated light rare earth abundances compared with the unaltered samples (TG3, TG4 and TG6).

c) Partial Melting of Sedimentary Material

The fact that granitic, granodioritic, trondhjemitic and tonalitic melts may be derived from sedimentary material has been established by a number of experimental studies (e.g. Tuttle and Bowen, 1958; Winkler, 1967). In more recent years similar propositions have been made by Ewart et al. (1968), for the evolution of the Taupo rhyolites of New Zealand, Alburquerque (1977, 1978), for the granitic suites of Portugal and Nova Scotia, Price and Taylor (1977) and White and Chappel (1977).

The granitic suites of Portugal are post-syntectonic and were emplaced during the Hercynian orogeny into a metasedimentary sequence of Proterozoic-Ordovician age. Two suites of granites are recognisable from field relationships and radiometric ages and they consist of hornblende-biotite granodiorites, pyroxene-hornblende diorites, biotite granites, biotite-muscovite granites and associated granodiorites. Samples collected from these intrusions have rare earth element fractionated patterns, $(Ce/Yb)_N$ = 13-35, with negative europium anomalies, $Eu/Eu^* \simeq 0.4$, and there is a general decrease in the abundances of the rare earths from granodiorite to granite. Alburquerque (1977) has presented models for the evolution of these suites by partial melting of greywacke, greywacke-pelite and gneiss compositions with their rare earth element abundances being that of the North American shale composite (Haskin et al., 1966). The residual minerals, after the removal of the batch melts, were considered to consist of quartz, plagioclase, garnet, orthopyroxene, apatite and cordierite.

The granitoids of Nova Scotia are intruded into a Cambro-Ordovician sequence of quartzites and greywackes metamorphosed to amphibolite facies. The proposed origin of the suite is that 30-60% partial melting of greywacke occurred and that the residual minerals were quartz, biotite, hornblende, plagioclase and orthopyroxene. The resulting rare earth patterns for the granitoids are moderately fractionated, $(Ce/Yb)_N = 5\text{-}19$, and they possess a Eu anomaly, $Eu/Eu^* = 0.2\text{-}0.7$.

Chappel and White (1974), White and Chappel (1977) and Chappel (1978) have made detailed field and geochemical studies of the batholiths of eastern Australia and they have found criteria which enable them to classify a compositionally narrow S-type or a compositionally broad I-type of granitoid. The S-type refers to granitoids derived from sedimentary material whereas the I-type depicts those granites and associated rocks which have formed from igneous material. The features which are found in studies of many igneous provinces are listed below and the criteria have been taken from Chappel and White (1974), Pitcher (1979) and Beckinsale (1979).

I-type	S-type
1) Relatively high Na_2O, $> 3.2\%$ in felsic varieties	1) Relatively low Na_2O, $< 3.2\%$ in rocks with 5 % K_2O.
2) Molar $Al_2O_3/Na_2O+K_2O+CaO<1.1$	2) Molar $Al_2O_3/Na_2O+K_2O+CaO>1.1$
3) C.I.P.W. normative diopside, or $<1\%$ normative corundum	3) $>1\%$ normative corundum
4) Broad spectrum of compositions from gabbro-granite	4) Restricted range of compositions, dominantly granites
5) Regular inter-element variations producing variation diagrams with good linear correlations	5) Irregular variation diagrams
6) Low initial $^{87}Sr/^{86}Sr$, $<.708$	6) High initial $^{87}Sr/^{86}Sr$ ratios, >0.708
7) Magmas possess relatively high oxygen fugacities: magnetite is a common phase	7) Magmas possess relatively low oxygen fugacities: ilmenite is a common ore mineral

8) Hornblende and biotite are common mafic minerals	8) Muscovite and biotite are common minerals; hornblende is absent
9) Sphene and allanite are common minerals in the felsic magmas	9) Monazite, cordierite and garnet are commonly present
10) Tungsten, molybdenum and porphyry copper deposits may be present	10) Tin mineralisation

The rare earth element pattern of the upper continental crust is assumed to be that obtained from determinations from clastic sediments. The North American shale composite, European shale average (Haskin et al., 1966), the post-Archean average sediment (Nance and Taylor, 1976) and other clastic sediments show a remarkable similarity in their rare earth patterns and abundances. The features of these patterns are light rare earth enrichment $(Ce/Yb)_N \simeq 6$, a small negative Eu anomaly (0.65) and almost no fractionation of the middle - heavy rare earths (Gd-Lu). It is noteworthy that Nance and Taylor (1977) have found that Archean clastic sediments possess lower abundances of the rare earths and they have a small positive Eu anomaly.

Some determinations, of the rare earth contents of Precambrian metasediments have been made by Thorpe (1970) in his study of Precambrian rocks from Wales and England. His determinations of La, Ce and Y in metasedimentary rocks from the Mona complex of Anglesey do not show any great differences from the North American shale composite (table 9.6; Thorpe, 1970). The $(Ce/Yb)_N$ ratio of Haskin et al.'s composite sample is larger than any found for the Snowdonian suite of intrusions and partial melting of such sedimentary material is unlikely to produce any magmas with a value less than 6. Most assemblages resulting from metamorphism of sedimentary material prior to melting may consist of quartz, plagioclase, orthoclase, biotite, garnet, sillimanite and minor apatite (Price and Taylor, 1977). The residual minerals just prior to the removal of a melt are likely to consist of plagioclase, garnet, alumino-silicates, pyroxenes and quartz. Most of these minerals possess higher rare earth distribution coefficients for the heavy rare earths than for the light rare earths and consequently any melts in equilibrium with such phases will possess

$(Ce/Yb)_N$ ratios larger than that of the parent.

The Snowdonian suite of intrusions bears a greater similarity to I-type granitoids than to the S-type. They display a fairly broad compositional range (tonalite-granite compositions have been sampled), possess greater than 3.2% Na_2O, except where secondary processes have altered this, their molar $Al_2O_3/Na_2O + K_2O + CaO < 1.1$ for most samples, hornblende and biotite are common mafic minerals and allanite and magnetite occur in accessory proportions in some intrusions. Thus, the rare earth element abundances and certain chemical and petrographic features suggest that the granitoids of the Snowdonian suite are unlikely to have formed by melting of sedimentary material of greywacke or shale composition.

d) Partial Melting or Remobilisation of Crustal Igneous Material

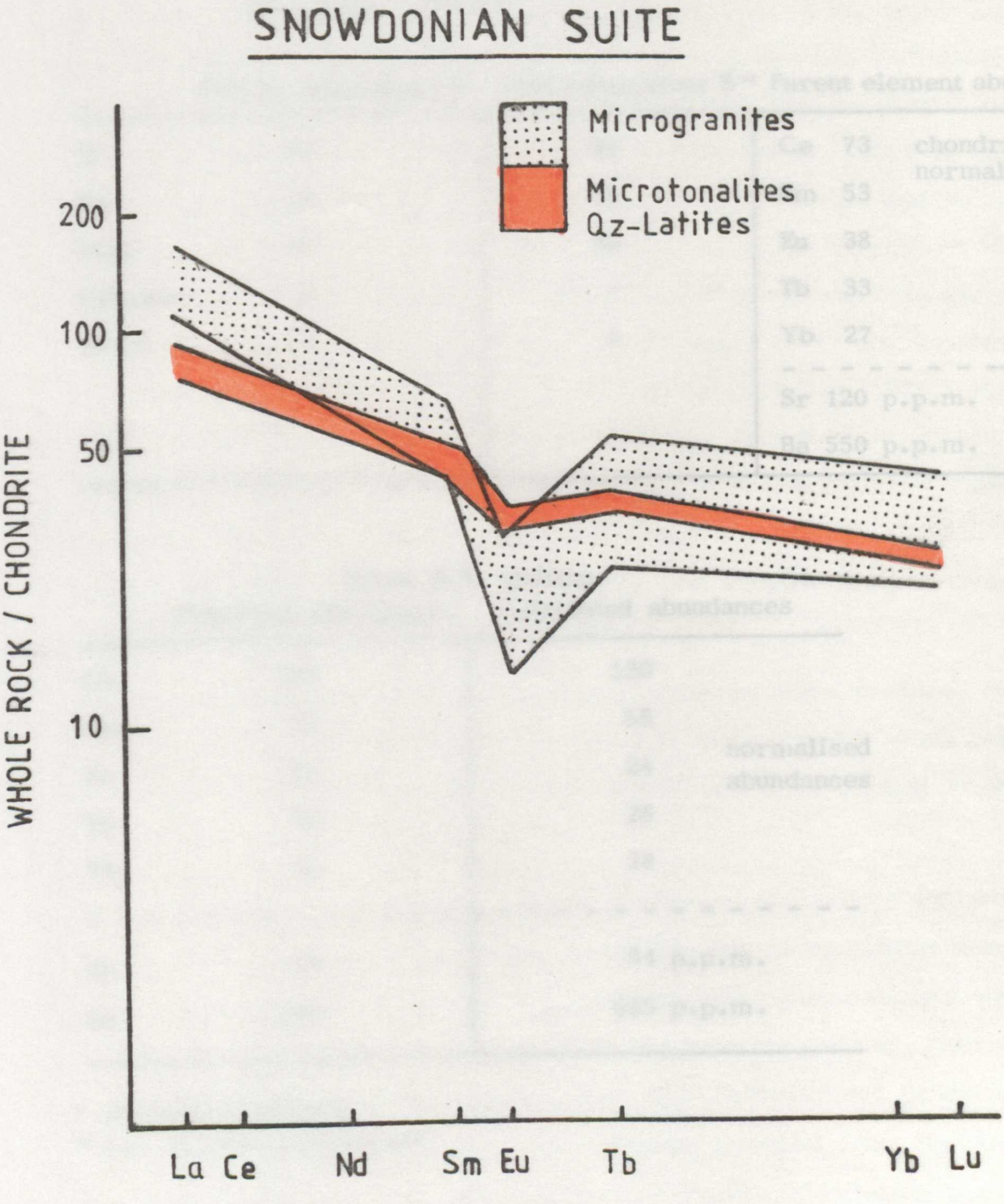
Large volumes of basic magma were available for eruption and emplacement throughout the Ordovician in North Wales and it is likely that the emplacement of dolerites in Snowdonia and around the Harlech Dome occurred at various times and were controlled by the local tectonic environment (Bromley, 1969; Lynas, 1977; Ridgeway, 1976). The fact that the basic magmatism is temporally and spatially associated with acid material led Rast (1969) and Bromley (1969) to the conclusion that a large body of basic magma had mobilised the crustal rocks, which were in its vicinity, to produce acid plutonism and volcanism. It is noteworthy that two lines of geophysical evidence support the basic body hypothesis, namely the gravity survey made by Griffiths and Gibb (1965) and the aeromagnetic survey made by the Geological Survey (Stubblefield, 1965). Composite intrusions, consisting of porphyritic microgranite enclosed by dolerite or quartz-dolerite, are emplaced as sills in the south-eastern limb of the Yr Arddu syncline (Bromley, 1968). Bromley observed that these bodies are stratigraphically higher than the quartz-latites associated with the Moelwyn Volcanic Series but that they have approximately the same lateral extent. The petrographic similarities of the acidic part of the composite sills with the quartz-latites of the Moelwyn Volcanics and their geographical relationship led Bromley (1968) to infer that the acidic portion represented remobilised quartz-latite from the Moelwyns by the ascending doleritic magma. The Moelwyn Volcanics, emplaced and erupted during the Llanvirn - Lower Caradoc (Bromley, 1965), have lateral equivalents in the Y Glog Volcanics south of Moel Hebog (Shackleton, 1959) and in the Migneint area which lies on the northern flanks of the Harlech dome (Lynas, 1977).

The acid members of the composite intrusions were sampled near Croesor and two samples (COMP1 and COMP7) were analysed for the rare earth elements. In view of the rather unusual chemistry of COMP 7 and its rare earth pattern, which shows that La in particular has been mobilised, the sample has been rejected from the Snowdonian suite population. COMP 1 shows a high degree of similarity to other composites (COMP2, COMP3, COMP5) and also to the samples collected from the Ogwen granophyre. At a slightly lower degree of similarity the previously named samples compare with samples from the Nant Gwynant and Castell intrusive rhyolites, the Bwlch-y-Cywion microgranite and the Tan-y-Grisiau microgranite (see fig. 40, page 176). There is a geochemical similarity between the Manod Bach quartz-latites (associated with the Moelwyn Volcanic Series), the Penmaenmawr microtonalite and the Drosgl micro-granodiorite and Lynas (1977) has stated that there is a close similarity between the quartz-latites of the Migneint area and those of the Ffestiniog area (Moelwyn Volcanics). It is apparent, therefore, that a considerable volume of this magma-type was available during Llanvirn-Caradoc times over a wide area of North Wales.

A consideration of Bromley's (1968) hypothesis, that the composite intrusions represent partial melts of quartz-latite by doleritic magma, is clearly merited. The rare earth elements, Ba and Sr abundances of the Manod Bach intrusion are used, along with its normative mineralogical components, to construct a batch partial melting model. Owing to the small grain-size of the groundmass and the chloritisation of the original mafic minerals it is not possible to determine the modal mineralogy and the proportion of mafic minerals is, therefore, assumed to represent the sum of normative hypersthene and diopside. Modelling procedures show that a reasonably good correspondence between the observed and calculated data for composite sample COMP 1 may be obtained by approximately 35 % melting of a source with the rare earth element, Ba and Sr abundances of Manod Bach. Although there is no direct evidence that amphibole and clinopyroxene were the mafic minerals and that they occurred in the proportions shown below, it is necessary to use minerals with high distribution coefficients for the heavy rare earths in order that these elements may be partitioned approximately equally between the melt and residue. The heavy rare earth abundances are similar for the Manod Bach quartz-latite and the granitic material of the composite minor intrusions, the Ogwen granophyre and the Nant Gwynant rhyolite and this suggests that the bulk distribution coefficients for the heavy rare earths are approximately unity. Their concentration in the samples from Tan-y-Grisiau and Bwlch-y-Cywion are higher than the remaining intrusions of Snowdonia (Ogwen etc.) and this could be a result of a source(s) with a lower proportion of hornblende. The reduction in the modal proportion of amphibole would lower the bulk distribution coefficients for the heavy rare earths.

The preceding account has demonstrated that the rare earths, Ba and Sr geochemistry of COMP 1 may be explained by 35 % partial melting of a quartz-latite and minor modifications to the source mineralogy would provide reasonably good fits for the other granitic intrusions of Snowdonia. A source such as Manod Bach is attractive since it possesses a low $(Ce/Yb)_N$ ratio (2.5), its magma type appears to be distributed over a fairly wide area and it was probably generated some time before the mid-Caradocian volcanism and plutonism. It is clearly recognised that the modelling procedures used above are poorly constrained, particularly owing to the uncertain nature of the source mineralogy, and that the solution is not unique.

Figure 42



Microgranites:	Tan-y-Grisiau, Bwlch-y-Cywion, Ogwen, Nant Gwynant, Croesor composite
Microtonalites etc.:	Penmaenmawr, Drosgl, Manod Bach

Table 7

Partial Melting Model

$$\text{Manod Bach (Qz-latite)} \xrightarrow[\text{melting}]{35\ \%} \text{composite (COMP 1)}$$

	Source mineralogy %*	Melt mineralogy %**	Parent element abundances		
Q	20	32	Ce	73	chondrite normalised
Or	10	33	Sm	53	
Plag	55	30	Eu	38	
Clinopx	5	-	Tb	33	
Amph	10	5	Yb	27	
			Sr	120 p.p.m.	
			Ba	550 p.p.m.	

After 35 % melting

	Observed abundances	Calculated abundances	
Ce	127	130	
Sm	57	55	normalised abundances
Eu	22	24	
Tb	32	28	
Yb	32	28	
Sr	54	54 p.p.m.	
Ba	695	635 p.p.m.	

* modal proportions

** i.e. if melt crystallised

Conclusions

The calc-alkaline nature of the Snowdonian suite has been demonstrated in section 3 of this discussion (page 186) although this feature may result from a number of evolutionary processes which are difficult or impossible to distinguish. These might include partial melting of the upper mantle, partial melting of an immature sequence of volcanoclastic sediments derived from calc-alkaline material and remobilisation or partial melting of calc-alkaline plutons which lay frozen in the crust. There is considerable evidence that, during the latter part of the Cambrian and the early part of the Ordovician, calc-alkaline activity occurred throughout North Wales and the Welsh Borders. Andesites occur at Arenig Mountain, Builth Wells and western Shropshire (Fitton and Hughes, 1970) and basalts-andesites-dacites-rhyolites occur at Rhobell Fawr (Wells, 1925; Kokelaar, 1979). Thus, there appears to be no shortage of material suitable for generating the intermediate-acid plutonic and volcanic material found in the mid-Ordovician of North Wales and around the Harlech dome. A number of points may usefully summarise and indicate the preference for partial melting of calc-alkaline plutons.

1) Considerable volumes of calc-alkaline material were produced over a wide part of North Wales, the Harlech dome and the Welsh Borders during the late Cambrian - Lower Ordovician (e.g. Rhobell Fawr, Arenig Mountain, Moelwyns).

2) The calc-alkalic material produced throughout the middle Ordovician of North Wales does not appear to include any compositions more basic than tonalite. This feature may indicate that the magmatism was generated at crustal depths and that the heat for melting, provided by large bodies of basaltic magma, was only sufficient for producing intermediate-acid magmas. Calc-alkaline material from the Andes, the Antarctic peninsula and the Western Pacific island-arcs generally includes a considerable proportion of basic compositions.

3) The existence of peralkaline granites (e.g. Mynydd Mawr, Nant Bodlas) is generally indicative of extensional tectonics, though not exclusively

(e.g. Smith et al., 1977). Their presence is consistent with the block-faulting and graben-like tectonics proposed by Rast (1969). Mitchell and Reading (1971) suggested that the North Welsh region probably evolved as a marginal basin behind a volcanic arc. In view of recent geophysical evidence, an ensialic (or incipient) back-arc basin is considered likely but this will be discussed in more detail later.

Chapter 8

THE INTRUSIONS OF THE LLEYN PENINSULA
(Group 2)

Introduction

The only important geochemical study of the intrusions of this area to have been undertaken are those of Tremlett's (1962, 1964, 1972). His most recent account (1972) involved the determination of the major elements and Rb, La, Ce, Sr, Ba, Zr, Nb, Ga, Y, Li and Cs for twenty-four of the intrusions. Tremlett's earlier field studies led him to the conclusion that many of the intrusions were emplaced subsequent to the faulting of the area, which he assumed to be of a Caledonian age (Devonian). His geochemical studies revealed that there were differences between 'known Ordovician' and 'known Caledonian' intrusions and on the basis of this evidence he felt confident that other intrusions of the area could be assigned to the Ordovician or the Caledonian (Sil.-Dev.). The Ordovician samples, he maintained, contain high SiO_2 and low Al_2O_3, Na_2O/K_2O and Zr, Nb and Y relative to the Caledonian samples.

Thomas and Briden (1976) conducted a preliminary paleomagnetic investigation of six intrusions along with samples from the Ordovician Cader Idris basalts and three Ordovician intrusions from northern Snowdonia. Their results suggested that an anomalous geomagnetic field had occurred during the late-Ordovician and that no differences in paleomagnetic directions could be found between the Lleyn samples and the Ordovician Cader Idris basalts. Roberts (1979) has also expressed his doubts concerning Tremlett's hypothesis for the Lleyn igneous suite and he favours an Ordovician age.

The geochemical results presented in the previous chapter have shown that there are clear chemical discriminants for the Lleyn and the Snowdonian intrusives. The Snowdonian suite has lower Al_2O_3, Na_2O, Na_2O/K_2O, Zr, Nb, rare earth elements (REE) and Eu/Eu*. The whole Lleyn sample population can be divided into three divisions on the basis of chemical variations and these will be explained in the following discussions. The divisions are:-

A. Garnfor (Garnfor, Yr Eifl Felsite, Moel-y-Penmaen)

B. Lleyn

C. Gurn Ddu, Moel Penllechog, Gurn Goch

DISCUSSION

A. The Garnfor Complex

The members of this group consist of the composite intrusion of Garnfor, the nearby Yr Eifl felsite boss and four samples of volcanic material from Moel-y-Penmaen. These last samples have been described as andesites (Tremlett, 1962; Roberts, 1979) but their trace element characteristics are not typical of orogenic andesites but they do have similarities with oceanic andesites (Thompson et al., 1974) and some mugearitic rocks (Baker, 1978) from oceanic islands. Tremlett (1962), Matley and Heard (1930) and Roberts (1979) have shown that the andesitic rocks of Moel-y-Penmaen belong to the Bala Volcanic Series (Ordovician) and it will be shown later that the samples collected from that locality are closely related to the intrusive rocks. This relationship provides strong evidence against a Silurian-Devonian age for the intrusive suites of Lleyn and the geochemistry of the andesitic rocks provides information for the origin of the suite.

A consideration of all the Lleyn data (figs 43 - 46) makes it apparent that the Garnfor Complex shows substantially lower concentrations of Y, Zr, Nb, La, Ce and Nd than the other two identified suites. The Harker diagrams also demonstrate that, for most elements plotted against SiO_2, there are strong linear relationships and the samples from Moel-y-Penmaen (PAND), and Yr Eifl lie at the ends of the trend lines.

A number of petrogenetic processes will be considered in the course of a search for an explanation of the evolution of this suite. These are:-

Figures 43 - 46

Harker diagrams of major and trace elements for the intrusions of the Lleyn Peninsula

. . . . . .

The red dots represent the intrusions of:

Moel Penllechog, Gurn Ddu and Gurn Goch.

The purple dots represent the Lleyn granitoids (excluding Garnfor).

The green dots represent the samples of the Garnfor complex.

The Moel-y-Penmaen andesitic rocks are marked as a green dot at the low -SiO_2 end of the diagrams.

. . . . . .

Some differentiation trends are marked on some plots.
The broken lines represent the Garnfor trend and the full line represents the Lleyn (ex. Garnfor) trend.
All components are oxide (wt. %) or element p.p.m.
The K+Na plot is K_2O + Na_2O (wt. %)

Figure 43

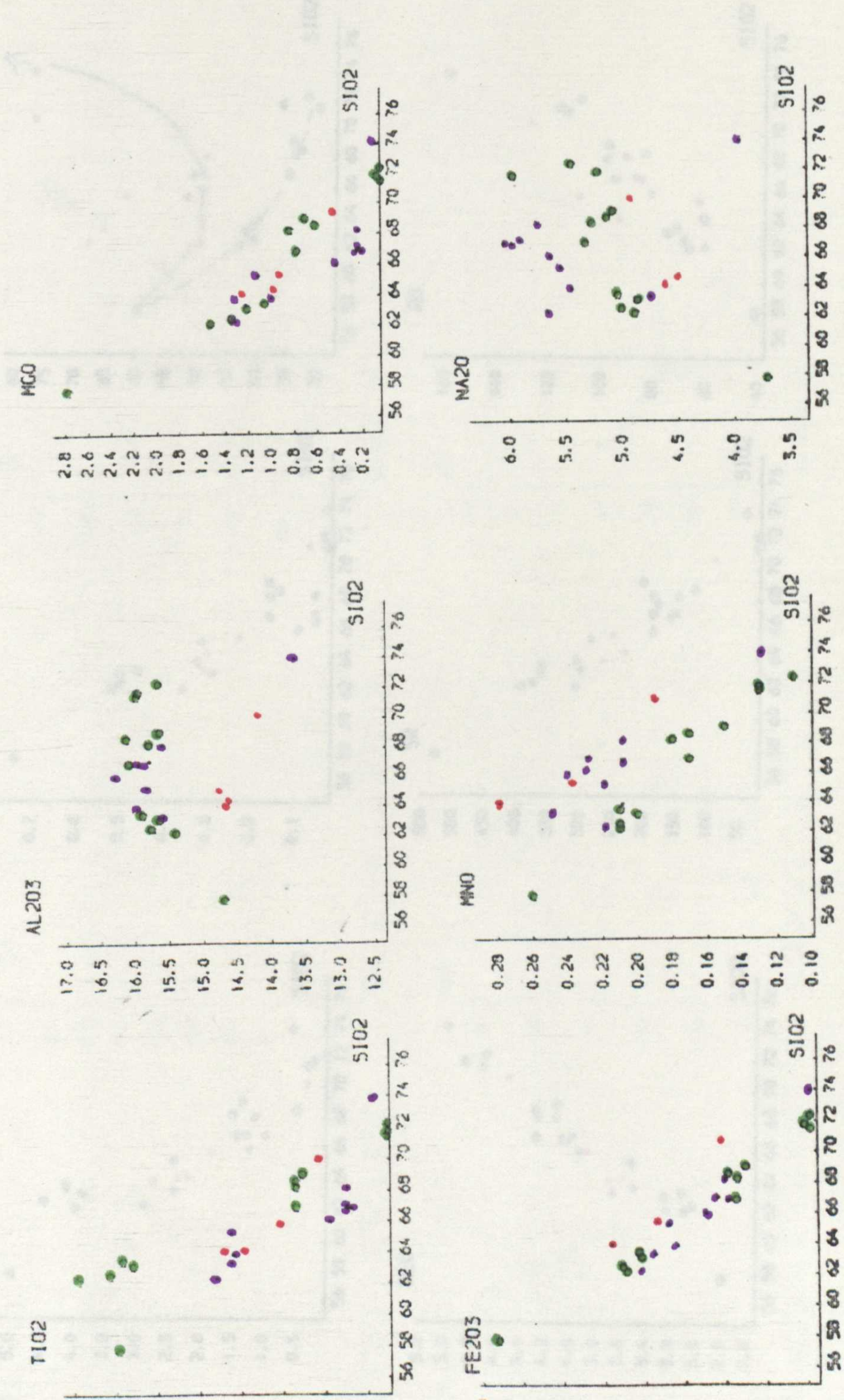

TIO2
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
AL2O3
17.0
16.5
16.0
15.5
15.0
14.5
14.0
13.5
13.0
12.5
MGO
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
FE2O3
10
9
8
7
6
5
4
3
2
MNO
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
NA2O
6.0
5.5
5.0
4.5
4.0
3.5
56 58 60 62 64 66 68 70 72 74 76
SIO2

Figure 44

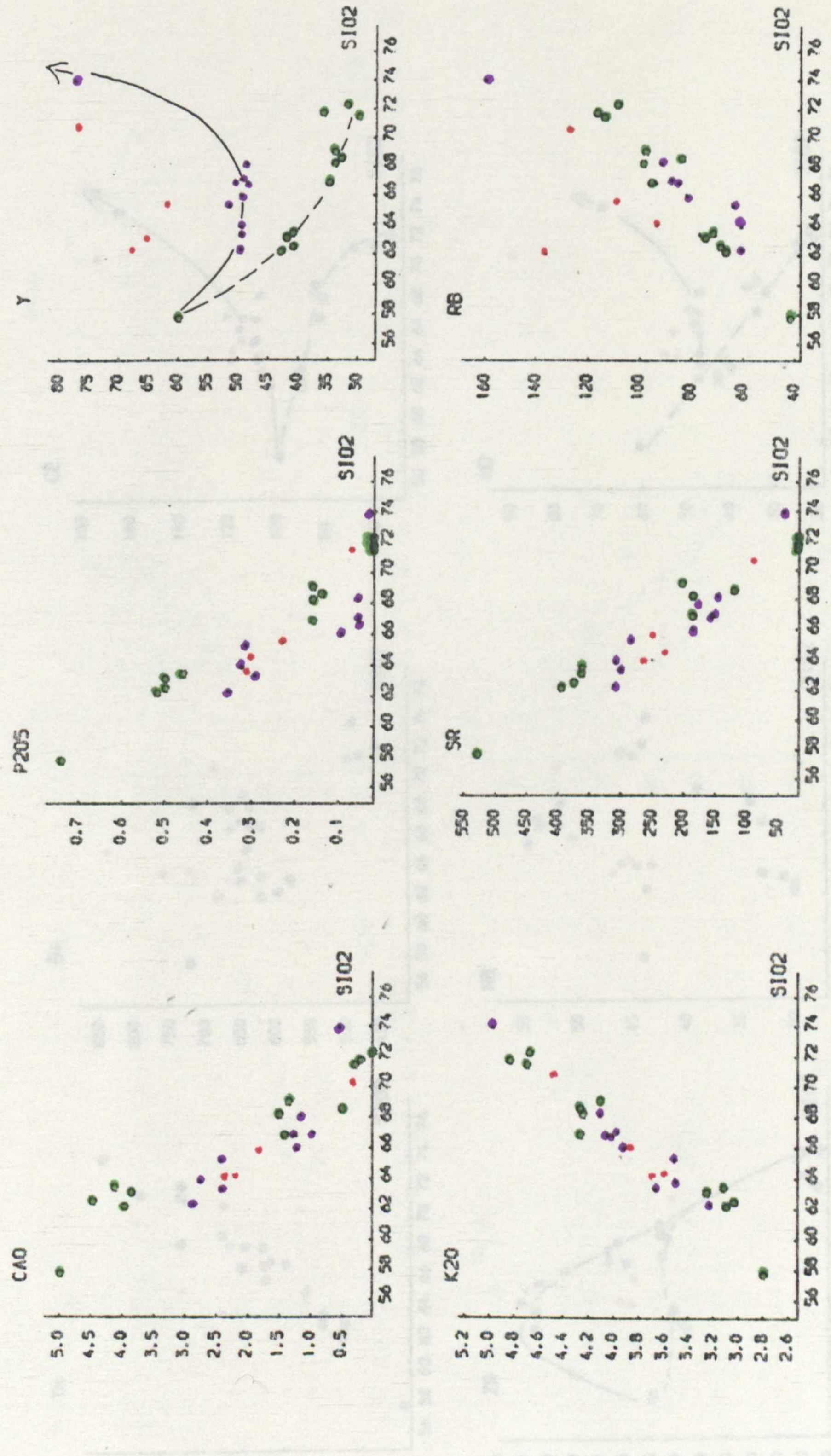

CAO
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
P205
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Y
80
75
70
65
60
55
50
45
40
35
30
K20
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
SR
550
500
450
400
350
300
250
200
150
100
50
RB
160
140
120
100
80
60
40
SIO2
56 58 60 62 64 66 68 70 72 74 76

Figure 45

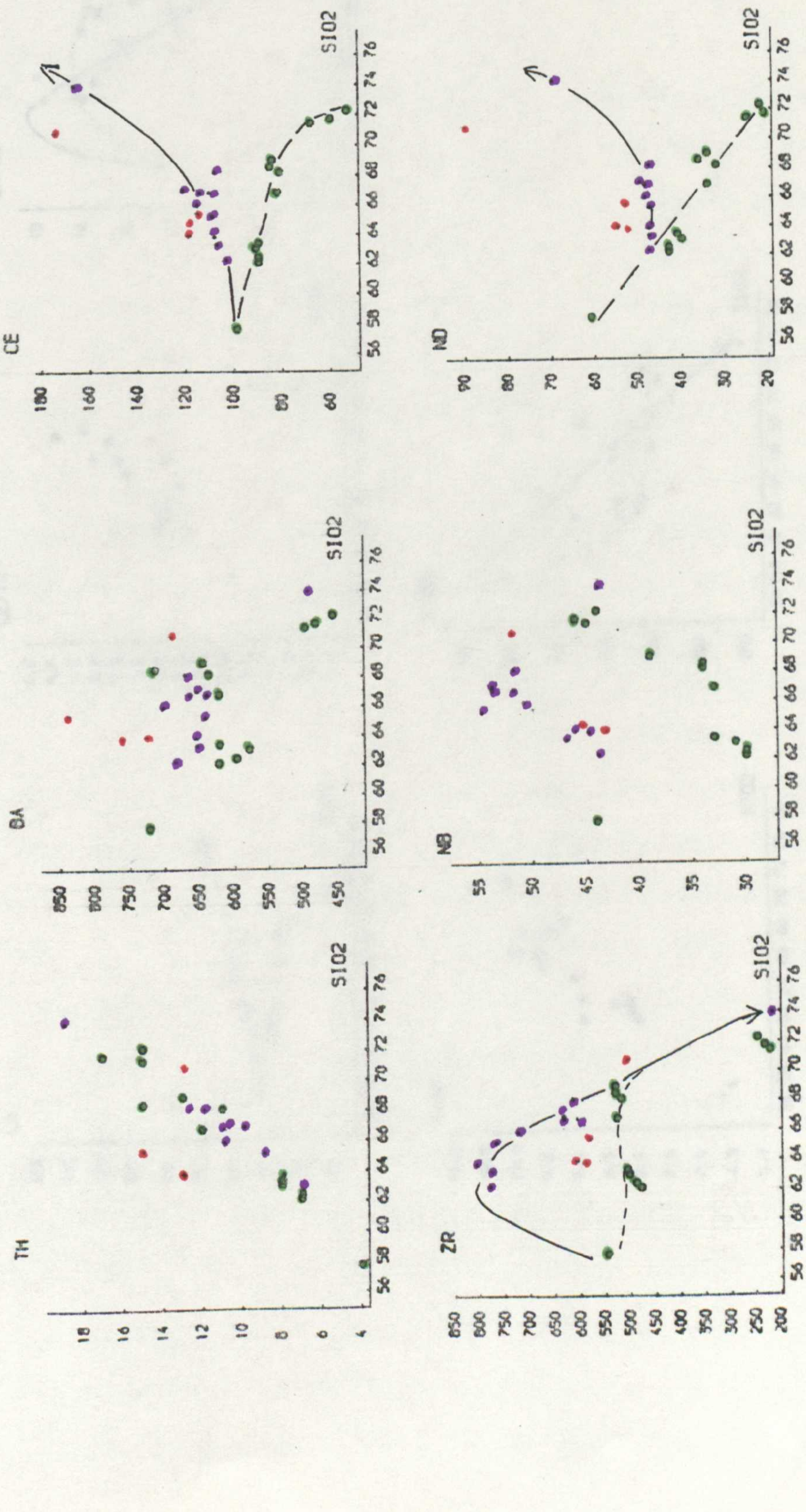
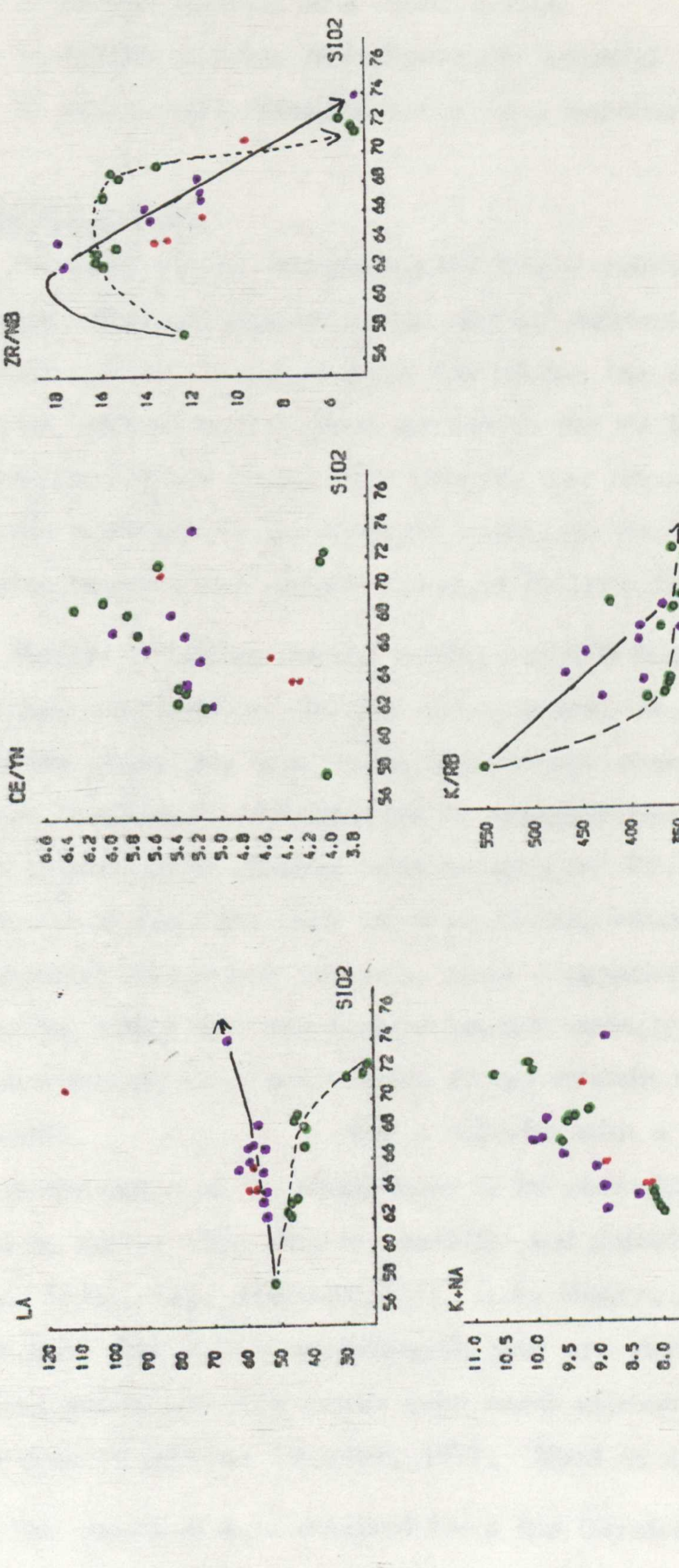

TH
18
16
14
12
10
8
6
4
BA
850
800
750
700
650
600
550
500
450
CE
180
160
140
120
100
80
60
ZR
850
800
750
700
650
600
550
500
450
400
350
300
250
200
NB
55
50
45
40
35
30
ND
90
80
70
60
50
40
30
20
56 58 60 62 64 66 68 70 72 74 76
SIO2

Figure 46


LA
120
110
100
90
80
70
60
50
40
30
SIO2
56
58
60
62
64
66
68
70
72
74
76
K+NA
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
CE/YN
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
K/RB
550
500
450
400
350
300
250
ZR/NB
18
16
14
12
10
8
6

1) Magma mixing
2) Magma unmixing
3) Partial melting of a mafic source
4) Partial melting of sedimentary material
5) Fractional crystallisation from a basaltic magma

1) Magma mixing

Tremlett (1962) recognised the linear relationships between plots of major elements against silica, and he suggested that the Garnfor complex (proper) resulted from the mixing (or assimilation) of doleritic material with an acid magma similar to the Yr Eifl felsite in composition. The reason for his choice of a dolerite was because the intermediate and acid members of the complex contained xenoliths of basic material and also because two narrow dykes of dolerite intrude the complex.

Models involving magma mixing require that all the hybrids lie on a straight line between the two end-members on element-element plots. Deviations from this may occur if additional processes have operated such as fractional crystallisation or contamination. There are many linear correlations although none is seen for Zr, Nb or Ba. The abundance of the light rare earth elements, which normally behave incompatibly in igneous systems, show a negative correlation with increasing silica and this feature argues strongly against a dolerite as an end-member since such rocks do not contain the high concentrations required. For a dolerite with a SiO_2 content of 48 % the concentration of Ce would have to be about 110 ppm for a mixing model to apply. The data for basaltic and doleritic rocks from North Wales, (PYG, CI1, Appendix VIII; G.L. Henry, personal communication, 1980) show that values exceeding 30 ppm are rare and even alkali basalts, which are rich in the rare earth elements, rarely contain more than 70 ppm Ce (Weaver, 1977; Wood et al., 1980).

The chemical data obtained from the Garnfor suite are inconsistent with a magma-mixing model involving a dolerite and the absence of strong linear correlations for Zr, Nb and Ba against SiO_2 argue against mixing involving another basic end-member.

2) Magma unmixing

The idea of unmixing or immiscibility of magmas had occurred to geologists as long ago as the late nineteenth century (Loewinson-Lessing, 1884) but the concept became unpopular owing to work by Bowen (1928) and others who considered that silicate liquids were completely miscible. Experimental work showed that small fields of liquid immiscibility exist in a number of silicate systems including $FeO-SiO_2$ (Greig, 1927) and $K_2O-FeO-Al_2O_3-SiO_2$ (Roedder, 1951). Strong evidence for the mechanism was obtained from lunar rocks and later from some terrestrial basalts (Roedder and Weiblen, 1970, 1971; De, 1974) and in recent years its applicability has been invoked by Philpotts (1976, 1978), Ferguson and Currie (1971), McBirney (1975) and Dixon and Rutherford (1979).

The development of small spheres of felsic material called ocelli are a feature of immiscibility and they are considered to have formed as droplets of immiscible liquid. Philpotts (1971) carried out melting and cooling experiments on samples containing ocelli which came from the Monteregian alkaline province of Quebec. The compositions of the suite range from nephelinite to quartz diorite for the basic members and nepheline monzonite and quartz monzonite to granite for the felsic members. The melting experiments showed that a homogeneous glass resulted and on cooling under hydrothermal conditions two liquids formed which had the same chemical compositions (electron microprobe analyses on glasses) as the matrix and ocelli of the natural samples. The proponents of magma unmixing point out that it provides a solution to the bimodal suites which are common in alkaline provinces (Sorensen, 1974). Weaver (1977), however, concluded that the 'Daly gap' present at Emuruangogolak volcano, Kenya can be explained by fractional crystallisation where the middle stages of crystallisation cause a rapid traverse of the compositional range resulting in few intermediate melts.

Philpotts (1975) has found evidence to suggest that unmixing of magmas occurs at a high level in the crust because the Monteregian dykes which were rapidly emplaced from a source at depth do not show a compositional gap in their range from basic to acid material. Nakamura (1974) came to the same conclusion from an experimental study of the fayalite-leucite-silica system. More recent work by Philpotts (1978) has shown that up to 32 % unmixing can occur in tholeiitic basalts subjected to melting and cooling and this demonstrates that the process is not confined to material of an unusual composition. He found that two liquids existed over a wide temperature interval at one atmosphere pressure and that the interval could be enlarged if the oxygen fugacity increased.

The behaviour of some major and trace elements between coexisting melts has been studied by Watson (1976) and Ryerson and Hess (1978) using synthetic and natural material. The distribution of the elements between the two phases appears to be controlled by the structural properties of the melts. Watson (1976)used the system K_2O-FeO-Al_2O_3-SiO_2 for his studies and his results showed how the melt-melt distribution coefficients for the elements vary with the changing composition and structure of the melt. Since natural systems are invariably more complex than that studied by Watson, owing to complex solid solutions and changing mineral compositions in response to changing melt composition, Ryerson and Hess (1978) considered it important to use natural rock samples. They investigated distribution coefficients for various major and trace elements between coexisting immiscible granitic and ferrobasaltic melts. Their interpretation of the measured distribution coefficients was that elements were partitioned between the two phases according to the degree of polymerisation of the melts. The basic melt, being rich in non-bridging oxygens,is less-polymerised while the acidic melt, containing few non-bridging oxygens, is more-polymerised. Highly polymerised melts possess a relatively small number of substitution sites for high charge density ions and their structure consists largely of

SiO_2, Al_2O_3, Na_2O and K_2O compared with the less-polymerised basic melts which contain Ti, Fe, Mn, Ca, Mg and P. The behaviour of trace elements is similar in that the low field strength ions (Cs, Rb, Li) are strongly partitioned into the acid melt while high field strength ions, HFS (Zr, Nb, P, Ta, Cr, Ni, Hf, rare earth elements) are strongly partitioned into the basic melt: Ba and Sr are partitioned equally between the two melts. Ryerson and Hess (1978) found that the concentration of phosphorus in the melts will affect the partitioning behaviour of the REE owing to complex formation and the higher the abundance of P_2O_5, the greater the partitioning of the REE into the basic melts.

An important discovery for immiscibility studies by Watson (1976) and Ryerson and Hess (1978) is that although the REE are more strongly partitioned into the less-polymerised basic phase, there is no fractionation within the lanthanide series i.e. the light, middle and heavy rare earths possess equivalent distribution coefficients. Watson found that the REE were about 4 x more abundant in the basic melt than the coexisting acid melt while Ryerson and Hess found a 10 x enrichment factor. This observation of non-fractionation of the REE is important for it shows that their variable distribution coefficients found for many minerals (clinopyroxene, hornblende, garnet, zircon) are not controlled by the structure of the melt but by the mineral's selectivity. The change in distribution content for a particular REE in a mineral in equilibrium with various compositions is dependent on the structure of the melt.

The behaviour of europium needs to be considered separately owing to its multivalent character. The oxygen fugacity, fO_2, of the melt determines whether Eu behaves as a trivalent or a divalent element. If the oxygen fugacity is high then Eu will be partitioned into the basic melt as a typical REE, and if the fO_2 is low its behaviour will be similar to that of Ba and Sr. Thus for a magma that is unmixing in a reducing environment the basic melt will develop a large negative Eu anomaly while the acidic melt will have a large positive Eu anomaly. In a strongly oxidising environment no anomalies will develop in the unmixing liquids while magmas with an intermediate fO_2 will develop an anomaly to a greater or lesser extent.

Although liquid immiscibility in magmas has been invoked, especially for some alkalic suites, it is as yet uncertain whether it could operate on a large scale. The evidence for unmixing to produce the variations seen in the Garnfor suite is very weak. The high field strength elements, P and Zr, are more enriched in the andesitic rocks from Moel-y-Penmaen than in the felsitic rocks but Nb is equally abundant in both end-members. The REE patterns of the andesite and the felsite do not show a parallelism as predicted by the experimental studies and a secondary mechanism would need to be invoked to account for this. Fractional crystallisation is the most likely secondary process but the extraction of hornblende or apatite, with their high distribution coefficients (table 1 , page 48) would be required to explain the depletion of the middle and heavy rare earths in the felsites. Any such fractionation would be very limited owing to the impoverished nature of the acid melt in the anions or cations that constitute those minerals and the high viscosity of the melt would possibly preclude efficient removal of those minerals. The absence of an Eu anomaly in the andesitic sample would require that the unmixing magma had a high oxygen fugacity, although Fe(II)/Fe(III) $\simeq$ 2.3 (Appendix V). The large negative Eu anomaly in the felsite (Eu/Eu* = 0.4) would require the removal of plagioclase and a considerable reduction in the previously high oxygen fugacity would be necessary to provide sufficient europous (Eu II) ions for entry into the plagioclase lattice (or orthoclase). The geochemical evidence and the lack of any petrographic criteria, such as ocellar structures, argue against a model of magma unmixing for the Garnfor suite.

3. Partial melting of a mafic source

In many geochemical studies of igneous suites it has been difficult to assign the chemical variations to a partial melting or fractional crystallisation process with any confidence owing to the similarity in behaviour of elements with $D < 1$. The behaviour of elements with $D > 1$

do permit a choice of process however, since partial melting is less effective than fractional crystallisation for altering the abundances of such elements, i.e. those with a large bulk distribution coefficient (see page 47). The partial melting process considered in this study is batch partial melting as this is considered to be a more reasonable geological mechanism than fractional melting (Hanson, 1978). Hanson argues that the first melt to form with batch partial melting will take most of the volatiles with it leaving an essentially refractory residue. Thus the addition of more heat or volatiles would be needed to produce further melting.

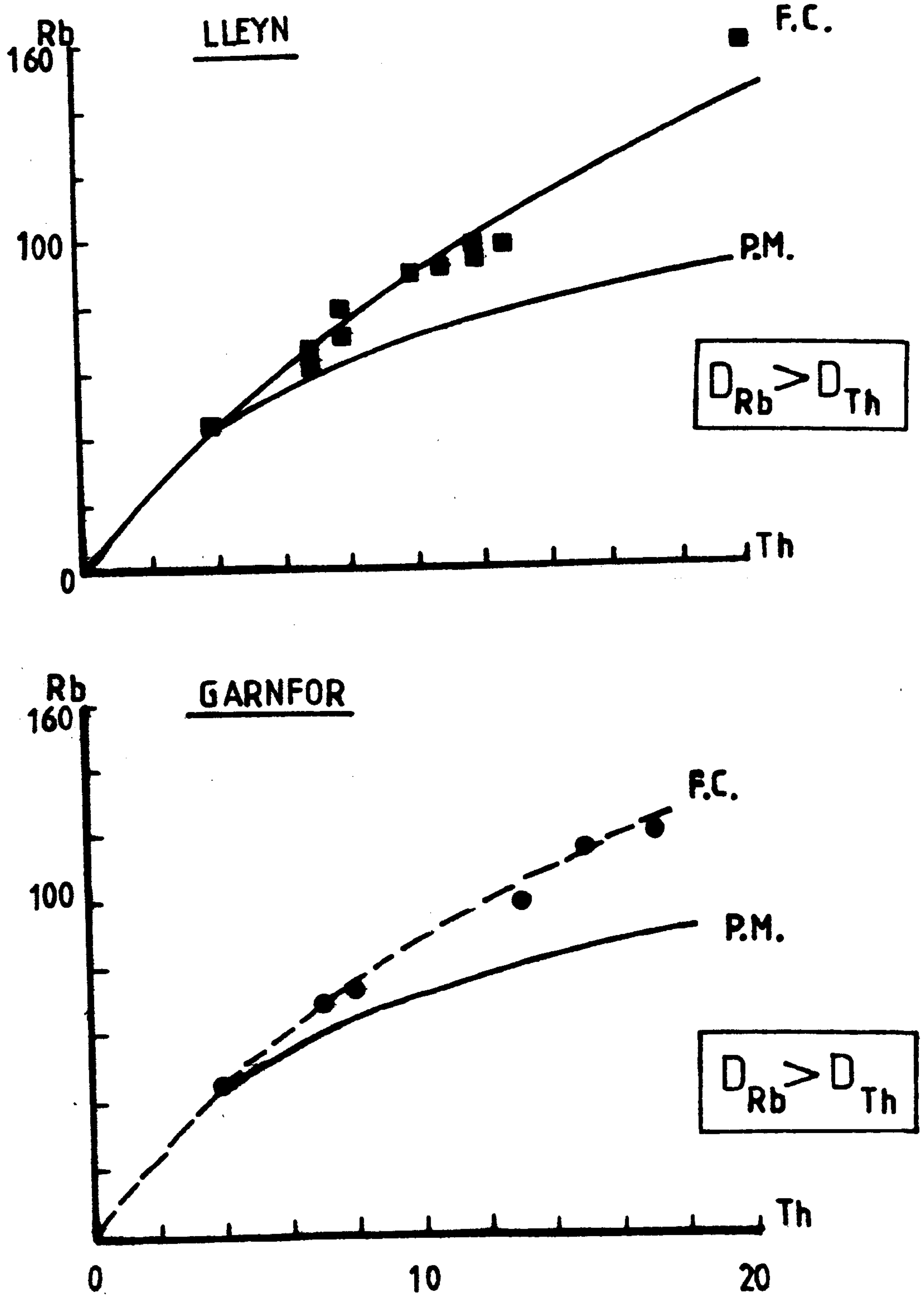
Minster,Allegre (1978) have provided a useful summary of the behaviour of various trace elements and their use in identifying the operative petrogenetic process.

1) Elements with high distribution coefficients, Kd's, are particularly useful for distinguishing between partial melting and fractional crystallisation because their abundance varies dramatically during the the latter processes but not the former.
2) Elements with very low Kd's behave similarly during partial melting or fractional crystallisation and their abundance is indirectly proportional to the extent of partial melting or the fraction of melt remaining.
3) Elements with intermediate Kd's behave differently during the two processes. When plotted against an element with a very low Kd the curve for a fractional crystallisation process is less variable than for a partial melting process. For low values of F (fraction of melt) the element with an intermediate Kd is less enriched during partial melting (fig. 8 , page 47).

With this understanding of trace element behaviour it should be possible to test whether the Garnfor data are consistent with a partial melting model. Chromium and nickel are two elements which possess large distribution coefficients in many igneous systems. They are strongly partitioned into early formed mafic minerals like olivine and the pyroxenes and their distribution coefficients are strongly temperature dependent for olivine and clinopyroxene. The Moel-y-Penmaen andesitic magma, PAND, would have to be formed from a source considerable more mafic than itself owing to the unlikelihood of generating a melt from a source of the same or similar composition to PAND. The solidus temperature of such an assemblage would be very high and low degrees of melting ($< 30\%$) of a more mafic source would be more reasonable. The proposed source would almost certainly contain appreciable Cr and Ni abundances and the partial melts produced would also contain measurable concentrations (see (1) above). Partial melting of a source similar to island arc tholeiites,with their characteristically low Cr and Ni contents,would produce melts with low abundances of these elements although measurable amounts should be present especially in any intermediate rocks produced. None of the samples from Garnfor, Yr Eifl or Moel-y-Penmaen has a Cr or Ni concentration that is measurable by the X-ray Fluorescence procedure used (lower limits of determination for Cr and Ni are approximately 5 ppm). Had melting of island arc tholeiite material been involved, the abundances of the high field strength elements (P, Ti, Zr, Nb) would be expected to be lower than observed since these elements are depleted relative to the large ion lithophile elements (Rb, Th, K, etc) in such source rocks. The abundances of the high field strength elements are high in this group and generally they show greater enrichment in the andesitic members than in the acid members (see figs 43,44,45, page 212-15).

Point (3) above has stated that a plot of a more incompatible element (more-HYG) against a less-incompatible element (less-HYG) could be used to distinguish between partial melting and fractional crystallisation. Thorium and rubidium are the only elements available from this study which satisfy the criteria for a more-HYG element (Th) and a less-HYG element (Rb). Owing to the large charge on Th (Th^{4+}; r = 1.08 A) and the large ionic radius of Rb (Rb^{+}; r = 1.57 A) neither of them can be readily accommodated in common igneous minerals and consequently their bulk distribution coefficient, D, is low or very low. The bulk distribution coefficient may be defined as the sum of the

figure 47



Rb versus Th data (p.p.m.) for the Lleyn and Garnfor Suites. The curves are those calculated for fractional crystallisation and partial melting assuming $D_{Th} = 0.01$ and $D_{Rb} = 0.25$ (see Ferrara and Treuil, 1975).

products of the modal proportions of minerals and their distribution coefficient for a particular element. Thorium which ranges from 4-17 ppm in this group is assumed to have a bulk distribution coefficient of 0.01 and Rb with a range of 42-110 ppm has a calculated D of 0.25. This value can be obtained from the relationship:

$$\frac{C_L}{C_o} = \frac{1}{F + D(1 - F)}$$

$$\frac{C_L}{C_o} = \frac{1}{D} \qquad \text{for small F}$$

N.B. Thorium determinations have a high relative error, approximately ± 1 ppm.

Hanson (1978) states that $C_o/C_L \longrightarrow \frac{1}{D}$ for F less than 0.4 and approaches it more closely as F decreases. F can be obtained from the abundance of Th in a sample from Garnfor divided by the abundance in the original parent.

$$\frac{C_L}{C_o} \simeq \frac{1}{F} \qquad \text{for } D \ll 1$$

Because the largest Th content obtained was 17 ppm and the smallest was 4 ppm, $F \simeq 23\%$ assuming PAND was the source. So long as the Rb/Th ratio of the mafic source is approximately the same as that of PAND (0.095) the following arguments hold. The plot of Rb .v. Th (fig. 47, page 223) shows that there is little change in the slope of the curve as it approaches the origin from the plotted point of PAND. Although this curve does not need to pass through the origin it will probably pass near it.

Thus it seems reasonable to use the Rb/Th ratio of the andesitic sample PAND as an approximation to the ratio in the unknown mafic source. To calculate D^{Rb} we require the Rb concentration at a small F or high Th concentration. This value can be obtained by extrapolation of the curve of fig. 47 and at Th = 25 ppm, Rb = 160 ppm. Thus a Th content of 25 ppm corresponds to a partial melt of 16 % of PAND

($\frac{C_o}{C_L} \simeq F$; $\frac{4}{25} \simeq .16$) although as previously stated the original source for this suite would need to be more mafic than PAND. However, if we assume that the ratio $\frac{Rb}{Th}$ is the same in the original source as it is in sample PAND then $D_{RB} \simeq \frac{42}{160} \simeq 0.26$. By using the formulation of Ferrara and Treuil (1975), the curve expected for a partial melting process can be calculated.

$$C^L_{Rb} = \frac{C^o_{Rb}}{C^o_{Th}} \cdot C^L_{Th} \left[\frac{F}{D_{Rb} + F} \right]$$

where C^L is the concentration of the element in a sample

C^o is the concentration of the element in the source

F is the extent of melting

D_{Rb} is the bulk distribution coefficient of Rb

The partial melting curve is shown in fig. 47 (page 223) and from this it is clear that, for these elements, the data do not conform to a partial melting model. The behaviour of Rb, Th, Cr and Ni suggests that their chemical variations cannot be explained by a melting process. The observed variations of the REE, Zr and Nb cannot be used in a definitive way owing to the apparent compatible behaviour of the REE in that their abundances fall with increasing differentiation, the fact that zircon is a mineral phase and the non-covariant behaviour of Nb with most elements.

Note: A rearrangement of the equation of Ferrara and Treuil (1975) can show that the partial melting curve is dependent on the Rb/Th ratio of the initial source. If this source is unknown and it is believed that a successive melt has an identical ratio then this sample may be used to construct the curve.

$$C^L_{RB} = \frac{C^o_{Rb}}{C^o_{Th}} \cdot C^L_{Th} \left[\frac{F}{D_{Rb}+F} \right] \text{ ----- Equation of Ferrara and Treuil (1975)}$$

$$= \left[\frac{D_{Rb} + F}{F} \right]^{-1} K \cdot C^L_{Th} \quad ; \quad K = \frac{C^o_{Rb}}{C^o_{Th}}$$

$$= \left[\frac{D_{Rb}}{F} + 1\right]^{-1} K \cdot C^{L}_{Th}$$

Since $D_{Rb} \;\; \frac{C^{o}_{Rb}}{C^{*}_{Rb}}$ and $F \;\; \frac{C^{Th}_{o}}{C^{Th}_{L}}$; C^{*}_{Rb} is the extrapolated value of Rb at a low F where C^{Rb} does not change greatly.

$$C^{L}_{Rb} = \left[\frac{C^{o}_{Rb} \cdot C^{L}_{Th}}{C^{o}_{Th} \cdot C^{*}_{Rb}} + 1\right]^{-1} K \cdot C^{L}_{Th}$$

$$= \left[K \cdot \frac{C^{L}_{Th}}{C^{*}_{Rb}} + 1\right]^{-1} K \cdot C^{L}_{Th}$$

$$= \left[\frac{C^{*}_{Rb}}{K.C^{L}_{Th} + C^{*}_{Rb}}\right] K.C^{L}_{Th}$$

Thus, if the Rb/Th ratio is constant and the same extrapolated Rb value were used, the partial melting curve remains the same. C_{Rb} varies little at low degrees of partial melting and C^{*}_{Rb} may be considered essentially invariable.

(N.B. The manipulations are those of the author.)

4) <u>Melting of sedimentary material</u>

The melting of typical sedimentary material has often been invoked for the generation of tonalitic-granodioritic-granitic melts (e.g. Winkler, 1967; Alburquerque, 1977). It is unlikely, however, that melting of such material could produce the geochemical characteristics and range of rock types found for the Garnfor group. Approximately total melting of such material (e.g. average shale of Wedepohl, 1971) could possibly reproduce the major element chemistry of the andesitic rocks from Moel-y-Penmaen, although such an extensive amount of melting does not seem reasonable. The trace elements, Zr, Nb, Y and the REE, do not bear any similarity with the data for Wedepohl's average shale shown below. The rare earth patterns for the Garnfor group do not show the high $(Ce/Yb)_N$ ratios expected from the melting of sedimentary material which would probably contain garnet ± amphibole (Arth and Hanson, 1975; Alburquerque, 1977). A detailed discussion of the likely characteristics of granitoids derived from the melting of sediments is given in the preceding chapter (pages 199-202) and it is not necessary to repeat them.

SiO_2	58.9	57.7
TiO_2	0.78	1.39
Al_2O_3	16.7	14.7
Fe_2O_3	6.9	9.6
MnO	0.09	0.26
MgO	2.6	2.78
CaO	2.2	5.00
Na_2O	1.6	3.71
K_2O	3.6	2.8
P_2O_5	0.16	0.74
Rb	140	42
Sr	300	530
Ba	580	722
Zr	160	546
Y	41	61
La	40	52
Ce	95	99
Th	12	4
	(1)	(2)

(1) Average shale (Wedepohl, 1971)

(2) Andesite, Moel-y-Penmaen (this study)

5) Fractional crystallisation from a mafic magma

Fractional crystallisation models assume equilibrium either between the surface of the crystallising phases and the melt or the total solid and the melt. The former model is known as Rayleigh fractionation and it is considered to be applicable to shallow level intrusions where cooling rates are rapid. The observation of graphic textures and zoned feldspars in the

Garnfor group of rocks suggests that they were undergoing crystallisation at relatively high crustal levels and the Rayleigh model will therefore be applied. This model may be expressed by:-

$$\frac{C_L}{C_o} = F^{D-1}$$

where C_L is the element concentrated in the sample
C_o is the element concentrated in the parent melt
D is the bulk distribution coefficient

The very low amounts of Cr and Ni in the Garnfor suite are explicable if there had been significant crystallisation of olivine, orthopyroxene or clinopyroxene. These three minerals have distribution coefficients greater than unity for these elements (chromium is not appreciably partitioned into olivine) and their crystallisation will result in a rapid reduction in the concentration of Cr and Ni. For example, 20 % crystallisation of a mineral assemblage with a bulk distribution coefficient of 4 for Cr will reduce the concentration of that element in the remaining liquid by about half.

The fractional crystallisation curve was determined for Th against Rb using the same bulk distribution coefficients as used for the melting model of section 3.

$$D^{Rb} = \frac{\log C_L^{Rb} - \log C_o^{Rb}}{\log F} \quad \text{where } F = \frac{C_o^{Th}}{C_L^{Th}}, \text{ for elements with } D \ll 1$$

and the equation from Ferrara and Treuil (1975)

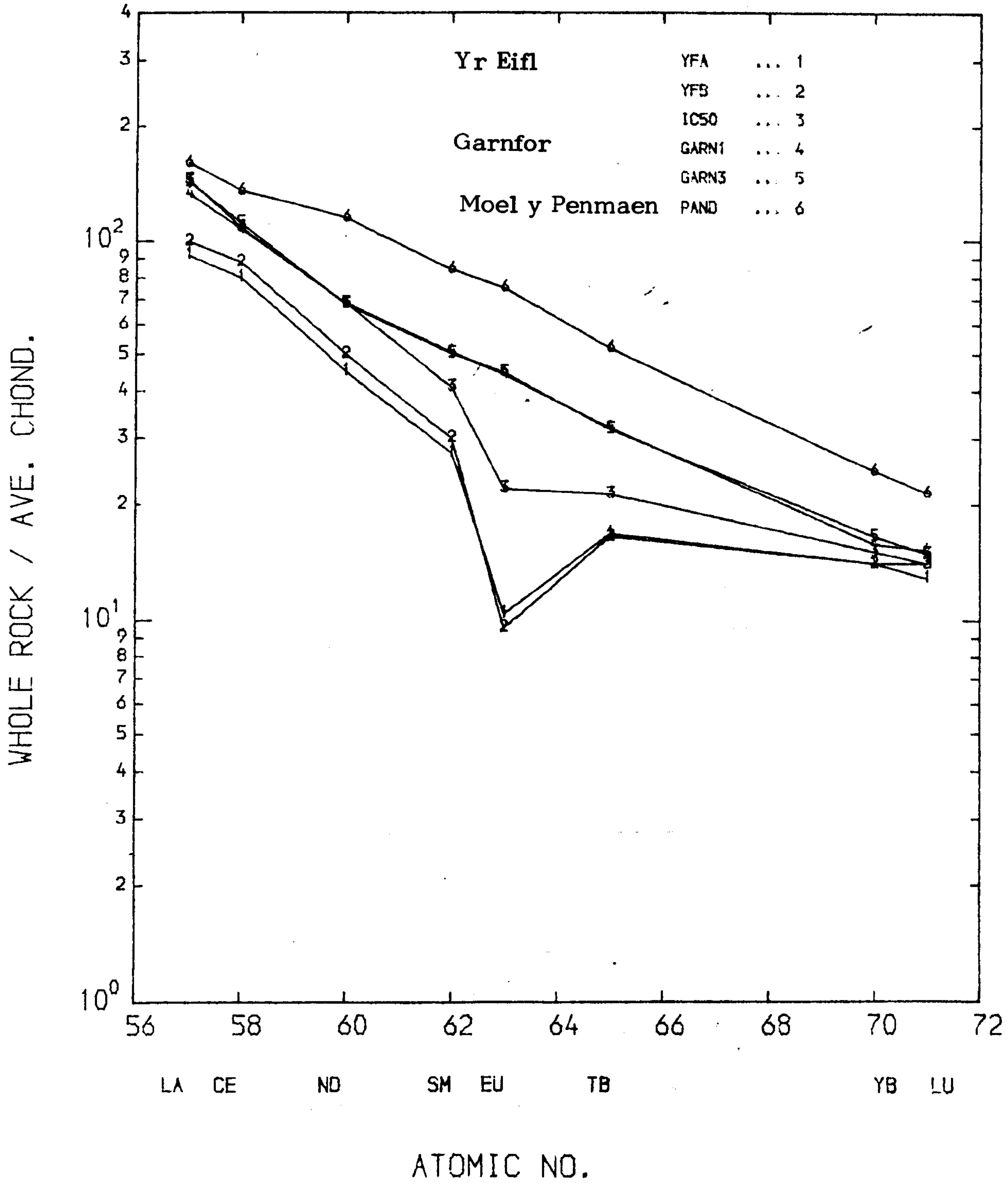
$$C_L^{Rb} = \frac{C_o^{Rb}}{C_o^{Th}} \cdot C_L^{Th} . (F^{D^{Rb}})$$

The calculated curve can be seen to coincide with the observed data for the Garnfor suite (fig. 47 , page 223) and therefore two chemical lines of evidence are found to support a fractional crystallisation model for the suite's evolution.

The rare earth elements and yttrium are particularly useful for solving problems in igneous petrology owing to their slightly different (except Eu) chemical behaviour. These differences are reflected by the preference a particular mineral shows for the REE; garnet, for example, prefers the heavy rare earths, HREE (table 1). The distribution coefficients of the REE in different minerals generally vary significantly and it may be possible to deduce which minerals have been residual or crystallising phases during partial melting or fractional crystallisation. Negative Eu anomalies indicate the involvement of feldspars although the extent of the anomaly is also dependent on the proportion of other mineral phases involved. The pyroxenes, amphibole, garnet and apatite have sizeable distribution coefficients for Eu although they are lower than for the adjacent elements, Sm and Gd. Consequently these minerals will tend to produce liquids with a positive Eu anomaly and if the correct balance of feldspar and one or more of these minerals is achieved during a petrogenetic process the resulting melt will not possess a Eu anomaly. The influence of garnet produces a dramatic effect on REE abundances owing to its large distribution coefficients for the HREE and hornblende involvement may also be detected owing to its relatively higher distribution coefficients for the middle rare earth elements (Arth and Hanson, 1975; Arth et al., 1978).

The abundances and patterns of the rare earth elements and yttrium (fig. 48, page 230) for the Garnfor suite show an unusual feature in that the REE abundances decrease with increasing silica. This observation is not unique, however, since Arth et al. (1978) reported similar findings for a tonalite-trondhjemite suite from S.W. Finland and Pankhurst (1979) found such a relationship in the Foyers and Strontian complexes of Scotland. Such variations indicate that all the rare earth elements are behaving in a compatible fashion with a bulk distribution coefficient greater than unity and this observation is important because hornblende, zircon and apatite are the only minerals which have distribution coefficients for the LREE which are greater than one. The petrology of the Garnfor rocks shows that orthopyroxene (hypersthene), clinopyroxene

Figure 48

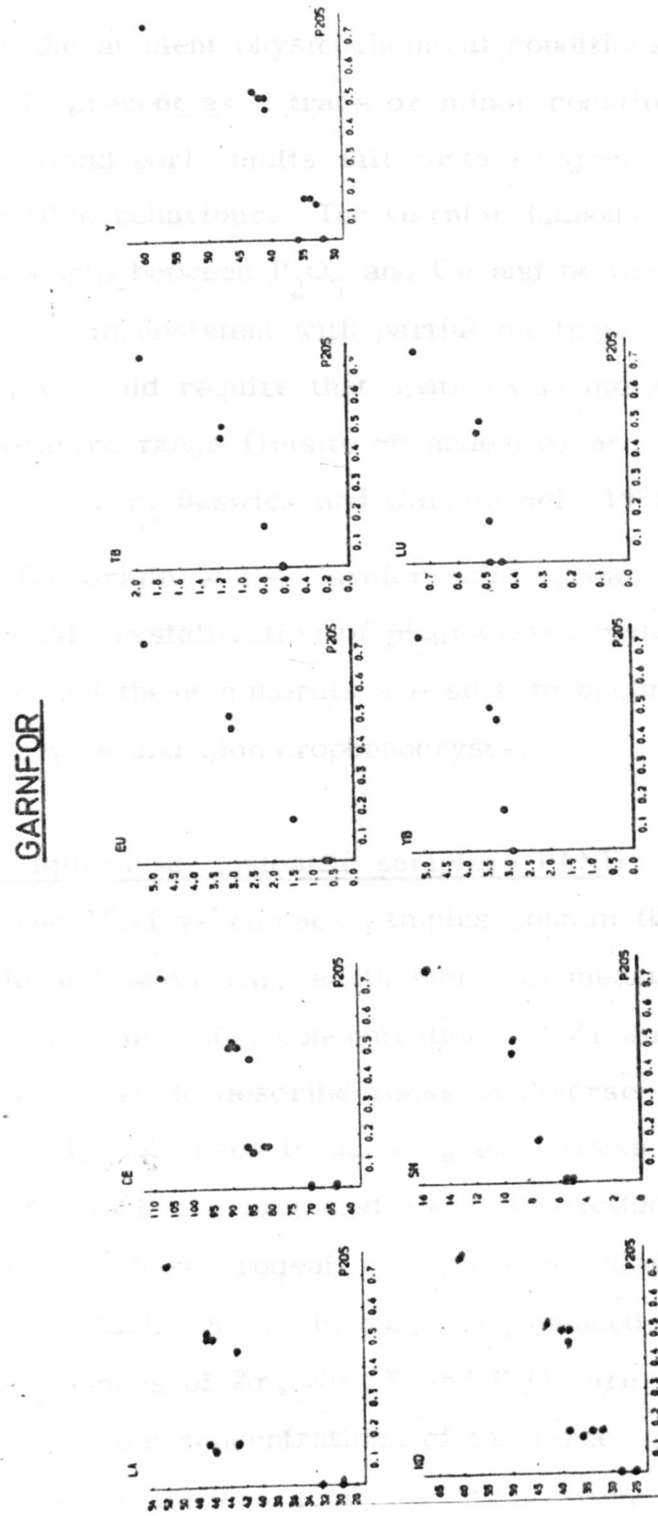

Yr Eifl
YFA ... 1
YFB ... 2
IC50 ... 3
Garnfor
GARN1 ... 4
GARN3 ... 5
Moel y Penmaen
PAND ... 6
WHOLE ROCK / AVE. CHOND.
10^0
10^1
10^2
ATOMIC NO.
56
58
60
62
64
66
68
70
72
LA
CE
ND
SM
EU
TB
YB
LU

(augite), plagioclase, magnetite, apatite, biotite, hornblende, sodic-amphibole, chlorite and K-feldspar are their main constituents. Hornblende, sodic-amphibole, biotite and chlorite, however, are late crystallising or alteration minerals and their influence on the rare earth element abundances is likely to be insignificant. Plagioclase-pyroxene-magnetite clusters with euhedral-subhedral outlines to the constituent minerals occur in the intermediate-acid rocks and plagioclase also occurs by itself in glomeroporphyritic clusters suggesting that these minerals are the main crystallising phases. That hornblende was not significantly involved in the evolution of the Garnfor suite can be demonstrated by the absence of a large increase in the $(Ce/Yb)_N$ and $(Ce/Sm)_N$ with increasing differentiation ($K_{hb}^{Ce} = 1.52$; $K_{hb}^{Yb} = 8$; $K_{hb}^{Sm} = 7.7$). $(Ce/Yb)_N$ increases from 5.5 in sample PAND to 6.3 in sample YFB (table 4) which would permit about 2 % removal of hornblende. Such a small value could not explain the evolution of the series from intermediate to acid compositions.

Removal of mafic phases such as the pyroxenes will account for the compositional evolution of the series although not the REE abundances since the Kd's for Ce in the pyroxenes are less than one and the observed bulk distribution coefficients for Ce are greater than one. The REE and Y show a strong positive correlation with P_2O_5 (fig. 49). This component is mainly accommodated in apatite for most igneous rocks and since this mineral is observed, fractionation of apatite is clearly suggested. The mineral has appreciable distribution coefficients for all the REE and Y although they are larger for the middle rare earths (Nagasawa, 1970) (table 1). The normative apatite content of these rocks varies from nearly 2 % in PAND to about 0.1 % in the felsites and this sizeable range demonstrates that apatite fractionation may have significant importance.

Sun and Hanson (1975) argue that if apatite were a residual phase during partial melting there should be no correlation between the degree of melting, F, and the P_2O_5 content of a melt but there should be a positive correlation between cerium and P_2O_5. However, if apatite is not a residual phase there should be a negative correlation between

Figure 49



P_2O_5 v. REE plots for the Garnfor Suite.

The strong positive correlations suggest that apatite fractionation controls the REE abundances.

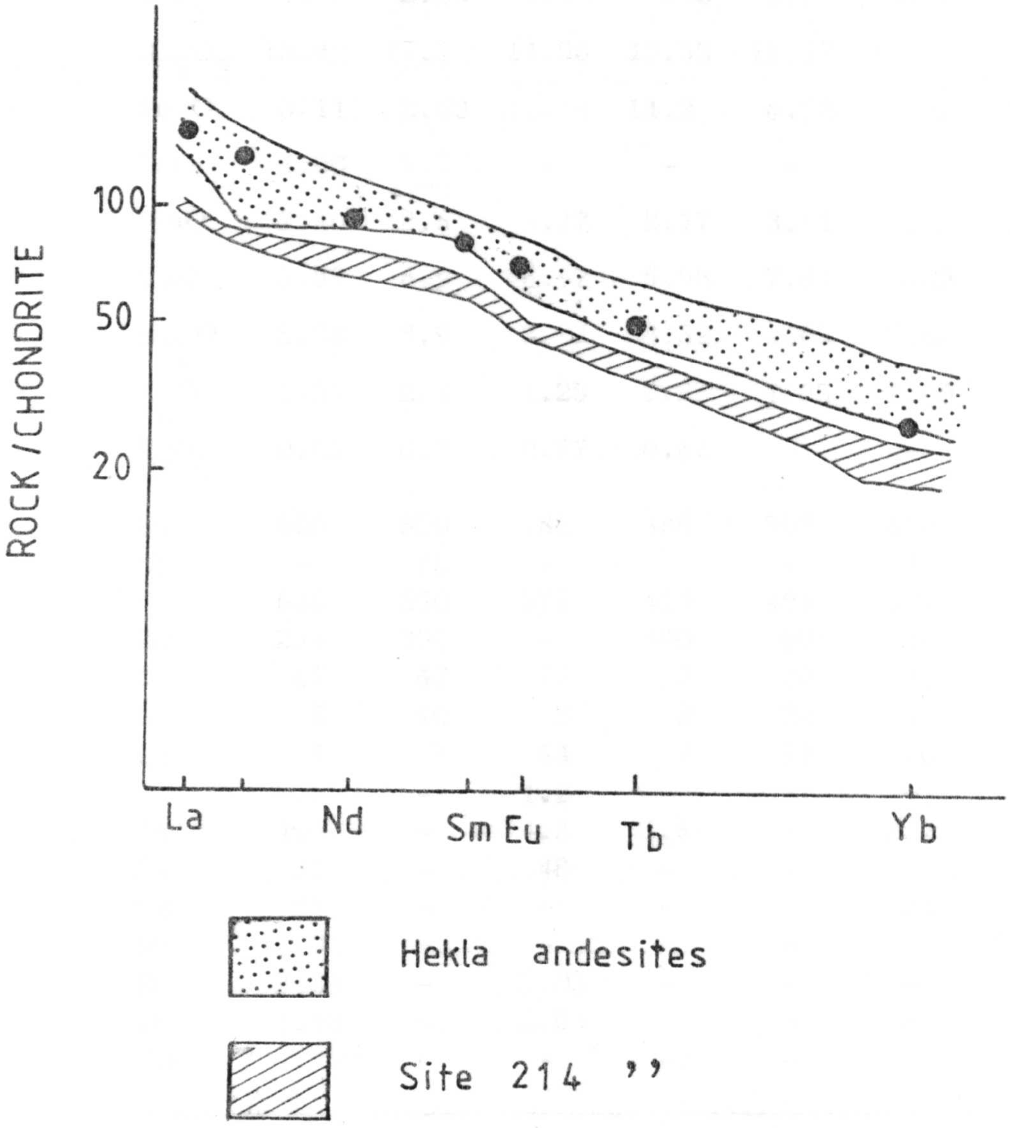
P_2O_5 and F, degree of melting, and a positive correlation between Ce and P_2O_5. In the former case P_2O_5 is a stoichiometric constituent of apatite and therefore enters the melt according to the stability of apatite under the ambient physicochemical conditions while in the latter case P_2O_5 is present as a trace or minor constituent in non-phosphate mineral lattices and early melts will contain higher abundances owing to its incompatible behaviour. The Garnfor igneous suite displays a positive relationship between P_2O_5 and Ce and between P_2O_5 and F (1/Th) and these facts are inconsistent with partial melting. For a partial melting model to apply would require that apatite was melted progressively over a wide temperature range (felsite — andesite) and this would seem to be unlikely (see however, Beswick and Carmichael, 1978).

The origin of the Garnfor suite appears to be best explained by fractional crystallisation of plagioclase, ortho- and clinopyroxenes and apatite and these minerals are seen to occur as euhedral-subhedral phenocrysts and glomerophenocrysts.

The origin of the andesitic samples - PAND

The Moel-y-Penmaen samples contain the highest abundances of the middle and heavy rare earth elements measured for the Garnfor suite and contain high concentrations of Zr and Nb. The term andesite has been used to describe rocks of diverse origin although currently the term is largely used to name igneous rocks with a silica content between 52-62 % which are produced above subduction zones. The chemical features of these orogenic andesites are distinctly different from those of PAND (table 8). In magmas produced above a subduction zone the abundances of Zr, Nb, Y and P_2O_5 are commonly depleted significantly relative to the concentrations of the large ion lithophile elements; LREE, Th, Rb etc (Saunders et al., 1980; Tarney et al., 1980). This important feature of orogenic magmatism is absent in the samples PAND and its origin is thus unlikely to be related to subduction (see pages 186-194) for a fuller discussion of subduction zone magma characteristics).

Figure 50



The data for Hekla volcano and Site 214 are taken from Thompson et al. (1974). The analysis for Moel-y-Penmaen is the author's.

Table 8

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
SiO_2	55.7	52.1	54.25	54.4	55.54	59.5	57.7
TiO_2	1.40	2.30	2.17	1.95	0.89	0.70	1.39
Al_2O_3	15.4	17.1	14.56	15.55	18.17	17.2	14.7
Fe_2O_3	3.11	2.00	11.54	11.2	8.73	6.10	9.62
FeO	4.00	8.7	-	-	-	-	-
MgO	2.40	2.6	3.17	2.17	3.81	3.42	2.78
CaO	5.59	6.9	6.97	5.98	7.41	7.03	5.00
Na_2O	3.88	4.9	3.97	4.32	4.63	3.68	3.71
K_2O	1.55	2.4	1.25	2.25	1.25	1.60	2.8
P_2O_5	0.63	0.7	0.77	0.65	-	-	0.74
Ba	600	800	482	480	508	270	730
Rb	-	10	-		-	31	42
Sr	625	650	379	419	491	385	530
Zr	255	390	-	490	99	110	546
Y	67	47	73	52	20	21	60
Ni	5	10	5	2	22	18	5
Cr	5	8	54	7	11	56	5
U	0.6	-	1.2	-	-	-	-
Th	4.5	-	4.3	5.8	-	2.2	4
La	31	-	48	-	-	-	52
Ce	85	-	-	-	-	24	107
Sm	10.9	-	-	-	-	-	15.6
Eu	3.35	-	5.03	-	-	-	5.18
Tb	1.98	-	2.04	-	-	-	2.44
Yb	4.85	-	-	-	-	-	5.12

(1) Site 214 - oceanic andesite; Thompson et al. (1974).

(2) Reunion Island - from Upton and Wadsworth (1972); Thompson et al. (1974).

(3) Hekla andesite - Wood et al. (1979).

(4) Bouvet Island - Mugearite; Verwoed et al. (1976).

(5) Andean andesite - Dostal et al. (1977).

(6) Circum-Pacific andesites; Taylor (1969).

(7) PAND - Moel-y-Penmaen (this study).

Comparisons with PAND may be found in a number of oceanic areas where rocks of similar composition are described as mugearites (Baker, 1976), oceanic andesites (Thompson et al., 1974) and intermediate differentiated rocks. The mugearites described by Baker are considered to be formed by crystal fractionation from a mildly alkalic or transitional basalt (T-type ocean floor basalt). Thompson et al. (1974) found basalts and oceanic andesites, collected from the Indian Ocean, to be genetically related and they suggested that the rocks were related by crystal fractionation. The oceanic andesites were also compared with andesitic rocks from Hekla volcano, Iceland and a similar evolution has been proposed for these by Jakobsson (1972). He favoured fractionation from transitional Icelandic tholeiites. Table 8 shows that the Moel-y-Penmaen andesites have the characteristics of andesitic rocks generated in oceanic areas.

The low abundances of Cr and Ni and the high concentrations of Zr, Nb, Y, P_2O_5 and the REE are not inconsistent with an origin for the andesitic rock by crystal fractionation. The close similarity of PAND with oceanic andesites, which have a relationship with transitional-type basalts, suggests that PAND was derived from such basalts. It has been suggested that the basaltic rocks of Snowdonia bear a resemblance to T-type (transitional) tholeiites and with this evidence an origin from such rocks is clearly acceptable. Since no samples of basaltic rocks from the Lleyn Peninsula were collected it is not possible to consider detailed models for the origin of PAND although by using data for T-type tholeiites from other sources it is feasible to estimate the degree of crystallisation which must have occurred to produce PAND. Wood et al. (1980) give a T-type tholeiite from the Reykjanes ridge with a Th content of 0.6 ppm and from $C_o/C_L = F$ it can be shown that PAND (Th = 4 ppm ± 1 ppm) could be derived from such a magma after about 80 % crystal removal. The Indian Ocean andesitic rocks seem to be produced by a similar amount of crystal extraction if the elements U, Th and La are used to estimate F (table 8 , page 235)

The recognition that the intrusive suite of Garnfor is related to the Ordovician volcanic rock from Moel-y-Penmaen is important for two reasons. Firstly, it demonstrates the probability that the intrusives have an Ordovician age (Caradoc ?) which is contrary to Tremlett's proposals (1962, 1964, 1972) and secondly, it shows that the suite's geochemistry can be explained by crystal fractionation from a basaltic magma.

Petrogenetic modelling for Garnfor suite

The mineralogy of the Garnfor suite shows that orthopyroxene, clinopyroxene, plagioclase and apatite are phenocryst phases and it is therefore possible to model the origin of each intrusion. Since PAND are the most basic samples collected these are used as the parental magma from which the successive melts were derived. The distribution coefficient data used are those of Arth and Hanson's (1975) which they obtained from various sources but because mineral distribution coefficients are scarce for intermediate rocks the data used are those for rhyolitic compositions. The procedure used for determining the proportions of minerals fractionating from PAND is similar to that used by Allegre et al. (1977) and both studies use matrix inversion techniques.

Method

1) Calculate F from $C_o/C_L \simeq F$ for elements with $D \ll 1$. Thorium is used in this study.

2) Calculate the bulk distribution coefficient for each sample.

$$D = 1 + \frac{\log C_L - \log C_o}{\log F}$$

where C_L is the concentration of an element in a sample
C_o is the concentration of an element in parent
F is the proportion of melt

3) Calculate n simultaneous equations for n crystallising minerals.

i) $aKd_1 + bKd_1 + cKd_1 + dKd_1 = D_1$
ii) $aK_2 + bKd_2 + cKd_2 + dKd_2 = D_2$
iii) $aK_3 + bKd_3 + cKd_3 + dKd_3 = D_3$
$\vdots \quad \vdots \quad \vdots \quad \vdots$
n) $aKd_n + bKd_n + cKd_n + dKd_n = D_n$

where D is the bulk distribution coefficient
a is the proportion of phase 1 extracted
b " " " " " 2 "
c " " " " " 3 "
d " " " " " 4 "
Kd_1 is the distribution coefficient for element 1 in phase a, b, c or d
Kd_2 is the distribution coefficient for element 2 in phase a, b, c or d
$\vdots \quad \vdots$
Kd_n is the distribution coefficient for element n in phase a, b, c or d
D_1 is the bulk distribution coefficient for element 1

4) The above formalism may be expressed in matrix notation,

$$[A] \cdot [X] = [B]$$

where A is a matrix of distribution coefficient data (square matrix)
B is a column vector containing the bulk distribution coefficients (D_1, D_2, D_3, D_4)
X is a column vector containing the unknowns or mineral proportions

5) The solutions of the equations are found by inverting the A matrix and multiplying it by the B matrix.

$$[A]^{-1} \cdot [B] = [X]$$

Matrix inversion is satisfied when $[A] \cdot [A]^{-1} = [I]$

I is an identity matrix with the same dimensions as $[A]$ and with all of its diagonal elements equal to zero.

Not all matrices are amenable to inversion because at some stage of the calculations division by zero occurs; such a matrix is called singular.

Initial attempts at solving the equations failed and it became apparent that this was due to the distribution coefficients used for apatite. The literature data for apatite show that the middle rare earth elements are more strongly partitioned into the mineral than are the light and heavy rare earths. When the distribution coefficients for the middle rare earths were reduced to values of about 36, compared with the literature values of about 60 for Sm and Gd, it was found that solutions were obtained, viz. Σ(mineral proportion) $\simeq$ 1. A comparison plot of apatite distribution coefficients is shown in fig. 50 (page 242). Although apatite is a minor mineral phase, its distribution coefficients are so large that its contribution to the bulk distribution coefficient exceeds the contribution from other minerals and the models are therefore sensitive to the distribution coefficients used for apatite. For this reason the mineral proportions obtained from the modelling are estimates and small variations in the distribution coefficients of apatite in particular may significantly modify the proportions of minerals predicted to have fractionated to form the Garnfor Complex.

The limitations associated with such modelling are appreciated and further studies on the chemistry of the phenocryst phases (e.g. microprobe analyses) would assist in constraining the system more adequately. The error sources for the models are derived from:-

a) Analytical errors associated with the trace element determinations, especially thorium.
b) Sampling errors. Do the samples represent liquid compositions? Allegre et al. (1977).
c) The use of a set of distribution coefficient data for rhyolitic rocks.
d) The apatite distribution coefficients used.
e) The use of a single set of distribution coefficient data for andesitic-rhyolitic compositions.

In view of the relatively smooth inter-element curves and element-Th plots, error sources (a) and (b) are considered to be less significant than those of (c), (d) or (e).

Table 9

Results of modelling calculations for Garnfor Suite

Bulk Distribution Coefficients calculated from: $D = \frac{\log C_L - \log C_o}{\log F} + 1$

$(D^{AP}_{Sm} \simeq 37; \quad D^{AP}_{TB} \simeq 37)$

	Yr Eifl Felsite	Garnfor (IC50)	Garnfor (Garn 3)	Garnfor (Garn 1)
Ce	1.29	1.16	1.43	1.33
Sm	1.71	1.61	1.94	1.73
Eu	2.42	2.05	1.92	1.77
Tb	1.79	1.76	1.88	1.69
Yb	1.39	1.42	1.86	1.69
F	.23	.31	.57	.50

Mineral proportions removed from PAND and recast to 100 %

	Yr Eifl Felsite	Garnfor (IC50)	Garnfor (Garn 3)	Garnfor (Garn 1)
Orthopyroxene	13	27	53	36
Clinopyroxene	37	37	28	45
Plagioclase	45	31	15	15
Apatite	2.76	2.5	3	3

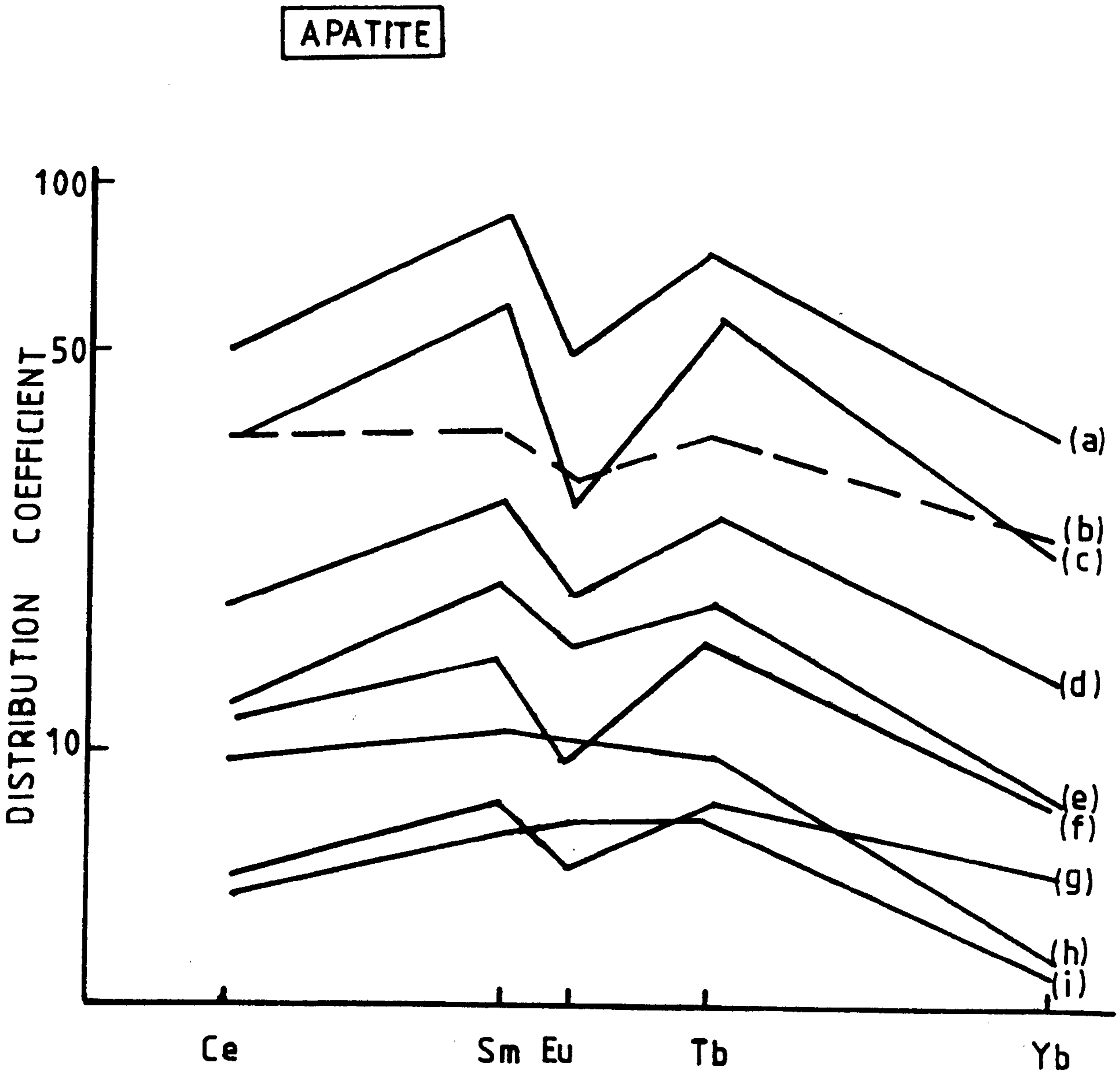
The use of distribution coefficients for rhyolitic rocks

Most trace element modelling studies in the literature use the distribution coefficient data shown in table 1 (page 48) which were taken from Arth (1976). The values are often no more than the average of three determinations and some uncertainty in their magnitude must exist. The review of published data by Irving (1978) has shown, however, that for some minerals there is a notable consistency in the pattern and size of distribution coefficients, at certain compositions, for determinations made on natural and synthetic samples. The literature reveals that data for intermediate rocks are scarce and clearly, considerable differences exist between the data for basaltic and rhyolitic compositions (table 1 , page 48). In view of the sizeable bulk distribution coefficients that were calculated for the Garnfor group it seems to be justified to use the distribution coefficient data for rhyolitic rocks. The use of a set of basalt/andesite data would require the involvement of a greater proportion of apatite than is found to be petrographically acceptable.

Apatite distribution coefficients

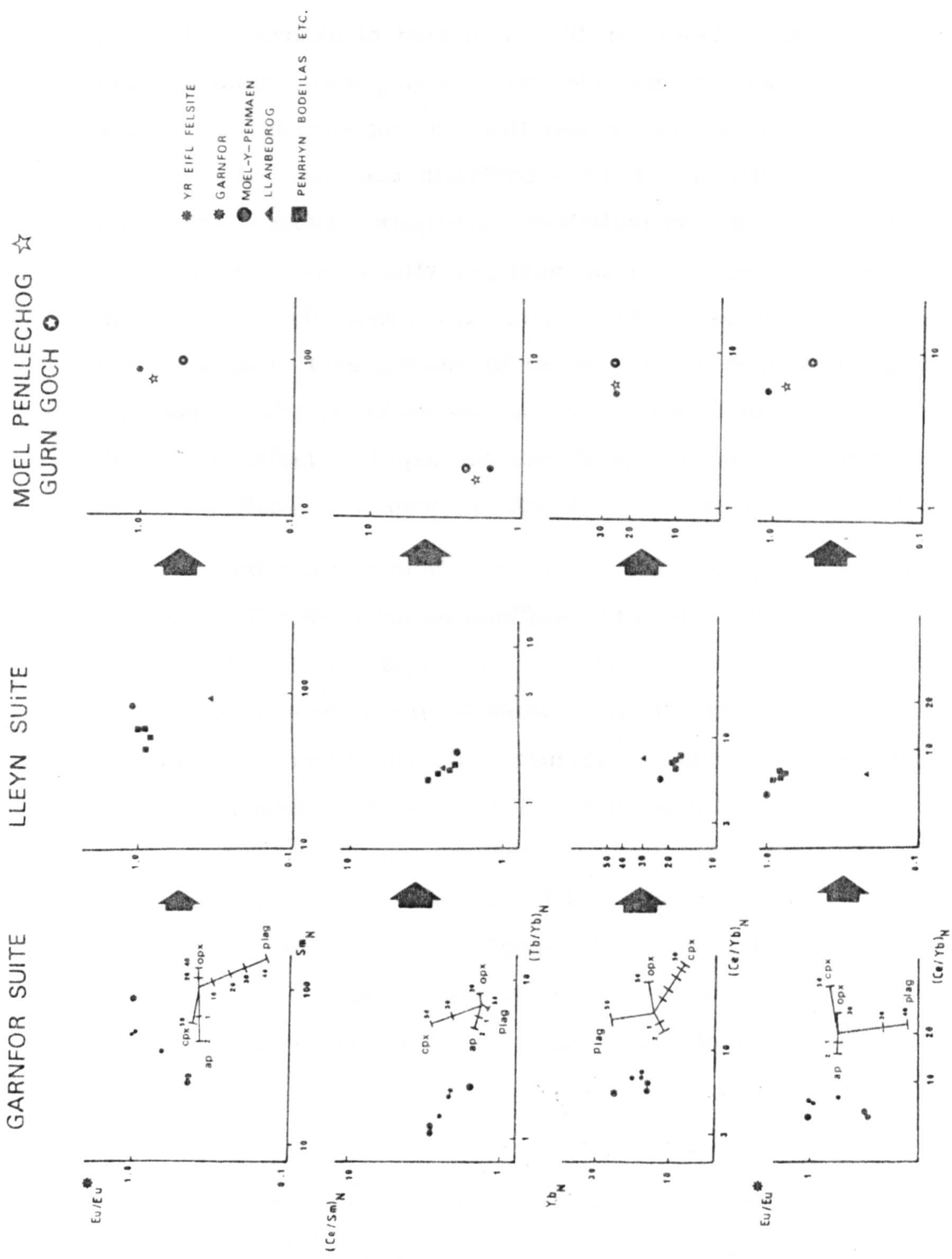
A literature search for apatite distribution coefficients revealed eight sets of data and these are shown plotted in fig. 50 (page 242). It is apparent that a considerable range of values exists, even for a narrow composition range, and that the form of the patterns is closely similar. A consistent feature is the higher distribution coefficients for the middle rare earths compared with those for the light and heavy rare earths. The predicted pattern, obtained from the modelling calculations, for the Garnfor Suite does not show greatly different values for the light and middle rare earths ($K^{Ce}_{Apatite} = 35$; $K^{Sm}_{Apatite} = 37$) although the magnitude of the predicted data do not seem unreasonable when compared with the literature values. The predicted Garnfor apatite pattern is controlled to some extent by the rare earth content determined in the samples and the distribution coefficients used for the other fractionating mineral phases. Adjustments to either of these could produce an apatite pattern more closely similar to those of the literature.

Figure 50



(a), (c) and (d) Dacites, Nagasawa (1970).
(e) and (g) Phonolite, Sun and Hanson (1976).
(f) Skaergaard, UZb; Paster et al. (1974).
(h) Basalt, Irving (1978).
(i) Norite, Roelands and Duchesne (1979).
(b) Calculated REE distribution coefficients for the Lleyn and Garnfor Suites (this study).

Figure 51



Various rare earth parameters are plotted on a log-log scale for the three granitoid suites from the Lleyn Peninsula. Fractional crystallisation vectors, calculated using the distribution coefficients of table 1 (except apatite where $D^{ap}_{Sm} = 40$), are also shown.

The use of a single set of distribution coefficients

It is well known that distribution coefficients vary according to physical and chemical changes (Ryerson and Hess, 1978) and these generally increase in magnitude with polymerisation of the melt. As the melt becomes more-polymerised, element species, particularly those with a high charge density, will tend to be excluded from the melt and consequently their bulk distribution coefficient will increase in size. For these reasons petrogenetic modelling of a suite of rocks with a wide composition range ideally requires the use of two or more sets of distribution coefficient data. In view of the absence of such data it is not possible to take account of the possibly changing distribution coefficients. The smoothly varying chemistry of the suite suggests however, that if the effect is important the changes must vary continuously rather than in a stepwise manner as found by Allegre et al. (1977).

Crystal fractionation vectors are calculated and plotted along with the data. The distribution coefficients for rhyolitic rocks were used for all calculations (fig. 51 , page 243). These diagrams are a particularly useful way of determining the influence of minerals during fractionation processes. For example the plot of Eu/Eu* .v. Sm_N shows that plagioclase is subordinate to pyroxene fractionation for the samples Garn 3 and Garn 1 which possess a Eu/Eu* ratio of approximately one. The proposed parental magma, PAND, also has a ratio of approximately unity. The data of table 9 (page 240) show that the modal proportions of plagioclase and pyroxenes which are removed, producing a melt with a composition corresponding to Garn 1 and Garn 2, are 15 % and 81 % respectively.

B. Discussion for Lleyn Intrusives (excluding the Garnfor Suite)

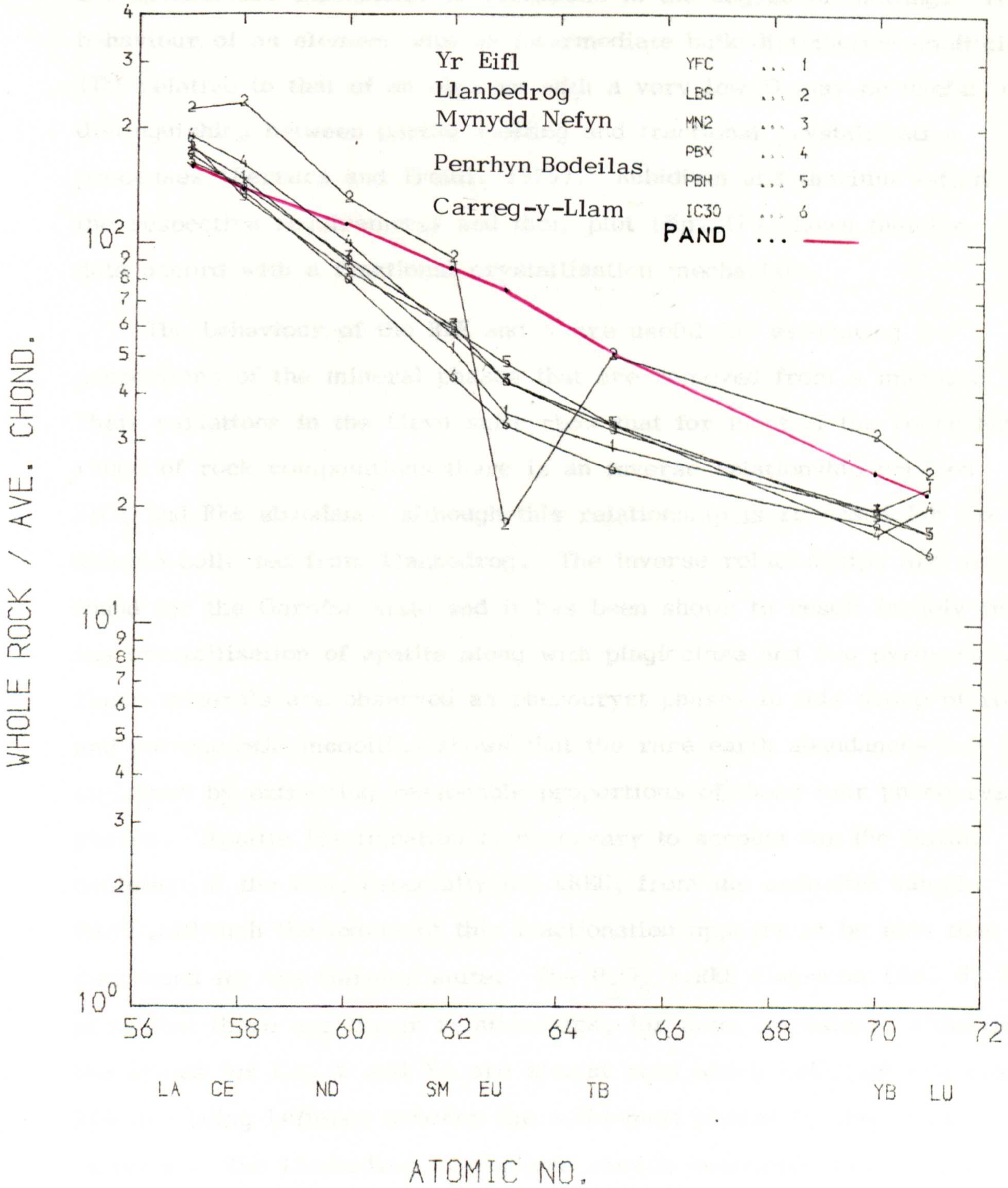
This group of intrusions consists of the earlier granodiorite suite (Tremlett, 1962; Roberts, 1979) which includes Penrhyn Bodeilas, Carreg-y-Llam, Nant, Pistyl and Mynydd Nefyn along with the granitic rocks of Yr Eifl and Llanbedrog. The Harker diagrams (fig. 43) show that most variations are smooth although there is a sharp increase in abundance of Y and the HREE at about 68 % SiO_2. This group appears to be related to the andesitic rock PAND although the chemical variations of the two suites are sufficiently different to suggest that their evolutionary histories are different in detail. The differences are enumerated below:-

1) P_2O_5 is depleted more rapidly with increasing silica than in the Garnfor group.
2) CaO and Sr are depleted more rapidly at first than in the Garnfor suite.
3) TiO_2 is depleted more rapidly in the Lleyn group.
4) Zr increases to a maximum at 62 % SiO_2 and is followed by a rapid decline suggesting zircon crystallisation whereas Zr abundances remain nearly constant in the Garnfor suite up to 68 % SiO_2 whereupon they fall.
5) Nb concentrations vary smoothly in the Lleyn suite rising to 54 ppm and then declining to 40 ppm. The variation in the Garnfor suites shows a fall initially and then Nb rises to about 45 ppm.
6) The rare earth elements and Y are less depleted at a comparable SiO_2 level than in the Garnfor suite.

The evolution of the Lleyn group of intrusions can be explained in a similar manner to that described for Garnfor. The differences in abundances of some elements may be accounted for by the different times at which mineral phases appeared and this could have been controlled by P, T, fO_2 and pH_2O. A closed-system fractional crystallisation model is proposed for the evolution of this suite although it is evident that the Garnfor and Lleyn suites did not share the same magma chamber.

The evidence for a fractional crystallisation origin for this group is similar to that cited for the Garnfor suite. The very low abundances of chromium and nickel for a suite with a broad composition range are more adequately accounted for by crystal fractionation than by a

Figure 52


Yr Eifl YFC ... 1
Llanbedrog LBG ... 2
Mynydd Nefyn MN2 ... 3
Penrhyn Bodeilas PBX ... 4
PBH ... 5
Carreg-y-Llam IC30 ... 6
PAND ...
WHOLE ROCK / AVE. CHOND.
10^0
10^1
10^2
ATOMIC NO.
56
58
60
62
64
66
68
70
72
LA
CE
ND
SM
EU
TB
YB
LU

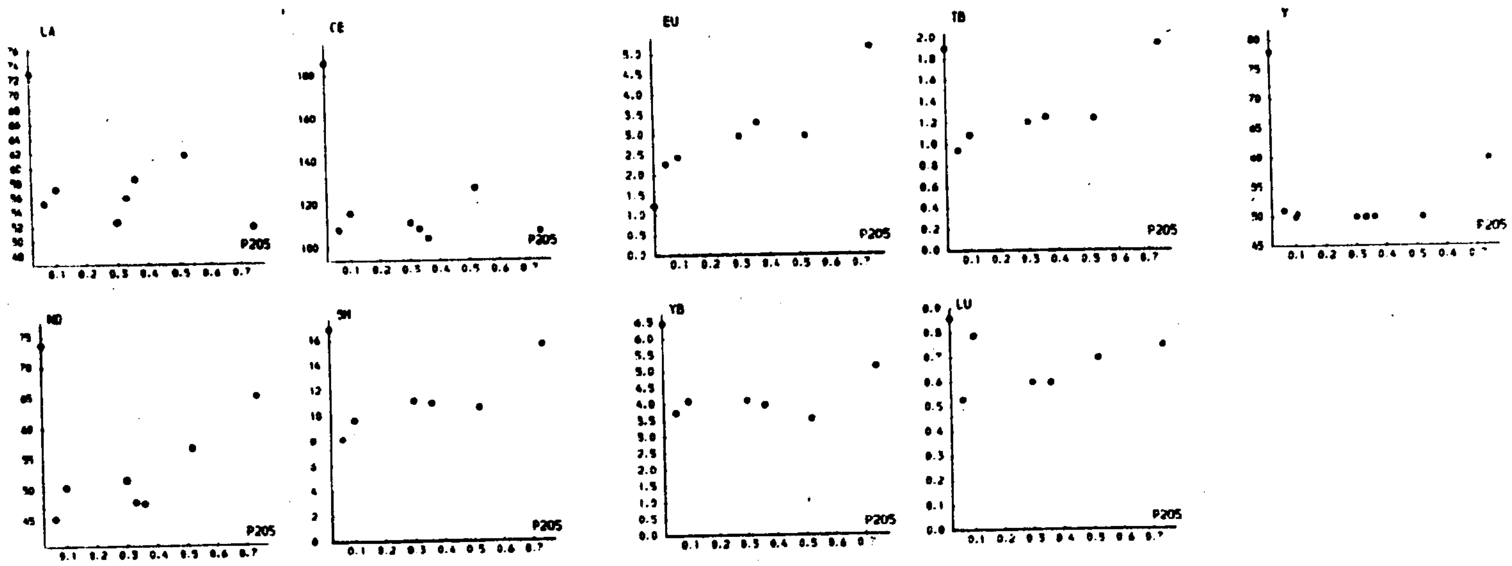
mechanism such as partial melting. Minster and Allegre (1978) have outlined the behaviour of trace elements during the evolutionary processes of igneous suites and they state that elements with high bulk distribution coefficients are insensitive to variations in the degree of melting. The behaviour of an element with an intermediate bulk distribution coefficient (D) relative to that of an element with a very low D may be useful in distinguishing between partial melting and fractional crystallisation processes (Ferrara and Treuil, 1975). Rubidium and thorium satisfy the respective requirements and their plot (fig. 47) shows that the data accord with a fractional crystallisation mechanism.

The behaviour of the REE and Y are useful for estimating the proportions of the mineral phases that are removed from a magma. Their variations in the Lleyn suite show that for most of the represented range of rock compositions there is an inverse relationship between SiO_2 and REE abundance although this relationship is reversed for the sample collected from Llanbedrog. The inverse relationships are also found for the Garnfor suite and it has been shown to result largely from the crystallisation of apatite along with plagioclase and two pyroxenes. These minerals are observed as phenocryst phases in this group of rocks and petrogenetic modelling shows that the rare earth abundances can be explained by extracting reasonable proportions of these four phenocryst phases. Apatite fractionation is necessary to account for the initial depletion of the REE, especially the LREE, from the andesitic sample PAND, although the extent of this fractionation appears to be less than that found for the Garnfor suite. The P_2O_5.v.REE diagrams (fig. 53) show that there are linear relationships, for most intrusions, although the slopes for Ce, Y and Yb are almost zero which indicates that the REE are being buffered between the solid-melt phases by the crystallising minerals. The Llanbedrog granophyre sample commonly lies off the linear trends and this is considered to result from a change in the proportion of crystallising phases.

The bulk distribution coefficients are calculated for the Lleyn samples using the same procedure outlined in the discussion of the

Figure 53

LLEYN



P_2O_5 (wt. %) v. REE (p.p.m.) plots for the Lleyn granitoids.
The good correlations suggest that apatite is controlling REE abundances.

Garnfor suite and the modelling scheme involving matrix inversion was carried out. The literature distribution coefficients for the middle rare earth elements in apatite were found to be too large to afford solutions to the simultaneous equations and by reducing the distribution coefficients for Sm and Tb to 40, it is possible to obtain reasonable solutions. The results of the modelling are shown in table 10 and the diminished importance of apatite may be seen from the lower bulk distribution coefficients compared with the Garnfor suite.

The fact that the Llanbedrog sample lies on most element-element plots suggests that it is a member of the fractionation sequence. Its chemistry is not dissimilar to the Yr Eifl felsites apart from its greater abundances of the REE, Y and Sr. All of these elements can be readily accommodated in apatite and if crystallisation of this mineral ceased or was reduced then Y, Sr and the REE would begin to increase in the residual liquids.

The influence of the four minerals on the various rare earth element parameters are shown as vectors in fig. 51 (page 243). For example, the log-log plot of Eu/Eu* against $(Ce/Yb)_N$ shows that the granodioritic samples may be derived from PAND along a path which lies between the vectors for plagioclase and ortho- and clino-pyroxene. Since apatite causes a reduction in $(Ce/Yb)_N$ but little change in the Eu anomaly its influence is masked by that of the pyroxenes and plagioclase and it serves to limit the change in $(Ce/Yb)_N$ which is caused by the removal of the pyroxenes. The change of direction of the trend from the granodiorites to the Llanbedrog granophyre is easily seen to be largely a result of plagioclase removal.

C. Discussion for Moel Penllechog, Gurn Ddu and Gurn Goch

These intrusions outcrop in northern Lleyn along the coast. The intrusions of Moel Penllechog and Gurn Ddu are granodioritic while Gurn Goch is a porphyritic granophyre. They possess the geochemical characteristics of the Garnfor suite such as high Zr and Nb concentrations but a number of features seem to be unusual. These features may be

Table 10

Results of modelling calculations for Lleyn Suite

Bulk Distribution Coefficients calculated from: $D = 1 + \dfrac{\log C_L - \log C_o}{\log F}$

$(K^{Sm}_{apatite} \simeq 40 \; ; \quad K^{Tb}_{apatite} \simeq 40)$

	Penrhyn Bodeilas	Mynydd Nefyn	Yr Eifl microgranite	Carreg-y-Llam	Llanbedrog
Ce	1.05	0.95	0.92	0.99	0.65
Sm	1.63	1.49	1.69	1.93	0.95
Eu	1.80	1.80	2.08	2.17	1.92
Tb	1.78	1.69	1.84	2.03	1.02
Yb	1.45	1.32	1.32	1.45	0.85
Melt remaining	0.57	0.5	0.36	0.33	0.21

Proportion of mineral phases removed (%)

e.g. If F = 0.57, then 43% of minerals have been removed.

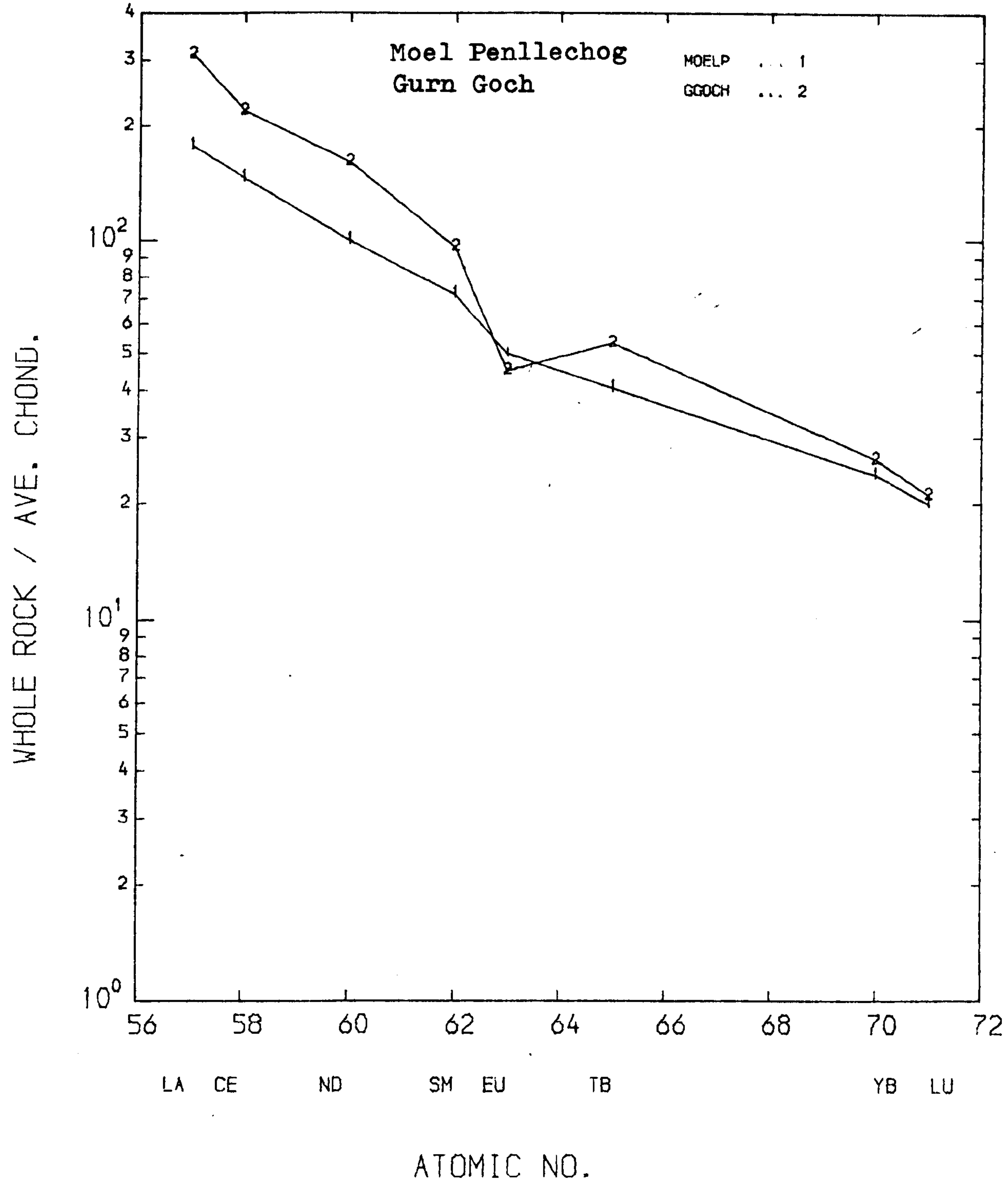
The proportions shown below represent fractions recast to 100%.

	Penrhyn Bodeilas	Mynydd Nefyn	Yr Eifl microgranite	Carreg-y-Llam	Llanbedrog
Orthopyroxene	35	32	35	30	21
Clinopyroxene	41	38	33	36	27
Plagioclase	23	29	30	32	54
Apatite	2	1.8	1.8	1.8	1.0

seen on the Harker diagrams (figs 43 - 46) and they include lower alumina and soda and higher MnO, Y, Rb, Th, Ba and REE. That the hygromagmatophile elements Th, Rb (and Ba) are more concentrated in these samples relative to the other intrusions may suggest that some other mechanism has operated during the evolution of this group of rocks. Assuming that the bulk distribution coefficients for Th and Rb are low and about the same value as that for the earlier discussed Lleyn groups then the abundances of the elements at equivalent SiO_2 should be the same if closed system fractional crystallisation were the operative mechanism. Since the sample population for this group is very small it would be presumptuous to propose a detailed petrogenetic scheme but it is possible to make a number of proposals.

Fractional crystallisation seems a likely mechanism since the abundance of Ni and Cr are below the detection limit for the method of analysis and the similarities in chemistry with the other Lleyn groups also lend support to this view. How the Th and Rb contents come to have higher values does require a special explanation. One means would be by way of open-system fractionation whereby a magma chamber is refilled after it has undergone some crystal fractionation. O'Hara (1977) provided a formulation for open-system fractional crystallisation which is useful but poorly constrained. The importance of the model is that it shows that the concentration of elements with $D<1$ can become considerably more enriched, and element with $D>1$ can become more depleted than would be possible via closed-system fractionation. The model is poorly constrained because the modeller has to provide values for the amount of crystallisation, the amount of magma erupted after this crystallisation and the amount of new magma input. This type of model has been used by Stern (1979) among others for the evolution of the Sarmiento and the Tortuga complexes of southern Chile. Owing to the small number of samples and because of the poor constraint of the model no attempt will be made to model since a large number of solutions could be obtained.

Figure 54


Moel Penllechog
Gurn Goch
MOELP ... 1
GGOCH ... 2
WHOLE ROCK / AVE. CHOND.
4
3
2
10²
9
8
7
6
5
4
3
2
10¹
9
8
7
6
5
4
3
2
10⁰
56
58
60
62
64
66
68
70
72
LA
CE
ND
SM
EU
TB
YB
LU
ATOMIC NO.

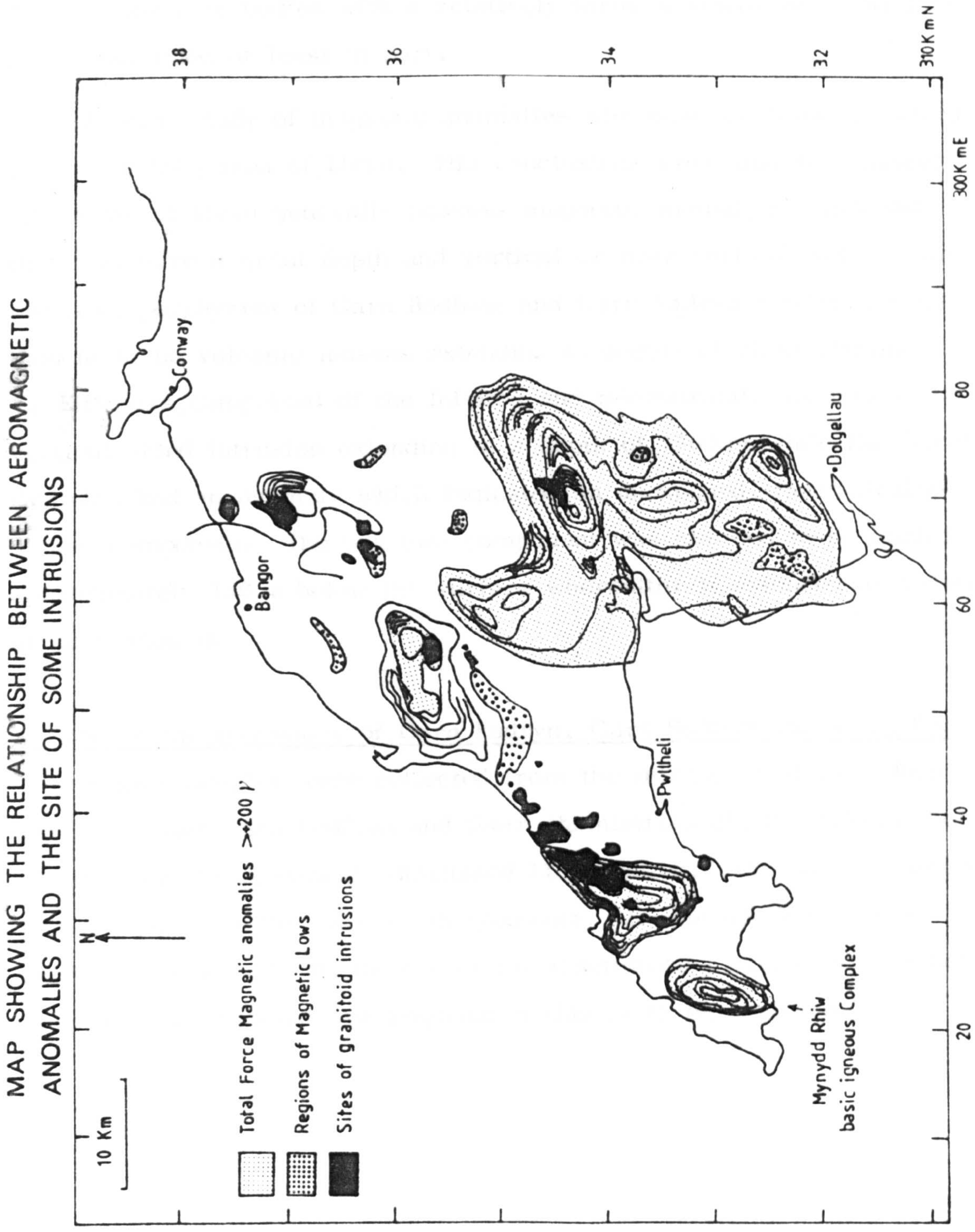
The two samples, Moel Penlechog and Gurn Goch, analysed for the REE, are plotted along with the fractional crystallisation vectors (fig. 51 , page 243). The main point of these diagrams is that Gurn Goch is probably derived from Moel Penllechog by way of plagioclase crystallisation. Eu/Eu* falls from 0.81 to 0.55 (Moel P — G Goch) and since K and Rb do not show any decrease in abundance it rules out any significant K-feldspar crystallisation. The influence of apatite and clinopyroxene crystallisation may be seen from the Eu/Eu* v Sm_N and $(Ce/Sm)_N$ v $(Tb/Yb)_N$ plots.

D. Geophysical Note

The arguments presented in the earlier sections have shown that there is good geochemical evidence to support a fractional crystallisation origin for the Lleyn granitoids. Analogues with the Lleyn suites have been identified from the Indian Ocean (Thompson et al., 1974) and Iceland (Jackobson, 1972) where the parental magma is claimed to be a tholeiitic basalt with the characteristics of T-type mid-ocean ridge basalt (Wood et al., 1980; Saunders et al., 1980). In view of these findings and the recognition of similar basalts in Snowdonia (sample PYG this study and G.L. Hendry, personal communication, 1980) it is felt that such a basaltic magma was parental to the Lleyn suites. It is unlikely that the silicic members of a fractional crystallisation sequence which formed from a basaltic parent represent greater than 10 % of the original volume of magma (O'Nions and Grönvold, 1973; Carmichael et al., 1974, p. 485). For this reason it is clear that a basic body, rich in mafic cumulates (pyroxenes, magnetite etc.), must be present in the Lleyn area and it must be of considerable size in order to account for the observed proportion of exposed silicic rocks.

The results of the aeromagnetic survey of the British Isles (Stubblefield, 1965) provides good supporting evidence for the notion that basic bodies underly areas of North Wales. A simplified form of the map is shown in fig. 55 (page 254). It may be seen that there is a remarkable correspondence between the sites of various intrusions or suites and

Figure 55



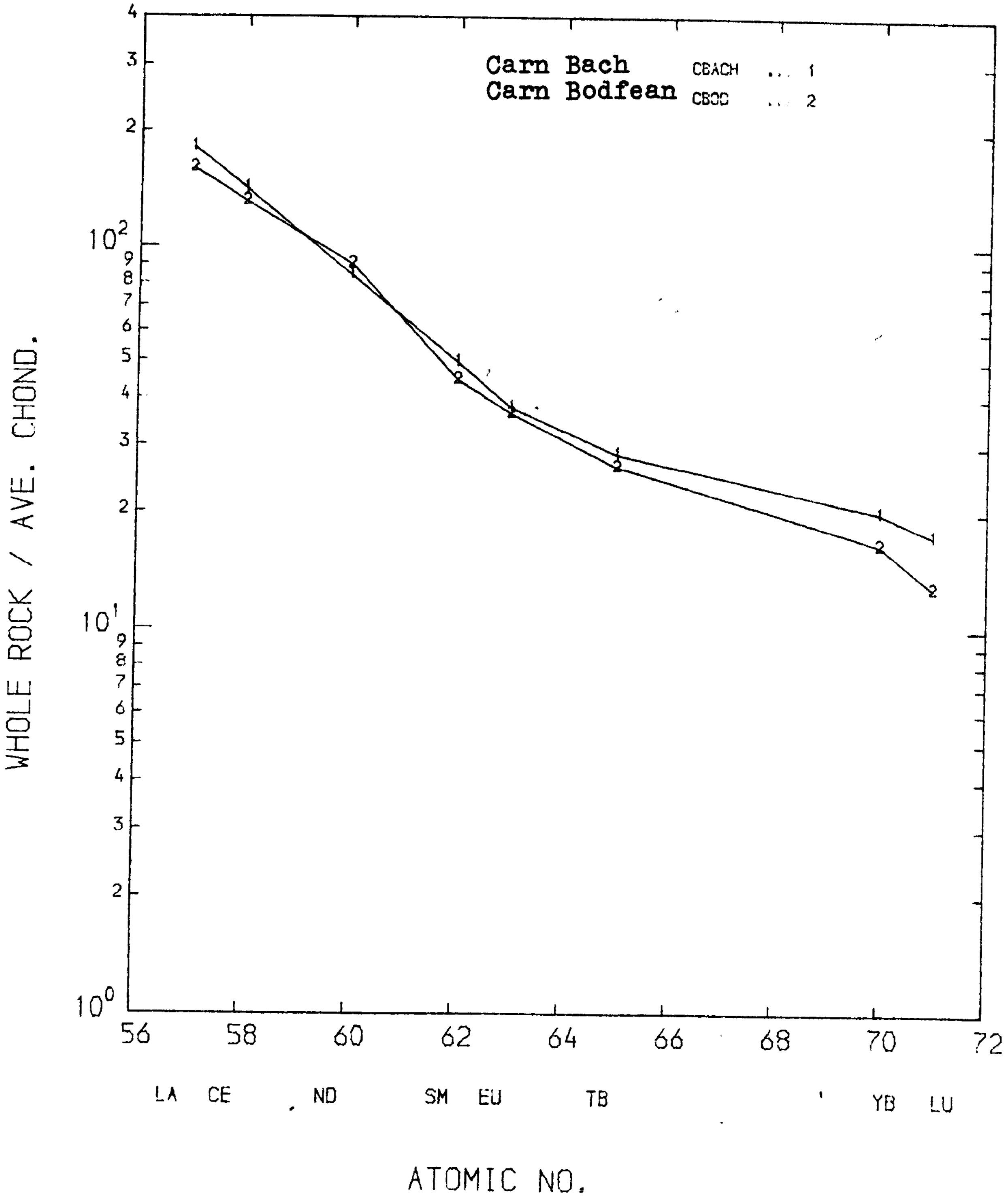
MAP SHOWING THE RELATIONSHIP BETWEEN AEROMAGNETIC ANOMALIES AND THE SITE OF SOME INTRUSIONS regions of magnetic highs. The contours in certain areas (Lleyn, Mynydd Rhiw, Mynydd Mawr and Tan-y-Grisiau) show that the inferred basic bodies, or bodies with a relatively large magnetic susceptibility, are steep-sided at least in part.

A local study of magnetic anomalies was made by Watkins (1958) in the Yr Eifl, area of Lleyn. His conclusions were that the various intrusions of Lleyn generally possess magnetic anomalies which indicate that they have a great depth and vertical or near vertical sides. The intrusive porphyries of Carn Bodfean and Carn Fadryn however, were thought to be volcanic masses extending to depths of about 600 m. The Yr Eifl boss, comprised of the felsites and microgranite, appears to be a vertical sided intrusion extending to a depth of 1500 m while the Garnfor Complex had an anomaly which indicated an unexposed, magnetically-strong component. The unknown component was claimed to be buried approximately 150 m below the surface whereafter it extended to a depth of over 1500 m.

A Note on the Intrusions of Carn Fadryn, Carn Bodfean and Carn Bach

Single samples were collected from the intrusions of Carn Fadryn, Carn Bach and Carn Bodfean and their chemistries clearly reflect their affinity with the previously discussed Lleyn suites. The samples were also analysed for the rare earth elements. It was not found to be possible however, to fit them into any fractionating series and further sampling and analyses are required if this is to be achieved.

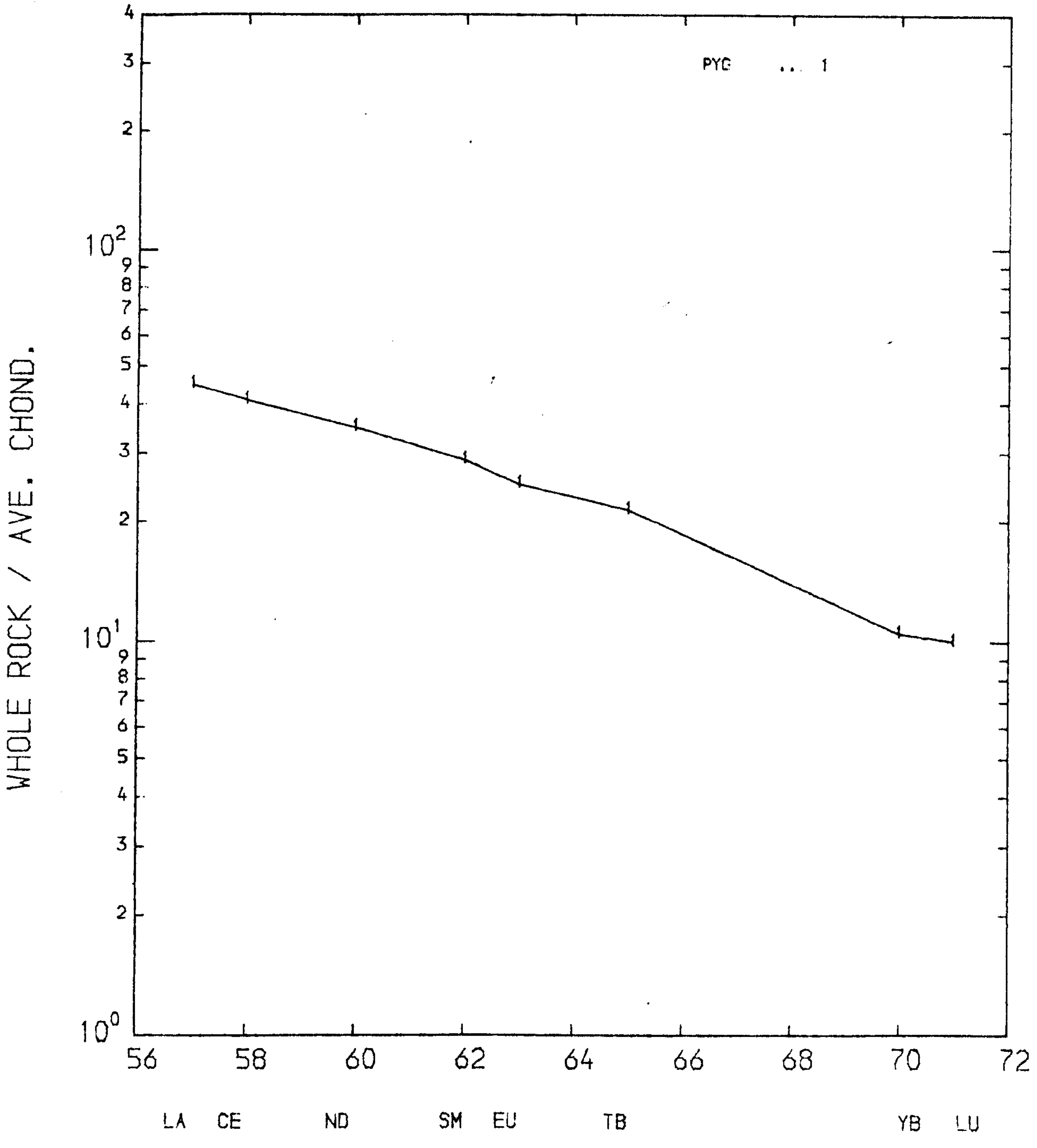
Figure 56


Carn Bach CBACH ... 1
Carn Bodfean CBOD ... 2
WHOLE ROCK / AVE. CHOND.
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
9
8
7
6
5
4
3
2
10^0
56
58
60
62
64
66
68
70
72
LA
CE
ND
SM
EU
TB
YB
LU
ATOMIC NO.

E. Conclusions

The geochemical investigation of the intermediate to acidic intrusions of the Lleyn Peninsula has provided some important information about their timing and petrogenesis. Tremlett's (1962, 1964, 1972) hypotheses about their derivation and Late-Caledonian age are not supported by the present study. The evidence against a Caledonian (or Silurian-Devonian) age has been provided by the geochemically distinctive volcanic rocks from Moel-y-Penmaen which are of a Caradocian age (Tremlett, 1964, 1970). It has been shown that there is overwhelming evidence that they are related to the intrusions of Lleyn and that there is fairly good evidence to suggest that both are derived by closed-system crystal fractionation from a tholeiitic magma of the T-type (Wood et al., 1980). The discussion of the implications of the geochemistry of these rocks to a paleoenvironmental setting will be given later.

Figure 57



ANALYSIS OF A DOLERITE FROM MOEL BERFEDD (NEAR PEN-y-GWRYD)

```
        SAMPLE         PYG       PYG       CI1

        SI02          56.4      51.0      48.9
        TI02           1.21      1.93      1.20
        AL203         13.6      13.1      13.2
        TFE203         9.80     12.57     12.82
        MNO            0.21      0.23      0.28
        MGO            7.53      8.36     11.95
        CAO            4.25      7.96      6.72
        NA20           2.24      3.68      2.27
        K20            3.20      0.80      0.30
        P205           0.24      0.30      0.22

        TOTAL         98.06     99.24     97.07
    AG. COEFF.         0.60      0.49      0.28

       TRACE ELEMENTS IN PPM
        CR               149       367       202
        NI                73        29        91
        SR               254       156       400
        BA               173       383        39
        RB                12        81         1
        Y                 35        49        23
        LA                23        15         9
        CE                60        34        26
        ND                32        21        14
        ZR               288       198        92
        NB                14         3         9
        TH                 3        13         1
        PB                 6         5         2
        U

       ELEMENT RATIOS
       K20/NA20        1.4       0.2       0.1
        K/RB        2213.       82.    2489.
        (CE/Y)N        4.2       1.7       2.8
        ZR/NB         20.6      66.0      10.2
        ZR/Y           8.2       4.0       4.0
        TH/NB          0.2       4.3       0.1
        NB/Y           0.4       0.1       0.4

       CIPW NORMS
        Q             10.9       0.0       1.4
        C              0.0       0.0       0.0
        OR            19.1       4.8       1.8
        AB            19.1      31.4      19.8
        AN            17.7      17.0      25.7
        DI             1.6      16.6       5.7
        HY            22.8      18.1      34.8
        MT             5.9       7.6       7.9
        ILM            2.3       3.7       2.3
        AP             0.6       0.7       0.5
```

Chapter 9

DISCUSSION OF THE TECTONIC ENVIRONMENT OF NORTH WALES DURING THE ORDOVICIAN

The preceding chapters have shown that the sampled granitoids of North Wales, belonging to three distinctive compositional groups, were generated by two main petrogenetic processes. The first of these involved partial melting of calc-alkaline material and the second was by fractional crystallisation (open- or closed-system) of basaltic magma.

1) Peralkaline Group

Modern views consider that many oversaturated peralkaline granites are derived by open or closed-system crystal fractionation from basaltic magma (Ferrara and Treuil, 1975; Baker, 1977; see however Bowden et al., 1979). The peralkaline granites of North Wales probably represent residual liquids formed after a considerable proportion of crystals (> 95 %) had been removed from a tholeiitic or mildly alkaline basalt. Post-magmatic processes may have modified the geochemistry of some parts of the Mynydd Mawr microgranite although its essential features of peralkalinity are clearly evident.

Rocks of peralkaline aspect are commonly found in environments associated with extensional tectonics or stable continental areas and their occurrence may therefore provide an indication of plate tectonic setting.

2) Sub-alkaline - alkaline Group

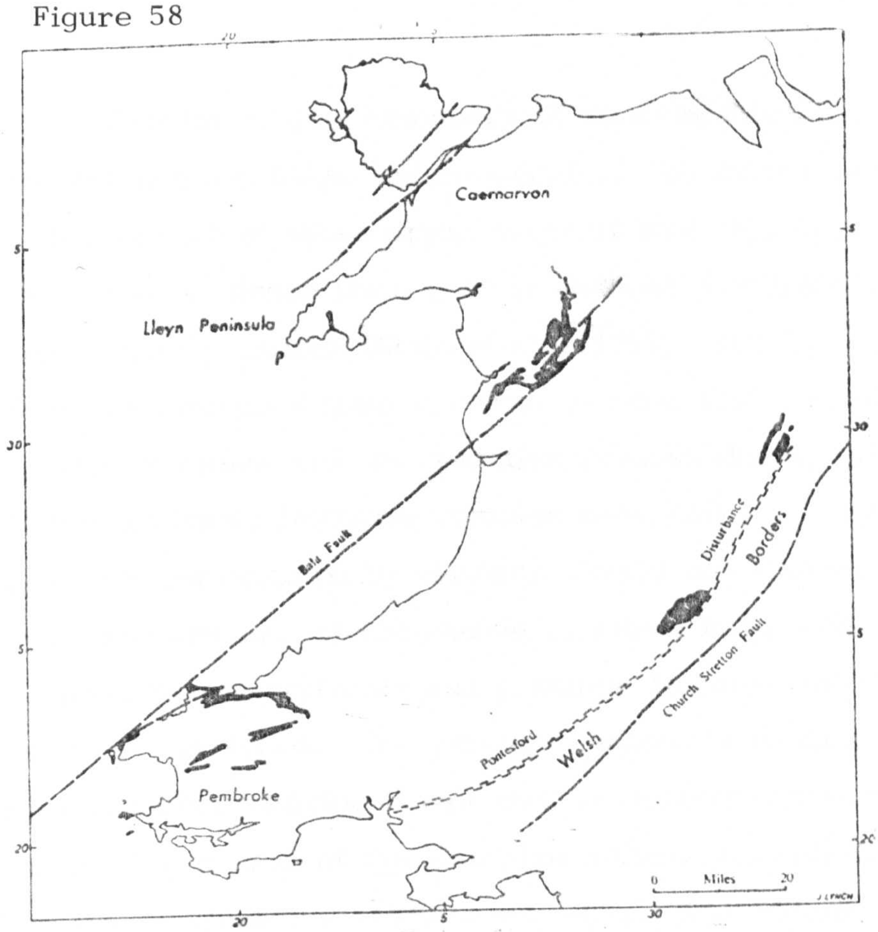
This group of intrusions includes those of central and northern Snowdonia and their geochemistry is typical of calc-alkaline rocks. The origin of this tonalitic-granitic suite is considered to be by remobilisation of calc-alkaline plutons which were generated during the earlier part of the Ordovician (pre-Caradocian). There is good evidence to suggest that the intrusive rocks are geochemically equivalent to the acid tuffs and ignimbrites that were produced throughout the Caradocian stage (Bromley, 1969; Olver, 1979). The remobilised plutons are likely to have had different compositions and they were probably subject to varying extents of partial melting and the subsequent melts to crystal fractionation. For these reasons a very close geochemical coherence among the intrusive and extrusive rocks is not expected although they would retain the calc-alkaline features of their source material.

3) Alkaline Group

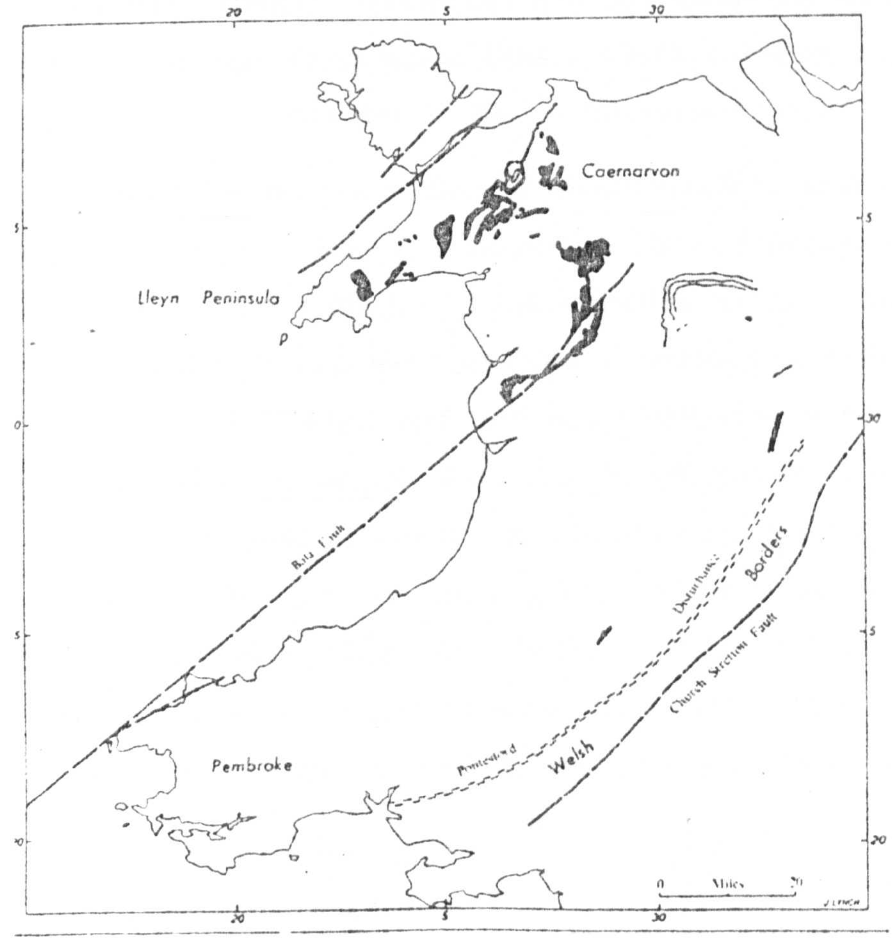
Three suites of alkaline rocks, ranging in composition from 'andesite' to granite, are recognised from the Lleyn Peninsula and similar rocks have been identified in Snowdonia. Their geochemical characteristics are strikingly different from the other groups and their variations within this group may result from differences in physico-chemical parameters (P, T, pH_2O, fO_2), proportions of crystallising phases and mechanisms of crystal fractionation. Evidence has been presented which shows that the geochemistries of the suites may be explained by open- or closed-system crystal fractionation from a basaltic magma of tholeiitic or mildly alkaline affinities. The crystallising phases were orthopyroxene, clinopyroxene, plagioclase and apatite, especially within the composition range, andesite - granite.

The occurrence of tholeiitic basalts (possibly bearing affinities with ocean floor basalts; Dr. G.L. Hendry, personal communication, 1980) peralkaline granites, graben-like tectonics and large, upper crustal magma chambers, where crystal fractionation operated, indicates that North Wales was an area of crustal extension. The relationship between volcanicity and structure in Wales has been outlined by Rast (1969). He demonstrated that volcanicity was closely linked to several major structural discontinuities (Bala Fault, Church Stretton Fault, Pontesford Disturbance; see fig. 58 , page 261) and that the Welsh basin could be viewed as a graben-like structure. This was bounded by the Menai Straits Fault and the Church Stretton fault and after a correction for Caledonian deformation the width of the graben was claimed to be approximately 160 km. This dimension compares favourably with those for parts of the Kenya rift, Rhine Graben, Red Sea rift and the Midland Valley of Scotland.

Figure 58



End Llanvirn volcanic rocks in Wales



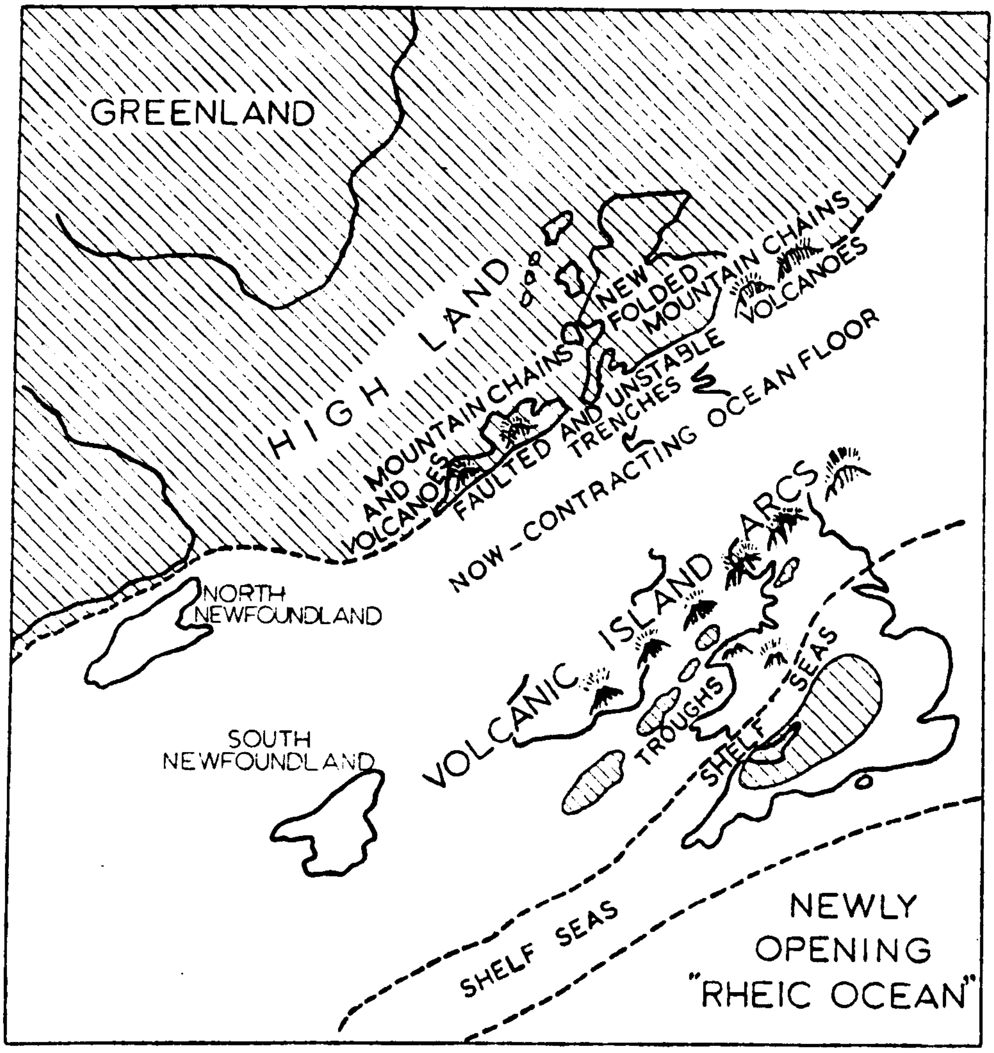
End Caradoc volcanic rocks in Wales

Crustal magma chambers of considerable size are probably present beneath Lleyn and Snowdonia. The existence of highly fractionated suites in both of these areas suggests that this is so and there is some supporting evidence from gravity anomaly (Griffiths and Gibb, 1965) and aeromagnetic studies (Stubblefield, 1965; see fig. 55, page 254). There is also good field evidence to show that crystal fractionation from basaltic magmas was an operative process during the Ordovician. A post-Llanvirnian intrusive complex near Rhiw, in south-western Lleyn, has been investigated by Hawkins (1965) and Cattermole (1969, 1976). The suite consists of hornblende picrites, hornblende dolerites, leucogabbros and granophyres and cumulate features such as rhythmic layering are well developed. The parental magma is thought to have been a hydrated alkali olivine basalt and its differentiation trend is claimed to be similar to that of the Hawaiian suites, viz. alkali olivine basalt - hawaiite - trachyte. Large, extensively fractionating magma reservoirs are commonly found in extensional or within-plate settings (Skaergaard, Kenya rift, Nigeria, Canaries) and this evidence along with the vertical tectonics of the Welsh basin (Rast, 1969) suggests an extensional tectonic regime for the area during the middle-upper Ordovician.

Prior to the production of alkali basalts, acid volcanism and the various intrusive groups discussed earlier, igneous activity in North Wales possessed a distinctly calc-alkaline aspect. Basalts, andesites, dacites and rhyolites were erupted at various centres (Arenig, Rhobell Fawr and Cader Idris) and they are claimed to have been generated at a destructive continental plate margin (Ridgeway, 1976; Kokelaar, 1979). Subduction related processes are invoked for the Ordovician calc-alkali volcanics of Ireland (Downes, 1974; Stillman and Williams, 1978) and the Lake District (Fitton and Hughes, 1970; Millward et al., 1978) and subduction is thought to have taken place, to the south-east, along a line from the Solway Firth to the Dingle Peninsula (fig. 59, page 263).

Thus the Welsh region lay south of an island arc or an environment midway between an island arc and a continental margin (Moseley, 1978). Within a relatively short time igneous and structural activity shifted from

Figure 59



Sketch map showing the probable paleogeography of Britain during the Lower Ordovician.

that associated with subduction to that associated with extension. Karig (1971), Karig and Jensky (1972) and Bruhn et al. (1978) have described similar changes in geological events in the western Pacific, Baja California and Southern Chile and the new environment is termed a volcano-tectonic rift zone. This is considered to be the precursor of a marginal basin where new oceanic crust is produced. Karig (1971) has discussed the possible origins of marginal basins and he found that their early stages are accompanied by the production of silicic extrusives in the form of ignimbrite sheets and a coeval or slightly later development of graben-like features. Calc-alkaline volcanic activity may persist where it is usually produced on the oceanic side of the rift zone. The following is a simplified sequence of events leading to the formation of a volcano-tectonic rift zone and marginal basins.

1) Operation of a trench-arc system with a calc-alkaline volcanic arc.
2) Production of large volumes of ignimbritic material with calc-alkaline characteristics. Extensional features may develop contemporaneously or slightly later than the acid volcanism.
3) Continental rifting occurs with the production of tholeiitic magmatism and basin-range topographic features are formed.
4) Subaerial volcanism confined to restricted regions overlying slivers of continental material.
5) Mafic igneous activity (calc-alkalic and tholeiitic) becomes dominant and an active back-arc basin is developed.
6) Basalts-rhyolites of the bimodal suite (Ewart, 1979) may be erupted.

The origin of back-arc basins is a contentious issue although there are two currently favoured models. Both involve the ascent of a diapir of mantle peridotite through the lithosphere (Oxburgh and Turcotte, 1970) although it is not established whether the diapir induces extension or vice versa (Kanamori, 1977; Uyeda et al., 1979). There is no evidence to suggest that the Welsh basin was an active back-arc basin although the geological features of the area are not inconsistent with the region being a volcano-tectonic rift zone. Wright (1976) stated that the Welsh basin never quite developed into a marginal basin although the Llanvirnian Strumble Head Pillow Lavas of Pembrokeshire may have marked its early development. It is probable that for one reason or another the sequence of events listed above terminated soon after the production of the middle-upper Ordovician ignimbrites, basic volcanics and the intrusion of intermediate-acid rocks. The postulated rising mantle diapir could have undergone partial melting, or more likely induced melting of upper mantle material to produce basaltic magma. This either collected and fractionated in crustal magma chambers (e.g. Lleyn intrusions) or was emplaced and erupted with little modification (augite-dolerites, pillow basalts etc.). Thermal energy derived from this considerable body (bodies) of mantle-derived material could have induced partial melting or complete remobilisation of earlier formed calc-alkaline plutons.

Some comments on plate-tectonic reconstructions during the Precambrian - Lower Paleozoic

Evidence has accumulated over the last decade or so which indicates that plate tectonics have operated as far back in earth history as the Precambrian. The geological associations found in S.E. Ireland, the Lake District, Wales and Anglesey suggest that their evolution was closely linked with subduction related processes. Many details of the tectonics however, remain unclear. Numerous models have been proposed for the evolution of the Welsh area from Precambrian - Lower Paleozoic times, although the main variant is the subduction direction. There is a consensus that the trench was oriented approximately NE-SW but the dip of the subduction zone has been claimed to be SE (Dewey, 1969; Wright, 1976) and NW (Ridgeway, 1976). A single south-easterly dipping Benioff zone (e.g. Dewey, 1969) cannot adequately account for the distribution of Ordovician calc-alkaline igneous rocks in Ireland, the Lake District and Wales. Modern observations have shown that volcanic arcs are most commonly situated about 100 km above the Benioff zone and their width is generally less than 50 km (Barazangi and Isacks, 1976).* Thus the

Welsh volcanic material requires a special explanation whereas the Lake District and Irish volcanic arcs may readily be accounted for by a south-easterly dipping subduction zone with a trench sited near Solway (Moseley, 1979).

Calc-alkaline volcanic material has been produced at various times and centres in Wales. During the late Precambrian calc-alkaline magmas were produced in Anglesey, Caernarvonshire (Bangor and Padarn Ridges) and the Harlech Dome area (see Allen and Jackson, 1978). The Rhobell Fawr and Cader Idris volcanic suites were generated during the early part of the Ordovician while later activity occurred in the Lleyn Peninsula and Snowdonia during the mid-Ordovician. The preceding section has argued that the silicic intrusions of Snowdonia were produced by remobilisation of earlier formed calc-alkaline material. The primary magmas may have been those generated during a late Precambrian subduction event which produced the blueschist facies metamorphism serpentinites, melange etc. in Anglesey and Lleyn. Alternatively they may have been derived from early Ordovician calc-alkaline magma (e.g. Rhobell Fawr, Moelwyns). These early Ordovician suites may either have formed from remobilised Precambrian calc-alkaline plutons or by partial melting of mantle material which was veined or conditional during the Precambrian (see Wood et al., 1980). In either case the ultimate heat source is considered to be the mantle diapirs.

The foregoing account suggests the possibility that the acid intrusions of Snowdonia may have evolved through complex multistage mechanisms and plate tectonic models are shown in the following figures.

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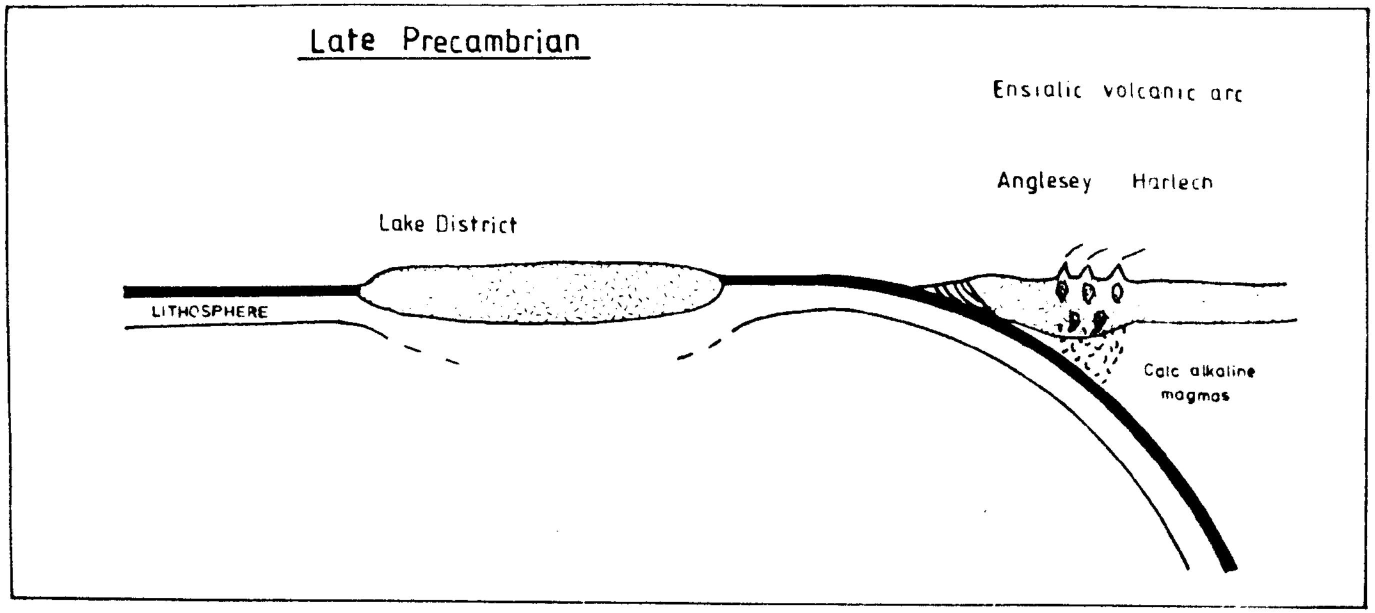
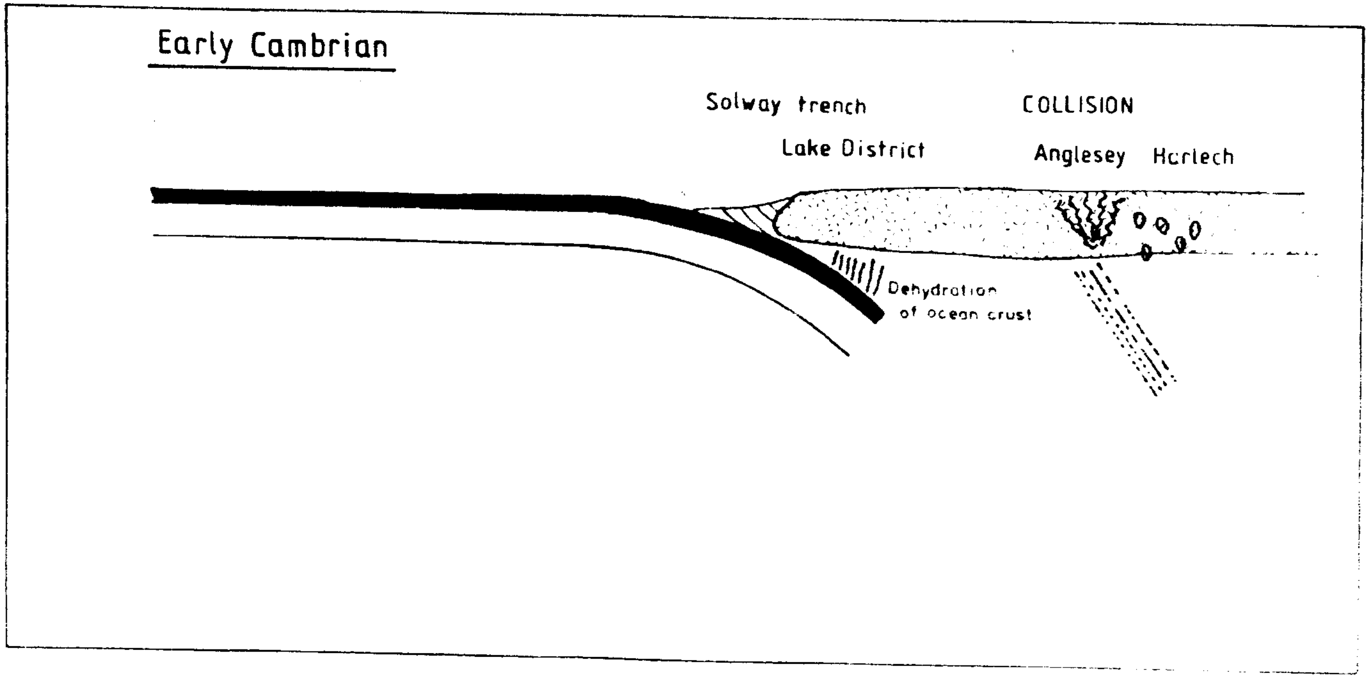
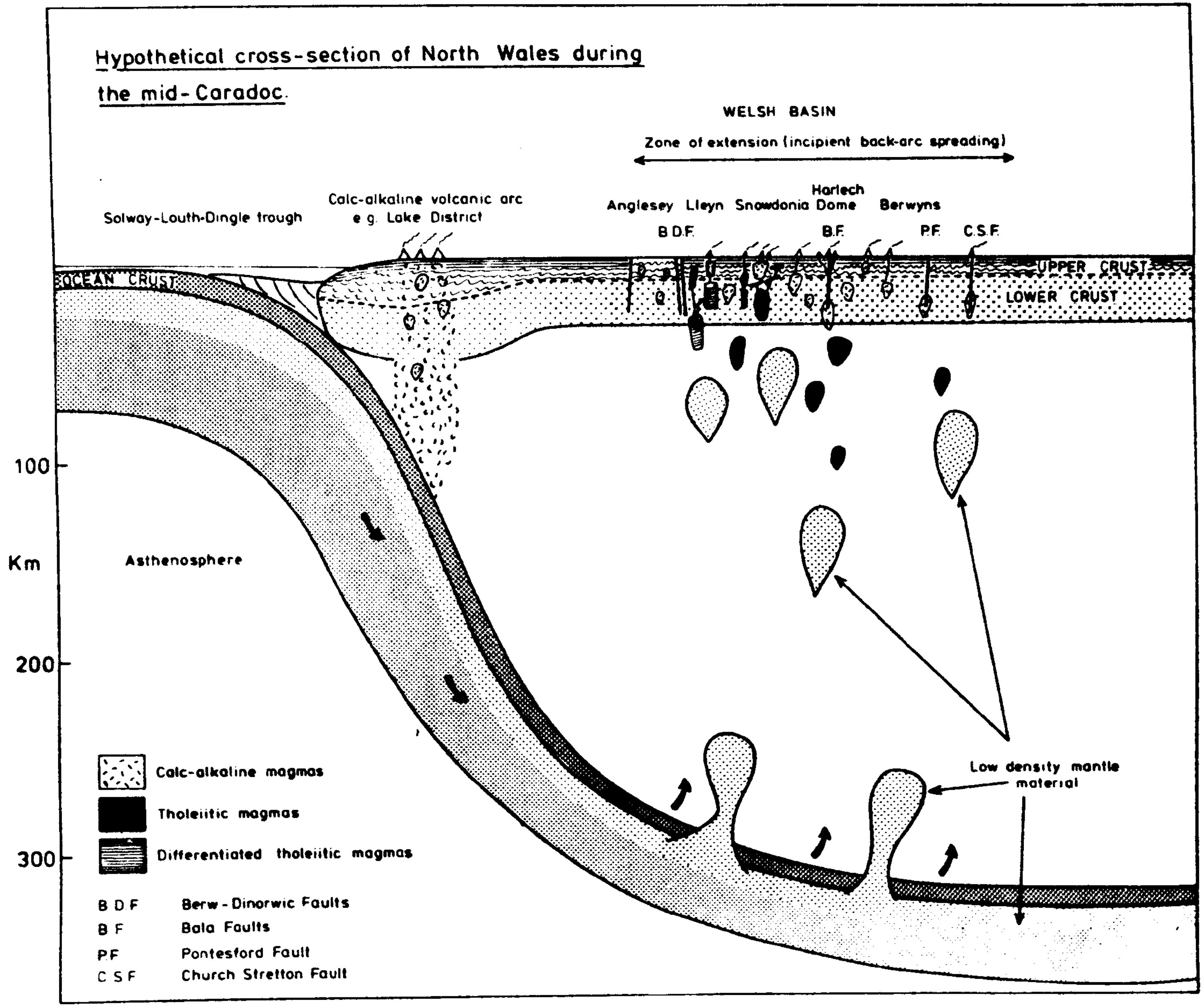
*Footnote to p.265 Barazangi, M. and Isacks, B.L. Spatial distribution of earthquakes and subduction of the Nazca plate beneath South America. Geology 4, 686-692, 1976.



Late Precambrian



Early Cambrian



Hypothetical cross-section of North Wales during the mid-Caradoc.

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Appendix I

Statistical Techniques

The chemical data were subjected to two main statistical procedures, namely correlation and cluster analysis. Correlation analysis is a relatively simple technique which is used to determine the degree of inter-relation between variables. It is concerned with linear relationships. Cluster analysis is a multivariate statistical technique used for classification purposes. That is, a relatively large body of data may possibly be separated into relatively homogeneous and distinctive groups on the basis of its measured variables.

a) Correlation analysis

The purpose of correlation analysis is to investigate linear relationships between variables. In order to compute the correlation coefficient (which gives an indication of the strength of the relationship between two variables), the variance and standard deviation must first be obtained. Variance of the sample is defined by the equation:

$$S^2 = \frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n - 1}$$

where n = no. of samples.

The standard deviation is the square root of the variance. The mutual variability of two variables is measured by a quantity called the covariance defined by:

$$\mathrm{cov}_{jk} = \frac{\sum_{i=1}^{n} (X_{ij} - \bar{X}_j)(X_{ik} - \bar{X}_k)}{n - 1}$$

where n is the no. of samples.

The number of degrees of freedom is written as n-1 rather than n as this is a sample,not a population.

The correlation coefficient r is calculated as the ratio of the covariance of two variables to the product of their standard deviations, where:

$$r_{jk} = \frac{cov_{jk}}{s_j s_k}$$

In the above form the calculation of the correlation coefficient is rather laborious. More convenient computational versions of these formulae are generally used (see Davis, 1973, p. 78).

The coefficients thus generated are generally arranged in the form of a symmetric matrix having 1's on the principal diagonal (each variable is perfectly correlated with itself).

The significance of each correlation coefficient was determined using the function:

$$t = r\sqrt{\frac{n - 2}{1 - r^2}}$$

which is known to approximately follow a t-distribution. The significance levels quoted in the tables of geochemical correlation are due to a two tailed test.

b) Cluster analysis

Cluster analysis may be performed in two ways depending on whether the interest is between the variables (R-mode) or between the samples (Q-mode). Both R- and Q-mode techniques have been used in the present study and correlation and cluster analysis are used together to simplify the data. Computer programmes written by Mr. A.C. Skinner and Mr. A. Erdogan (University of Birmingham) were used. The clustering procedure used the equally weighted pair-group method and the results are graphically displayed in the form of dendrograms. These are the most commonly used way of displaying the results of clustering.

The following account is a simple description of the procedures for performing Q-mode cluster analysis. By transposing the initial raw data matrix, the analysis becomes R-mode.

If we have n objects (samples) and these have m characteristics the data set forms an n x m matrix. The raw data matrix is standardised prior to further calculations. This ensures that each variable is equally weighted, otherwise, the variable with the greatest magnitude will strongly influence the subsequently calculated measure of similarity. The computation of a similarity measurement (e.g. correlation coefficient) between all possible pairs of variables results in an n x n symmetrical matrix. However, it is necessary to first transpose the nxm raw data matrix to an mxn matrix otherwise clustering will be R-mode and not Q-mode. The next step is to arrange the objects of the similarity matrix into a hierarchy such that objects with the highest mutual similarity are placed together. Groups or clusters are associated with other groups which they resemble and so on until all objects have been classified. The method for doing this is the equally weighted pair-group method using arithmetic averages. The mutually highest correlations in the matrix are first determined and these form the centres of the clusters.

1)

	A	B	C	D
A	1	0.57	0.12	-0.65
B	0.57	1	0.46	-0.79
C	0.12	0.46	1	-0.58
D	-0.65	-0.79	-0.58	1

Thus object A and B form mutually high pairs because A most closely resembles Ba and B most closely resembles A. Now, C most closely resembles B but B does not most closely resemble C; it resembles A. D most closely resembles C but C does not most closely resemble D; it resembles B.

The similarity matrix is now recomputed treating grouped or clustered elements as a single element. Only A and B showed mutually high correlations with one another. The new matrix is shown below:

2)

$$\begin{array}{c|ccc|} & AB & C & D \\ \hline AB & 1 & 0.29 & -0.72 \\ C & 0.29 & 1 & -0.58 \\ D & -0.72 & -0.58 & 1 \\ \hline \end{array}$$

The recalculated correlation coefficient between AB and C = (0.46+0.12)/2=0.29

" " " " " AB and D = (-0.65-0.79)/2=-0.72

C and D remain the same.

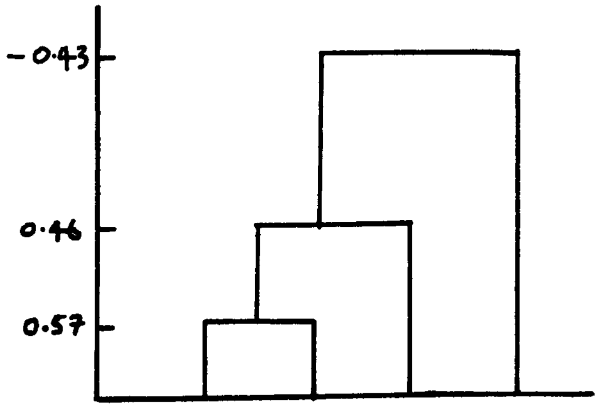
The similarity matrix is recomputed for the last time.

3)

$$\begin{array}{c|cc|} & ABC & D \\ \hline ABC & 1 & -0.43 \\ D & -0.43 & 1 \\ \hline \end{array}$$

The recalculated correlation coefficient between ABC and D = (-0.72-0.58)/3=-0.43 Since ABC comprises three components division by three is carried out. Had division by two occurred the method would be called an <u>unequally weighted pair-group</u> method.

The dendrogram resulting from the above analysis is shown below:



The Closure Problem

This phenomenon occurs when variables summing to a constant (e.g. percentage data) are considered. The theoretical background has been discussed by Chayes (1964). The situation results simply from the relative decrease in size of a variable if another increases. For some variables there are therefore induced negative correlations which may be so large as to be significant. The effect is obscured if many variables are included. Since it influences all operations performed on the variables it may invalidate the results of an entire analysis. This problem is often dismissed (Beach and Tarney, 1978) but this does not reflect the insignificance of the problem it merely demonstrates that no satisfactory means exist for its solution. Chayes (1971) has proposed some equations which provide a partial solution to the problem but they fail when more than four variables are considered. Thus, great caution is required when interpreting geochemical correlations whether they are expressed graphically (Harker diagrams) or statistically.

APPENDIX II

X-Ray Fluorescence Analytical Procedure

Sample Preparation

Samples, weighing between 2-5 kg, were collected and this was sufficient to provide material for a hand-specimen, a thin-section and for analytical purposes. The material was initially broken in a jaw-crusher and most of the weathered surfaces were removed at this stage. Approximately 1 kg of sample was chosen for crushing in a fly-press which was fitted with hardened steel crushing surfaces. Any weathered or lichened chips were removed and portions of the remaining material were crushed in a tungsten carbide "Tema" swing mill for one minute. The coarse-powder obtained was placed on a sheet of clean paper and homogenised by repeated folding. 50 cm^3 of this powder were sampled and then crushed for 2 minutes. This produced a fine-powder suitable for analytical purposes which was approximately 240 mesh B.S. 15 g of this material was mixed with 25-30 drops of a 7 % (w/v) poly-vinyl alcohol solution (binding agent) and this was pelleted by compressing the mixture in a special die to 20 tons between two hardened steel faces (I.D., 46 mm). In order that mineralogical and matrix absorption differences between the samples could be minimised, fifteen samples were selected which covered the range of compositions sampled. These were made into glass discs by fusing 0.8 g of sample with 4.0 g of a special flux (Johnson-Matthey Spectroflux 100B; 80 % lithium metaborate - 20 % lithium tetraborate). Fusion to 1150°C was facilitated using a vertical tube electric furnace and Pt/Au crucibles. The sample was fused and swirled for 20 minutes after which it was poured into aluminium molds using equipment similar to that described by Harvey et al. (1973). Both the powder briquettes and the fusion beads were stored in sealed plastic bags and the latter were kept in a dessicator to reduce contamination and water absorption.

X-Ray Fluorescence Analysis

The equipment used was a Philips PW 1450 automatic spectrometer with a PW 1466 60-position sample changer. The count data obtained from the spectrometer are punched onto 8-channel paper tape by an on-line "Teletype". This is then read into either a Digital PDP 11-03 or an ICL 1906A computer where the data are processed using a computer program written by Mr. P.D. Marsh.

The analytical, instrumental and operative procedures used are similar to those described by Leake, Hendry et al. (1969) and details of various settings may be found in tables 11 ,12 , 13 (page 308,309 ,310). Samples are generally measured twice, such that possible erratic results may be identified and corrective action taken. Counts are normalised to a ratio standard which eliminates all but short-term instrument drift. Four "house standards" are included in all sample runs and these are used to monitor long-term precision (table 14 , 311). The ratio standard for major element analyses, analysed every fourth sample, is a silicate enamel reference sample. For trace element analyses an epoxy resin base (Araldite MY 753), containing silica, iron oxide and appropriate trace elements, is used as a ratio standard and it is only analysed once throughout a particular "run" ($\leqslant$ 60 samples).

Major-Element Analysis

Major-element analyses are carried out on all the samples using a chromium anode X-ray tube. Most of the major-element analyses are determined on powder briquettes. However, potential errors, caused by mineralogical effects, are inherent in the use of powder samples for major-element analysis. To minimise these, a set of representative samples, covering the range of compositions, was selected for analysis using fusion bead discs. These are analysed in parallel with beads of international standard reference samples, and the determined concentrations are used to establish short-range calibrations for the remaining powder samples.

Trace-Element Analysis

To obtain maximum sensitivity and to avoid interferences from the X-ray tube target, the samples are excited using both molybdenum and tungsten anodes. The fluorescent radiation is dispersed using a LiF_{220} analysing crystal to achieve maximum peak separation.

Wavelengths and choice of tube anode are as follows:

Mo target: $Y(K\alpha)$, $Sr(K\alpha)$, $Rb(K\alpha)$, $Th(L\alpha)$, $Pb(L\beta_{1,2})$, $Ba(L\beta_{1,4})$, $W(L\beta_1)$, $U(L\alpha)$

Corrections were made for the overlap of $RbK\beta$ on $YK\alpha$, $CeL\alpha$ on $BaL\beta$, and $YK\beta$ on the $MoK\alpha$ Compton peak. Background profiles and contamination arising from the X-ray tube target were determined using ultra-pure samples of SiO_2, Al_2O_3, and MgO. The minor overlap of the second-order $WL\beta_1$ escape peak on Ba was removed by careful setting of the pulse-height window.

W target: $Ni(K\alpha)$, $Cr(K\alpha)$, $Ce(L\beta_{1,4})$, $La(L\alpha)$, $Zr(K\alpha)$, $Nb(K\alpha)$, $Nd(L\alpha)$

Corrections were made for the overlap of $SrK\beta_{1,3}$ on $ZrK\alpha$ and the target contamination on Ni and Cr. Because of the lack of precision inherent in the correction of $CrK\alpha$ for $VK\beta$, involving the separation of $VK\alpha$ from the overlapping Ti $K\beta$, the results for chromium are presented uncorrected.

Calibration: Initial calibrations are prepared from a wide range of rock types spiked with the appropriate pure element compound (Leake, Hendry, et al., 1969). The element that was spiked had a minimum purity of 99.99 %. These values are then related using either the WL or MoK Compton peaks scattered by the sample to provide correction for total mass absorption for all emission lines shorter than the iron absorption edge (Reynolds, 1967). The slightly inferior method of correction using the W Rayleigh peak was adopted in the automatic analysis procedure to give immediate results. As a check on the values, especially where tungsten was detected in the sample (from

(from tungsten carbide crushing equipment), the concentrations were also calculated using the MoKα Compton peak. Rb and Sr calibrations were obtained using samples which had these elements determined by isotope dilution. A check was then made against international reference samples. No detectable improvement resulted from absorption corrections using tube scatter lines and the count rate on the FeKα peak designed to determine the absorption coefficient at wavelengths longer than the Fe absorption edge (Walker, 1973).

Precision and accuracy: The instrumental precision with the techniques used is high, even at relatively low trace-element concentration (table 14 , page 311). The accuracy can only be judged, however, against international reference samples and some estimates may be obtained from table 15 (page 312); further data on a wider range of reference materials are given in Hendry (1975).

TABLE 10

Lower limits of determination (100 sec counting time)

Y	5 ppm
Sr	3 ppm
Rb	3 ppm
Th	5 ppm
Pb	5 ppm
Ba	12 ppm
Zr	3 ppm
Nb	5 ppm
Ce	10 ppm
La	10 ppm
Nd	12 ppm
Ni	5 ppm
Cr	5 ppm
U	6 ppm

TABLE 11

Spectrometer Conditions for the CR-Programme

Element	Line	Peak $^{o}2\theta$	Background(s)	Crystal	Detector	Coll.	kV	mA	Time(Peak)
Ti	$K\alpha_{1,2}$	36.54	+3.16	PE	F	f	50	20	4 secs.
Ca	Kα	45.06	-1.80	PE	F	f	20	10	4
K	Kα	50.58	+3.75	PE	F	f	60	30	4
Si	Kα	108.94	+3.00	PE	F	c	60	30	20
Al	Kα	144.75	-4.80	PE	F	c	60	30	20
P	Kα	140.92	+2.70	GE	F	c	60	30	20
Fe	Kα	85.74	+4.83	LIF 220	F	f	60	30	10
Mn	Kα	62.98	+3.02	LIF 200	F	f	60	30	20
Mg	Kα	45.21	-2.30 +3.20	TLAP	F	f	60	30	20
Na	Kα	55.20	-2.20 +1.30	TLAP	F	c	40	45	40
S	Kα	75.74	-2.64	PE	F	c	60	30	20
CL	Kα	65.32	+2.00	PE	F	c	60	30	20

TABLE 12

Machine Conditions for the Mo-Programme

Element	Line	Peak °2θ	Background(s)	Crystal	Detector	Coll.*	kV	mA	Time(Peak)
Y	$K\alpha_1$	33.83	-0.85 , +0.93	LIF 220	S	f	60	30	20 secs
Sr	$K\alpha_1$	35.79	-1.03 , +0.84	LIF 220	S	f	60	30	20
Rb	$K\alpha_1$	37.92	-1.29 , +0.90	LIF 220	S	f	60	30	20
Th	$L\alpha_1$	39.22	-0.40 , +0.80	LIF 220	S	f	60	30	20
Pb	$L\beta_2$	40.35	-0.33 , +0.90	LIF 220	S	f	60	30	20
Mo	Compton	30.10	-1.66	LIF 220	S	f	60	30	20
Ga	$K\alpha_1$	56.12	-1.82 , +1.28	LIF 220	F + S	f	60	30	20
Zn	$K\alpha_1$	60.50	+1.27	LIF 220	F + S	f	60	30	20
Cu	$K\alpha_1$	65.52	+1.04	LIF 220	F + S	f	60	30	20
Ba	$L\beta_1$	128.67	+2.69	LIF 220	F	C	60	30	20
U	$L\alpha_1$	37.27	-.64,+.55	LIF 220	S	F	60	30	20

* Fine = 0.15 mm

Coarse = 0.55 mm

TABLE 13

Spectrometer Conditions for the W-Programme

Element	Line	Peak $^{\circ}2\theta$	Background(s)	Crystal	Detector	Coll.	kV	mA	Time(Peak)
Ni	$K\alpha_{1,2}$	71.25	WLL	LIF 220	F	f	60	30	20 secs
Cr	$K\alpha_{1,2}$	107.13	-2.22	LIF 220	F	f	60	30	20
Ce	$L\beta_1$	111.68	-1.75	LIF 220	F	c	60	45	20
La	$L\alpha_1$	138.95	-2.20	LIF 220	F	c	60	45	20
W	$L\beta$	53.48	-1.18	LIF 220	S	f	60	30	20
Zr	$K\alpha_{1,2}$	32.04	-0.94 +0.57	LIF 220	S	f	60	30	20
Nb	$K\alpha_{1,2}$	30.36	+0.74 -0.55	LIF 220	S	f	60	30	20
Nd	$L\alpha_1$	112.8	-3.87	LIF220	F	C	60	45	20

TABLE 14

Measured Precision of Cr Excited Elements (n >10)

	OB	UB	T-y-G	HA1
SiO_2	50.63 ± 0.06	56.94 ± 0.05	71.52 ± 0.12	66.51 ± 0.09
TiO_2	1.35 ± 0.005	0.67 ± 0.005	0.209 ± 0.005	0.313 ± 0.002
Al_2O_3	15.35 ± 0.05	15.01 ± 0.02	14.44 ± 0.035	17.07 ± 0.05
Fe_2O_3	9.23 ± 0.03	10.01 ± 0.05	2.74 ± 0.02	4.52 ± 0.03
MgO	7.90 ± 0.06	2.72 ± 0.02	0.377 ± 0.01	0.571 ± 0.01
CaO	11.52 ± 0.05	6.42 ± 0.03	2.89 ± 0.08	0.944 ± 0.05
Na_2O	3.26 ± 0.01	2.41 ± 0.01	3.00 ± 0.01	1.55 ± 0.01
K_2O	0.38 ± 0.01	2.43 ± 0.03	2.398 ± 0.01	4.91 ± 0.03
P_2O_5	0.130 ± 0.005	0.266 ± 0.001	0.040 ± 0.001	0.289 ± 0.001

Measured Precision of Mo Excited Elements (n >10)

	OB	UB	T-y-G	HA1
Y	27.7 ± 0.5	21.4 ± 0.8	46.6 ± 0.5	64.2 ± 0.9
Sr	200.8 ± 1.0	277.3 ± 1.5	65.0 ± 1.9	61.7 ± 1.7
Rb	4.5 ± 0.5	80.6 ± 1.0	67.7 ± 2.0	228.7 ± 1.3
Th	0.3 ± 1.5	6.6 ± 0.8	23.0 ± 1.2	28.4 ± 1.3
Pb	4.0 ± 1.3	48.9 ± 2.0	4.5 ± 1.0	27.9 ± 1.0
Ga	17.5 ± 1.0	17.9 ± 1.0	16.9 ± 0.8	27.7 ± 0.9
Zn	61.5 ± 2.0	174.5 ± 2.1	61.0 ± 1.4	57.7 ± 1.8
Ba(+Ce)	69.6 ± 3.0	977.0 ± 7.8	558.4 ± 6.7	1069.0 ± 8.3
W	70.9 ± 2.5	45.4 ± 2.2	431.0 ± 8.5	85.8 ± 2.3

Measured Precision of W Excited Elements (n >10)

	OB	UB	T-y-G	HA1
Ni	119.0 ± 3.	6.0 ± 1.	2.0 ± 1.	1.8 ± 1.
Cr/V	236. ± 3.	16.5 ± 2.0	2	2
Ce	14. ± 2.	29.0 ± 1.	130.7 ± 1.	141.5 ± 1.
La	6. ± 1	13.5 ± 1.	64.0 ± 1.	84.7 ± 2.
Nd	9.8 ± 1.	17.1 ± 1.	56.7 ± 1.	85.8 ± 1.
Zr	100.9 ± 2.	62.0 ± 2	186.1 ± 1	345.5 ± 4.
Nb	8 ± 1	5 ± 1	13 ± 1	23.5 ± 3.

TABLE 15

Analyses of Standard Reference Samples[a]

Component (% or ppm)	Standard BOB-1	AVG-1	JB-1
SiO_2	51.02 ± 0.078	60.19	53.13
TiO_2	1.28 ± 0.004	1.01	1.30
Al_2O_3	16.55 ± 0.012	17.44	14.48
Fe_2O_3	8.48 ± 0.013	6.98	9.02
MnO	0.14 ± 0.001	0.10	0.15
MgO	7.58 ± 0.030	1.56	7.79
CaO	11.39 ± 0.027	4.87	9.41
Na_2O	3.10 ± 0.074	4.40	2.87
K_2O	0.37 ± 0.003	2.99	1.45
P_2O_5	0.16 ± 0.001	0.49	0.25
Total	100.07	100.03	99.85
	BOB-1	BCR-1	JB-1
Ni	106.4 ± 2.1	19	134
Cr[b]	257 ± 10	18	359
Rb	4.8 ± 0.6	48	42
Sr	202.1 ± 1.0	329	442
Y	26.9 ± 0.5	36	23
Zr[c]	107.6 ± 3.0	191	150
Nb	5.3 ± 1.6	12	35
Ba[d]	50.4 ± 3.6	695	500
La	6.4 ± 1.9	26	38
Ce	16.6 ± 1.7	55	66
Zn	61.5 ± 2.1	120	80
Ga	17.6 ± 0.7	25	17

[a] Fe_2O_3 is total iron as Fe_2O_3; mean and 1 sigma standard deviation of six fusion beads of BOB-1, and means of three fusion beads of international reference samples; All values are for ignited samples; average concentration of BOB-1 determined on 22 consecutive days (with 1 sigma variation); average concentration of two samples of international reference material.

[b] Not corrected for V interference.

[c] Corrected for Sr interference.

[d] Corrected for Ce interference.

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Notes on the Interpretation of Data from the MON Program

The majority of interferences encountered in the analysis of the elements Y, Sr, Rb, Th, Pb, W, Ga, Zn, Cu, Ba are corrected by the computer program. These notes are provided to allow the detection of possible errors due to extreme rock types or contamination.

Line Overlaps

Y	Peak overlap from RbK_β, corrected.
Sr	Background interference from U > 50 ppm, Rb > 1000 ppm.
Rb	Background interference from Sr > 1500ppm.
Pb	Slight contribution from spectrometer, corrected *
W	Contribution from X-ray tube, corrected *
Ga	Background overlap from W > 800 ppm, from crushing.
Zn	Contribution from X-ray tube, corrected * Background overlap with W > 800 ppm.
Cu	Major X-ray tube contamination equivalent to 200 ppm. partially removed by Al filter, corrected *
Ba	Peak overlap (2nd order escape peak) from W in crushing, corrected in spectrometer by PHA. Overlap from very high Ti. Ce Lα OVERLAP MUST BE CORRECTED EXTERNALLY using equation on output page 2.
MoCo	Compton, Scatter peak for absorption correction. Y K_β Nb Kα overlap corrected. Background overlap with Zr > 800 ppm. Position effect from [illegible] Y + Nb.

* The contribution of W, Zn, Cu from the X-ray tube alters each time the tube is changed, as does the MoCo peak intensity, these values will alter the background correction, and calibration (MoCo) with time.

Absorption Correction

This is performed by the program using a modification of the technique of Reynolds (1963, 1967) employing the Mo K_α Compton peak to estimate μ., and is applied to all elements with the exception of Ba which is on the long wavelength side of the iron absorption edge.

For Ba a choice is offered of Acid, Intermediate, Basic calibrations allowing the user to select the appropriate rock type. (Strictly to chose the correct μ governed by Fe (Ti, Ca) contents).

Precision

Figures are given for all elements on the 'house standards' OB (Ocean Basalt) UB (Intermediate) TyG (Granite) H Al (High Alumina Dacite) which are run on each program. Those elements e.g. Y, involving peak overlap corrections will obviously have lower precision, as will those with concentrations near the instrument lower limit of determination.

Cu has a low count rate due to the Al filter, and these figures should be treated as an order of magnitude.

For greater sensitivity and precision on important elements a special program may be set up. This is costly and samples and elements should be selected with extreme care.

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Notes on the Interpretation of Data from the RhT Program

The majority of interferences encountered in the analysis of Ni, Cr, Nb, Zr are corrected by the computer program. These notes are provided to allow the detection of possible errors due to extreme rock types, or contamination.

Absorption Corrections

The Rh K_α Compton scatter line is used to correct all elements, using the relationship $^1/\mu \propto$ Rh Compton intensity. In the case of Cr the Fe absorption edge is crossed and the relationship is $^1/(\mu \times \text{Rh Compton}) \propto$ Fe intensity.
NB. In unusual rock types the absorption coefficient (μ) is only proportional to the scatter line intensity for wavelengths shorter than the absorption edge of a major element. For example Ni could not be corrected using the Rh Compton line in the presence of high Zn (> 2000 ppm) unless the Zn counts were also determined.

Tube Anode Contamination

The anode contains measureable amounts of Ni, Cr, Fe. The amount of this contamination changes each time the x-ray tube is removed from the spectrometer, and is corrected using peak/background ratios determined from blank samples.

Individual Elements

Ni Values over 1000 ppm may be in error due to mineralogical effects. The concentrations would be better determined on a fusion bead.

Cr The Cr K_α peak is overlapped by VK_β. The error introduced by ignoring the overlap is less than that of the correction, therefore all Cr values are high by ~6% of the V concentration.
Cr values over 1000 ppm may be in error due to mineralogical effects. The concentrations would be better determined on a fusion bead.

Zr Zr K_α is overlapped by Sr K_β. The overlap is corrected in the program.

Nb Levels of Th greater than 500 ppm could cause errors in the Nb concentration.

Sr The Sr overlap on Zr requires the removal of ~ 0.03 of the Sr K_α intensity. As the correction is small only a short time need be spent on the analysis and precision is consequently low. Sr concentrations are therefore produced only for information and not to replace those from the MoN program.

The Sr K_α peak lies on the $^3/2$ Rh K hump. The background is estimated using the Rh Compton peak.

February 1980

Appendix III

Preconcentration Technique for REE and Ba from Rock Samples

(Zielinski, 1975)

Add $\simeq$ 1 ml deionized H_2O to platinum dish or teflon beaker. Add aliquot of Ce^{144} tracer (ICN#63010, t 1/2 = 285 D, 1 mc → 200 ml, aliquot = 50µl = 0.6µCi).

Sample dissolution in HF-$HClO_4$

Add 0.5 grams of powdered (200 mesh) rock to platinum dish. Add 20 ml of conc HF, 10 drops of 60-70% $HClO_4$. Stir with teflon rod, cover with teflon watchglass and place on hotplate at $\approx$80°C. Allow to digest overnight.

Solution in 1N HCl

Remove watchglass and evaporate to dryness. Continue heating until white fumes of volatilized SiF_4 cease being produced. Add 15 ml of 1N HCl. Evaporate solution to dryness with occasional stirring. Repeat addition of 1N HCl. If, after gentle heating, the solution becomes clear, remove from hotplate and cover.

Note: Clear solution is yellow from dissolved iron chloride.

If solution remains cloudy, transfer to polyethylene centrifuge tube and centrifuge. Decant off clear liquid and save. Return precipitate to platinum dish and add 15 ml of 1N HCl. Heat gently with stirring until solution becomes clear and combine with saved solution above.

If some undissolved material remains, repeat centrifuge step before combining liquids and transfer precipitate to machined teflon container (bomb).

HF dissolution in teflon bomb

Add 5 ml of conc HF and seal teflon container. Place in steel jacket and screw halves of jacket together to hand tightness. Place in oven at 150°C overnight. Quench jacket with distilled H_2O, unscrew, and wash out teflon container with HF into platinum dish.

Evaporate to dryness and dissolve residue in 1N HCl. Combine with rest of dissolved rock solution.

> Note: Difficultly soluble minerals include spinels, zircon, chromite.

Ion exchange

Cation exchange resin AG50W-X8, hydrogen form, 100-200 mesh is equilibrated with 6N HCl followed by 2N HCl.

Column preparation

Resin is loaded as a slurry in 2N HCl into 25 ml glass burettes (1.0 cm diameter) fitted with glass wool frit. Resin column length is adjusted to 20 cm. This is equivalent to ≃ 5 grams of dry resin of 25 meq capacity. Column is rinsed with 100 ml of 2N HCl.

> Note: A liquid reservoir for eluent in the form of a 250 ml separatory funnel may be attached to the column tope by means of an appropriate connector of tygon or rubber tubing. Squeezing of tubing expels trapped air from column and allows liquid from reservoir to enter column. See diagram.

> Note: A length of glass tubing of ≃ 5 mm diameter is a useful tool for addition or removal of small amounts of resin slurry or stirring of resin bed.

Loading of dissolved rock

Make rock soln. vol. as small as possible.

Combined solutions of 1N HCl are loaded onto columns with eye droppers and eluted until last solution reaches top of resin bed. Do not disturb the resin bed.

Elution of most cations

Reservoir is attached and column is eluted with 100 ml of 2N HCl at a drop rate of ≃1 ml/minute.

> Note: This elution removes all cations except REE, Ba, Zr, Th, some Sc. Ce tracer moves down column about 4 cm. Furthest advance of less tightly held heavy rare earths is 15 cm down the column (determined by geiger counter monitoring of Lu, Yb tracers).

Elution of REE and Ba

Reservoir is eluted with 125 ml of 6N HCl at same drop rate.

> Note: Rare earths are eluted in the order Lu, Yb 4-16 ml; Eu 10-40 ml; La, Ce 10-60 ml. Ba elutes with middle rare earths. Yields of rare earth tracers in tonalite rock matrix were Ce 96%, Yb 94%, Sr, Th remain on column.

6N HCl eluent is evaporated to $\simeq$ 5 ml and transferred with 5 ml H_2O rinse water to a 4 dram polyethylene vial.

An aliquot of Ce^{144} tracer of volume equal to that added to rock is combined with a solution of rare earth carriers to a volume of 10 ml in a 4 dram vial.

Yield determination

Standard and sample are counted in a NaI 3x3"well detector coupled with a multichannel analyzer. Areas of Ce^{144} γ ray peak of 133 KeV are compared to determine chemical yield factor for REE and Ba. Non-fractionation of elements in this procedure is assumed.

> Note: Non-fractionation observed in tracer experiment. Also, values of REE and Ba calculated using constant yield factor agree well with literature values for standard rocks BCR-1, G-2 analyzed by this method.

Preparation for irradiation

Rock solutions plus Ce tracer are evaporated to dryness overnight in a drying oven. Residue is dissolved in 2 ml of 6N HNO_3 and again evaporated to dryness. Sample vials are heat-sealed and submitted for irradiation with a vial containing an evaporated residue of REE and Ba standard solution.

Vials are irradiated in lazy susan for 16 hours at 1,000 KW.

> Note: Rocks of anomalously low REE content may require longer irradiations.

Post-irradiation removal of Br interference

Vials are allowed to cool for 4 hours after irradiation. They are opened and rinsed with 6N HNO_3 and deionized H_2O. Rinsings are transferred to a clean 4 dram vial.

Note: This transfer allows removal of 97% of Br^{82} activity caused during irradiation. Br contamination is introduced with HCl eluent. Br^{82} remains in vial because it combines with organic molecules of the vial polyethylene. Transfer of REE and Ba is quantitative however.

Counting schedule

Transferred solutions are now ready for analysis by Ge(Li) detector.

Note: Only additional impurities noted are Na^{24}, Sc^{46}. Columns may be re-equilibrated with 2N HCl and re-used for other rocks.

Note: Advantages of procedure include 1) good sensitivity for REE and Ba, 2) minimum handling of "hot" samples since Na, Mn, other major elements are removed prior to irradiation, 3) rapid processing of as many as 8 rocks at one time by one researcher, 4) elimination of re-irradiation technique for chemical yield determination, 5) low (<.1% for BCR-1) blank since only reagents are purified acids.

Appendix IV

BROOKHAVEN NATIONAL LABORATORY

MEMORANDUM

DATE: 8/25/70

TO: Files

FROM: P. F. Palmedo

SUBJECT: The Gamma Spectrum Analysis Code, BRUTAL

The computer code BRUTAL is widely used at BNL for the analysis of gamma ray spectra measured with Ge(Li) detectors. The code as used here was modified by B. R. Erdal from an original code written by Gunnink, Levy and Niday at Livermore. Except for a brief description by Gunnink et al.(1) no detailed description of the code seems to exist. This memo is intended to fill this gap at least partially by describing the procedures followed by that portion of the code used by the Safeguards Group.

This description hopefully avoids unnecessary detail; there are numerous tests for significance, checks for errors, etc. that will not be mentioned. It is hoped, however, that this description will allow the average user of the code to make appropriate use of the rather complete output provided by the code.

Many of the variables and constants used in the FORTRAN version of the code are also used in the output. The code will thus be described using these same variable names. Appendix A provides a list of these names and the page of this memo in which they are mentioned. Appendix B presents a description of the input to the code and, in fact, provides a complete description of the various options available in running the code.

I would appreciate being informed of any corrections or additions to this memorandum.

ANALYS

BTST

The subroutine which performs the actual data analysis is called ANALYS. The first step of the analysis is to calculate a quantity at each point of the spectrum which will indicate the direction and statistical significance of the slope at that point. The quantity is termed BTST and is defined as

$$BTST_i = (y_{i+1} - y_{i-1}) \Big/ \sqrt{(y_{i+1} + y_{i-1})}$$

where y_i is the count at channel i.

WTSIGB(I)

This quantity is used throughout the analysis, being compared with appropriate constants, WTSIGB(I)*. The WTSIGB are internally defined and are part of the print-out. The initial search for possible peaks, for example, is made by looking for points having BTST > WTSIGB(1) followed, within 10 points by a point with BTST < - WTSIGB(1) where, in the current version WTSIGB(1) = 1.4.

ISTART
START
IEND
END
XPK
YPK

Similar criteria are used to define the starting point of a peak, ISTART (printed out as START) and the end of a peak, IEND (or END). Four point interpolations are used to locate both fractional channel number XPK and the total height of the peak, YPK.

WOPT

WOPT is basically the width of the top of a peak, i.e. the number of channels required for the significant positive slope to change to a significantly negative slope. In a Ge(Li) spectrum, for single well-defined peaks (with usual channel widths) WOPT should be 1 or 2. The variable WOPT is also used to "tag" peaks having suspicious characteristics such as excessive width or asymmetry.

---

*For the sake of clarity the nomenclature used in this description corresponds to FORTRAN usage and, in particular that usage in BRUTAL. WTSIGB(I), for example, is a subscripted variable with subscript I. The print-out generally uses the same nomenclature as is used internally in the code.

If the peak is found to be asymmetric 100 is added to WOPT. Asymmetry is defined as existing if

$$1 < |XPK - PKAV| \leq 0.5\ (IEND - ISTART)$$

PKAV

where PKAV = 0.5 (ISTART + IEND).

If the peak is too wide, i.e. if

$$(IEND - ISTART) \geq 15$$

200 is added to WOPT. A peak may be found to be tainted by both these conditions, in which case 300 is added to WOPT. If a peak is too narrow, i.e. if

$$(IEND - ISTART) < 2$$

then XPK is set to zero.

PKGROS

PKGROS is simply the sum of the counts, y, between ISTART and IEND. The background for each peak is found by examining the seven points before ISTART and the seven points following IEND. In each set, the average of the three consecutive points having the lowest sum is chosen as the background. Thus defining BKGD1 (in front)* and BKGD2 (behind the peak)*. The central channel of those used for BKGD1 is termed FORE and the central channel of BKGD2 is termed AFT. These quantities, and related ones, are shown for a peak of a Ge(Li) spectrum in Fig. 1. (the 414 keV peak of a ^{239}Pu sample$^{(2)}$).

BKGD1
BKGD2
FORE
AFT

The background under the peak is assumed to be linear between BKGD1 (at channel FORE) and BKGD2 (at channel AFT). An appropriate amount of background is subtracted from YPK to give the net peak height, PEAKHT. Similarly, the appropriate background under the entire peak, PEAKBGD, is subtracted from PKGROS to give the net counts in the peak, PKNTOT (printed out as NETCTS).

PEAKHT
PEAKBGD
PKNTOT
NETCTS

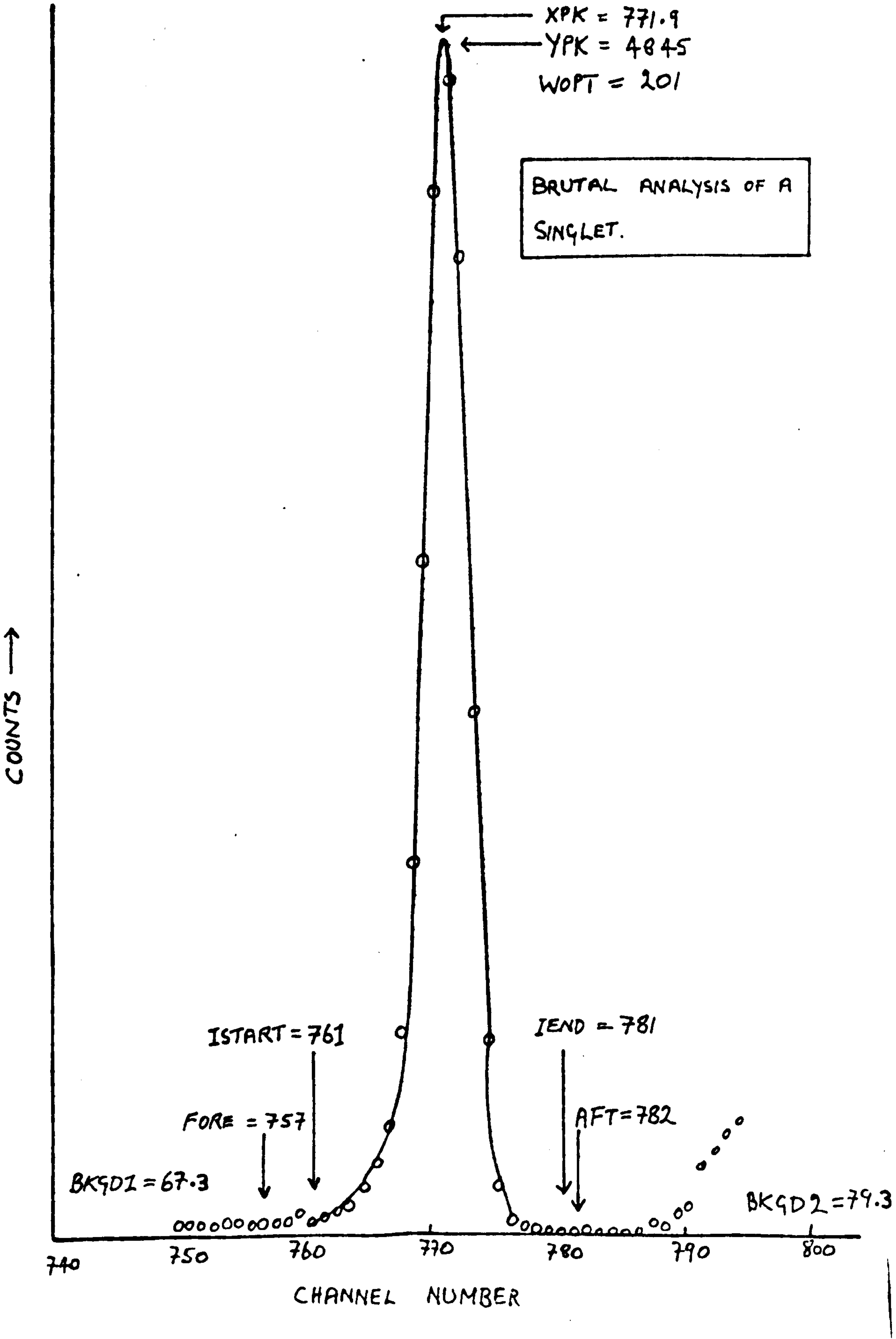
The standard deviation of the net counts in the peak, SIGPNT is defined as

SIGPNT

$$SIGPNT = (PKGROS + PEAKBGD \cdot \frac{R}{3})^{\frac{1}{2}}$$

---

*The front of the peak as implied by BRUTAL is the low energy side.


XPK = 771.9
YPK = 4845
WOPT = 201
BRUTAL ANALYSIS OF A SINGLET.
ISTART = 761
FORE = 757
BKGD1 = 67.3
IEND = 781
AFT=782
BKGD2=79.3
COUNTS →
740
750
760
770
780
790
800
CHANNEL NUMBER

where R is the number of points in the peak. Note that since PEAKBGD is based on the average of six points, the approximation used for the standard deviation of the background is somewhat conservative (overestimating the over-all uncertainty).

CHAN

The significant quantities defined up to this point comprise the third major block of print-out under "Summary of Peaks with Significant Net Totals". Peaks with PKNTOT ≤ 2 x SIGPNT are rejected from this list. The heading CHAN obviously refers to XPK.

REPEAK

At this point the subroutine REPEAK is used to fit a Gaussian to each peak to more accurately define its characteristics. The fit is made to points on the front of the peak within 0.3 of the peak height and at the rear of the peak within 0.2 of the peak height.

PNTS

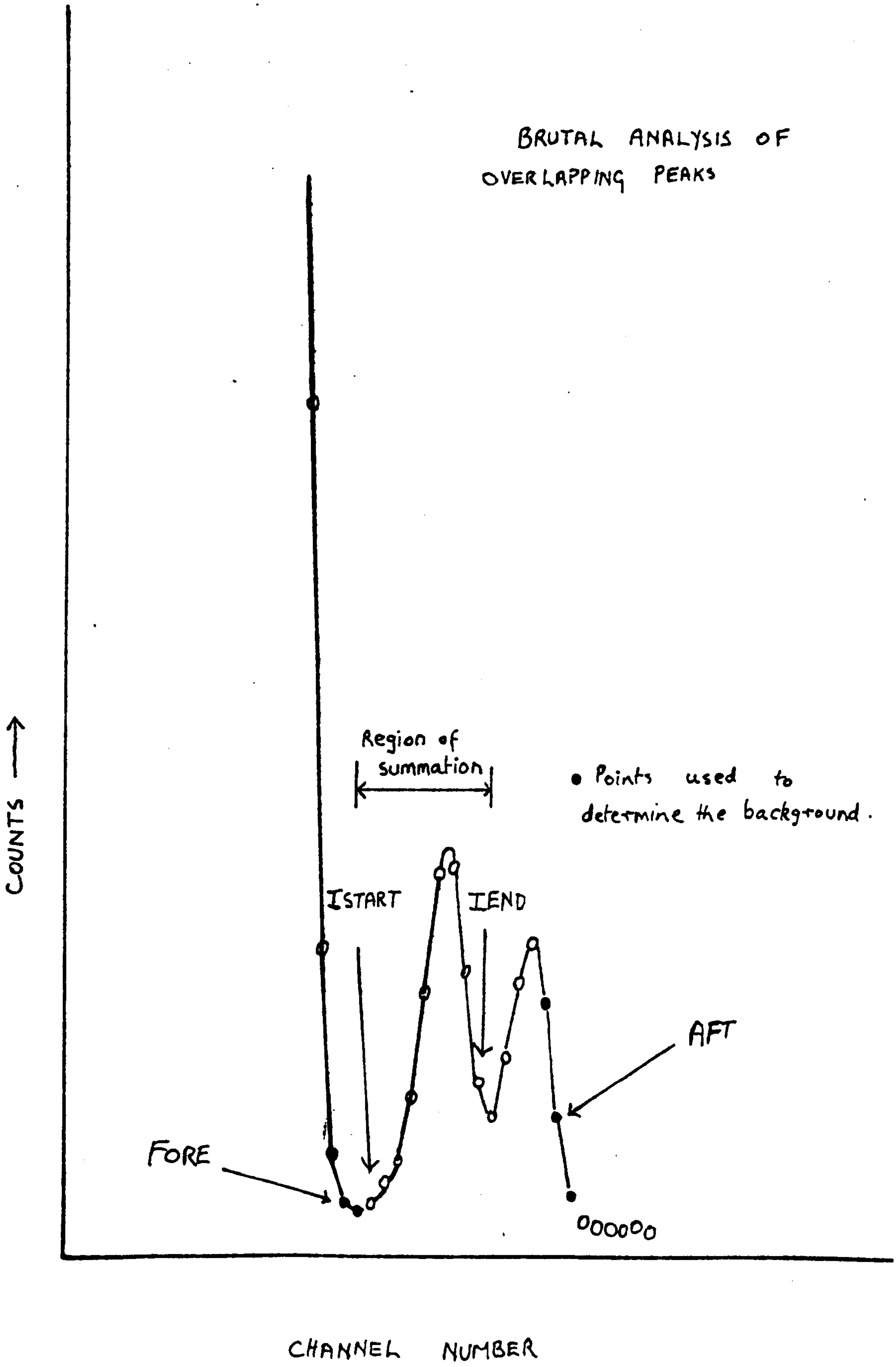
CHANNEL

SIGXPK
PCTERR

FWHM

The number of points used, PNTS, is included in the next block of print-out. If the peak is too broad (having more than thirty points within the limits described) or asymmetric (having no points to one side) PNTS is set to 0. PNTS is set to -1 if the fitted σ of the Gaussian is non-positive. Also included in this print-out is the new (fitted) channel number (fractional) of the peak center, XPK (printed out as CHANNEL). If no fit is made, XPK is left at its previously determined value. The uncertainties, both the absolute standard derivation, SIGXPK, and the percentage σ, PCTERR, of the fitted XPK are also printed out. The quantities A, B and O are intermediate parameters of the fit whereas FWHM, not unexpectedly, is the FWHM of the peak defined as 2.354 x the fitted σ.

Although under certain circumstances the results calculated by BRUTAL up to this point may be useful, their limitations should be recognized. In particular, the method of calculating the background under a peak is subject to large error. For example, Figure 2 shows the preliminary analysis of the 380 keV peak in the same ^{239}Pu spectrum shown in part in Fig. 1(2). The peak is summed from channel 683 to channel 692. The background points, shown as full circles in the figure, are seen to be inaptly chosen. In this case the criteria for the choice of background points described above are inadequate.


BRUTAL ANALYSIS OF OVERLAPPING PEAKS
COUNTS →
Region of summation
• Points used to determine the background.
ISTART
IEND
AFT
FORE
000000
CHANNEL NUMBER

The difficulty is due, of course, to the peak in question not being sufficiently isolated from its two neighboring peaks. Even the gross count is affected by the neighboring peaks, particularly that at 382.8 keV.

MULTIPLE PEAKS

MULTPK
ODGROS
XST
XND
ODBKGD

The next section of the code is devoted to solving this difficulty by considering overlapping peaks. The subroutine involved is MULTPK. It first seeks doublets which are defined as two peaks, N and N+1 in which the starting channel of peak N+1 [ISTART (N+1)] is within five channels of the final channel of peak N [IEND (N)]. Some of the variables used are shown in Figure 3. The total counts in the doublet, ODGROS is summed between the beginning of the first peak, at channel XST, and the end of the second peak, at channel XND. The total background of the doublet, ODBKGD, is based on the background in front of peak N, BKGD1(N) and that behind peak N+1, BKGD2(N+1), and the total number of channels in the doublet. The net counts in the doublet is then defined as

ODNTOT

$$ODNTOT = ODGROS - ODBKGD.$$

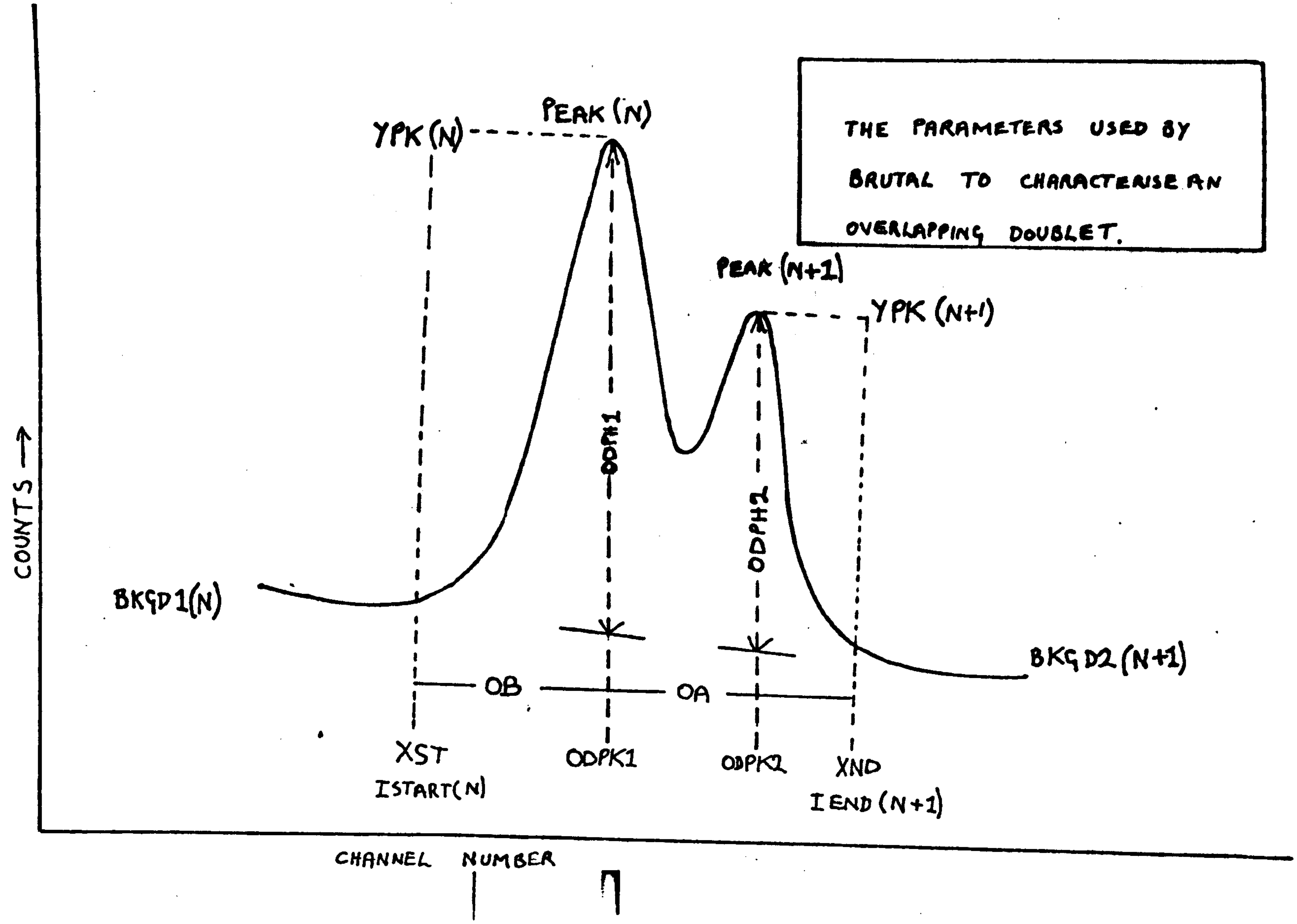
ODPNT1
ODPNT2
SGDPN1
SGDPN2

The net peak heights are then recalculated assuming that the background is linear between BKGD1(N) and BKGD2(N+1).* The total net counts in the doublet are then distributed to the two peaks proportional to the net peak heights. These net counts are termed ODPNT1 and ODPNT2. The uncertainties (actually the standard deviations) of these quantities are also calculated and are printed out as SGDPN1 and SGDPN2.

The code then proceeds to look for triplets. All of the peaks found in the first part of the analysis are examined once more. A triplet is defined as three peaks in which the beginning [ISTART(N+1)] of the second peak is within five channels of the end of the first [IEND(N)] and the beginning of the third [ISTART(N+2)] is within five channels of the end of the second [IEND(N+1)].

---

*An adequate assumption is made here that BKGD1(N) occurs at the same distance to the left of XST as BKGD2(N+1) occurs to the right of XND. See Fig. 3.



THE PARAMETERS USED BY BRUTAL TO CHARACTERISE AN OVERLAPPING DOUBLET.

Missing pages are unavailable

The analysis proceeds completely analogously to that for doublets. Again the background is assumed to be linear between the front of the first peak and the back of the third, and the total net counts under the triplet are apportioned to the peaks in proportion to the net peak heights.* The terminology is as defined above for doublets with D replaced by T in the variable names (ODPNT1, 2 becomes OTPNT1, 2, 3, etc.).

PKCTS

As currently dimensioned, the code will analyze up to 150 triplets, 200 doublets and 300 singlets. A given peak may find itself appearing in six different analyses: as a singlet, in two possible positions in a doublet, and in three possible positions in a triplet. In establishing its final list of peaks, BRUTAL choses that appearance of a peak in which it has the largest net total counts, and the variable name PKCTS is assigned to that quantity. This criterion is reasonable given the possibility of overestimating the background (see Figure 2), but each particular case should be checked for its applicability.

NUMPTS

TYPE

The "Final Summary of Peaks with Significant Net Totals" presents the selected peaks. CHANNEL refers to the peak position as determined by the Gaussian fit if one was made. NUMPTS is number of points used in that fit, referred to above as PNTS. Under the heading TYPE is specified whether the appearance of a peak as a singlet (S), in a doublet (D) or in a triplet (T) has been selected for this final summary.

The last two entries in this table, KEV and INTENSITY, are calculated optionally, as described below.

---

*It should be pointed out that there is an error in one statement in at least one version of BRUTAL at this point; Statement MLPK-176 (the second statement following 111 in Subroutine MULTPK) should read:

```
PB3 = (BKGD1(N) * OA + BKGD2 (N+2) * OB)/DIST
```

THE ENERGY CALIBRATION

IEN

If the input quantity IEN is set = 1, energies are assigned to the various peaks found above in one of two ways. If the input quantity IFIT is set = 1, the coefficients of the equation

$$E = a_1 + a_2c + a_3c^2 + a_4c^3$$

AA(I)

are specified in the input. E is the energy of channel c and the a_i are the input quantities AA(I) (see Appendix B). If IFIT = 0, the AA(I) of the previous case are used again.

FINDE

Alternatively, for IFIT = 2, 3, or 4, certain peaks (up to 20) are preselected as calibration peaks and assigned energies and approximate channel numbers in the input. The code (in subroutine FINDE) then locates the peak which is closest to each channel number and assigns it the corresponding energy. A least-squares fit is then performed to a [straight line] (if IFIT = 2), a second order (IFIT = 3) or a third order (IFIT = 4) polynominal, whose coefficients are again AA(I).

STD ENERGY
EXPK
CALCD ENERGY
DELTA E

The output at this point (which occurs before the "Final Summary") includes the coefficients of the fit, the input energies (STD ENERGY), and channel numbers (CHANNEL), the fit energies (EXPK, printed out as CALCD ENERGY) and the absolute difference between the input channel number and the channel number that had been assigned by BRUTAL, XPK (DELTA E).

PEAK INTENSITIES

The final calculation performed by the code (in subroutine FINDE), if the option is selected, is the determination of the intensities (relative or absolute) of the various peaks. Since the calculation involves the energies of the peaks, this option can be used only if the energies have been calculated as described above.

RLEF

The first step is to assign a detection efficiency, RLEF, to each peak on the basis of energy-efficiency data read in to the code. The input is in the form

EFEN(I) XRLEF(I)	of pairs of data: energy, EFEN(I) and the efficiency (relative or absolute), XRLEF(I) at that energy. (Efficiencies of unity may be specified by setting INTS = 2). A linear interpolation is performed between these data points; the peaks below EFEN(I) and above the maximum EFEN are assigned an efficiency of zero.

The intensity of each peak is then calculated on the basis of the net number of counts under the peak (PKCTS) and the efficiency. For those peaks who have been assigned an efficiency of zero, the intensities are set = -1.

BRUTAL will then proceed to the next spectrum to be analyzed.

References

(1) R. Gunnink, H. B. Levy and J. B. Niday, "Identification and Determination of Gamma Emitters by Computer Analysis of Ge(Li) Spectra" UCID-15140, presented at the American Chemical Society's Symposium on Nuclear Methods of Chemical Analysis, April 10-14, 1967.

(2) Memorandum of August 7, 1970 from P. F. Palmedo and R. Sher to W. A. Higinbotham on the subject of gamma and neutron measurements on PNC (Pu) plates.

Example of final output table produced by the program MEGRASPEC

```
SAMPLE IS   .IC830 LABELLED #23
*********************************************************************************************************
FINAL SUMMARY OF PEAKS WITH SIGNIFICANT NET TOTALS

INDEX   CHANNEL    KEV     NET AREA    STD DEV    SIGMA    TYPE    PEAKHT     INTENSITY      GAUSS FIT    WIDTH
  1     188.916   80.664   30312.8     1055.0      3.48     D      5014.3 *     0.000            0          20
  2     204.603   87.228   47148.4     1388.6      2.95     T      8279.8 *     0.000            0          18
  3     214.823   91.478   35824.2     1199.3      3.35     T      6688.7 *     0.000            0           7
  4     223.130   94.932   26469.2     1107.0      3.89     T      5315.4       0.000            4           8
  5     231.934   98.593   55580.0     1382.8      2.49     T     11913.5       0.000            4          11
  6     243.566  103.429   30800.7      935.7      3.04     T      6602.1       0.000            4          12
  7     260.441  110.446   67467.4     1181.5      1.75     D     12313.4       0.000            3          13
  8     268.043  113.608   89348.3     1397.2      1.56     D     16306.8       0.000            3          12
  9     279.641  118.430    4471.1      580.9     12.99     T       829.7       0.000            3           6
 10     289.194  122.403   15569.0      655.0      4.21     S      3228.1       0.000            2          15
 11     309.619  130.296   38253.8      614.4      1.61     D      9322.2 *     0.000            0          13
 12     316.501  133.757  156067.5     1480.4      0.95     D     38032.6       0.000            4          13
 13     345.034  145.622  325776.9     1076.7      0.33     S     76562.0       0.000            4          25
 14     378.776  159.653    4700.5      525.3     11.17     S       762.3       0.000            6          16
 15     394.847  166.335    1575.0      328.0     20.82     S       319.0       0.000            6          10
 16     421.919  177.592   53915.5      715.8      1.33     S     12927.4       0.000            4          24
 17     471.591  198.247   87296.2      675.5      0.77     S     19345.6       0.000            5           8
 18     496.752  208.709   59756.8     1083.0      1.81     D     14882.6       0.000            4          23
 19     514.361  216.032   10058.2      339.4      3.37     D      2505.0       0.000            5          19
 20     540.031  226.706    2372.8      319.9     13.48     S       267.8       0.000            9          12
 21     570.815  239.506     897.0      226.7     25.27     S       200.8       0.000            5          13
 22     583.917  244.954    3502.6      452.4     12.92     D       635.2 *     0.000            0           6
 23     591.183  247.976    3639.4      334.7      9.20     S       482.8       0.000            9           9
 24     622.893  261.161    3115.2      249.1      8.00     S       715.5       0.000            5           6
 25     658.173  275.872     400.1      191.0     47.74     D        97.0 *     0.000            0          14
 26     674.578  282.653   13902.2      684.1      4.92     D      3371.1       0.000            4          11
 27     713.622  298.888   48425.0     1012.3      2.09     D      9038.8       0.000            7           3
 28     735.213  307.866   16082.7      370.2      2.30     D      3747.9       0.000            4           6
 29     745.261  312.044   67714.0      915.1      1.35     D     15779.9       0.000            4          16
 30     765.051  320.273    4907.5      290.3      5.92     S       881.7       0.000            7           8
 31     785.864  328.928    2584.9      225.9      8.74     S       602.3       0.000            4           3
 32     813.975  340.617    6548.2      362.5      5.54     D      1654.4       0.000            4          20
 33     823.221  344.462    5256.2      310.4      5.90     D      1327.9       0.000            3          12
 34     892.825  373.405     717.8      189.6     26.41     D       217.6 *     0.000            0          15
 35     897.934  375.529    1029.0      164.4     14.03     S       257.4       0.000            5          15
 36     939.773  392.926    2388.6      212.7      8.91     T       504.9 *     0.000            0          12
 37     948.363  396.498   22753.0      657.7      2.89     D      4795.1       0.000            5           9
 38     984.500  411.525     415.5      160.6     38.66     T       304.3 *     0.000            0          12
```

Appendix V

Ferrous iron

Ferrous iron was determined by taking the rock powder into solution followed by titration with ceric sulphate.

About 0.2 g of 240 mesh rock powder was digested with a HF/50% H_2SO_4 mixture. Where it was necessary to dilute or dissolve reagents, boiled distilled water was used. This practice ensured that dissolved oxygen would not introduce errors.

Digestion was carried out on a hot-plate at 180° C for 5 mins. The solution was transferred to a beaker containing 100 cm^3 of boric acid solution. This served to complex any excess HF.

This solution was titrated with ceric sulphate using "Ferroin" indicator (1, 10-phenanthroline ferrous complex).

Sample	% FeO	Sample	% FeO
CYLL	2.34	OG1	1.09
G1	1.90	OG2	1.18
IC42	2.17	OG3	1.29
G2	4.39	BC1	3.18
MN1	2.75	BC2	1.83
MN2	2.60	BC3	0.45
C.Bach	2.19	BC4	0.17
C.Bod.	3.93	BC5	1.10
YYF	0.39	BC6	0.89
YFA	0.22	BC7	0.98
YFB	0.36	BC8	0.63
YFC	1.76	TG3	1.73
DR1	3.96	TG4	1.16
DR2	3.75	TG6	1.77
MW1	3.54	MM1	0.48
GN1	2.97	MM3	0.31
FF1	4.06	MM4	0.97
FF2	4.43	MM6	0.37
FF3	3.93	MM2	0.82
GI1	8.76	MB1	4.64
CI2	7.95	MB2	4.90
PYG	5.71	MB6	4.99
PYG	8.11	FG1	1.84
MP1	3.31	X	1.36
MP2	3.16		
MP3	3.03		

Appendix VI

Sample Locations

Sample	Intrusion	Locality	Grid Ref.
TG11	Tan-y-Grisiau	Ty Newydd	695447
TG12	"	Cwm Bowydd	697453
TG13	"	"	697453
TYG1	"		696453
TG14	"	Cwm Bowydd	698453
TG6	"		689444
TG3	"	Moel Ystradau	683441
TG4	"	"	684441
BC1	Bwlch-y-Cywion		636607
BC2	"		636604
BC3	"	Bwlch-y-Cywion	629606
BC4	"		629606
BC5	"		629607
BC6	"		629607
BC7	"		629608
BC8	"	Y Llymllwyd	631609
BC22	"	"	636606
BC20	"	"	637605
CAS1	Castell	Clogwyn Coch	638478
CAS2	"	"	638477
CAS3	"	"	638477
CAS4	"	"	638478
NGWY	Nant Gwynant	Clogwn Melyn	625506
COMP1	Croesor Composites	Garth Llwynog	631450
COMP2	"	"	632450
COMP3	"	Ffynion Helen	631449
COMP4	"	Cae-glas	628447
COMP5	"	"	629448
COMP6	"	"	628447
COMP7	"	"	628446
OG1	Ogwen		654605
OG2	"		654605
OG9	"		654606
OG10	"		656607
IC15	Manod Bach	Manod Quarry	71344
IC16	"	"	71244
MB1	"	"	71344
MB2	"	"	71444
MB3	"	"	70944
DR1	Drosgl		659685
DR2	"		659686
DR3	"		660686
PM1	Penmaenmawr		705755
PM2	"		705755
PM3	"		704756
PM4	"		706754
PMA	"		706754
PMB	"		697757

Sample	Intrusion	Locality	Grid Ref.
PMC	Penmaenmawr		698748
PMD	"		698747
PME	"		707753
PMF	"		707752
PMBT1	"		700762
PMBT2	"		700762
PMGDL	"		697755
PMDGL	"		697755
NANB1	Nant Bodlas	Inkerman Bridge Quarry	287329
NANB2	"	"	287329
Foel G	Foel Gron	Foel Gron Quarry	301309
IC38	Nant Bodlas	Inkerman bridge	287329
IC39	"	"	287329
LBG1	Llanbedrog	Tan-y-Mynydd Quarry	326305
IC37	"	Tir-y-Cwmwd	329309
IC37	"	"	329309
YFA	Yr Eifl	Tre'r Ceiri	375444
YFB	"	"	374443
Y YF	"	Graig Ddu	355442
IC46	"	Tre'r Ceiri	375443
IC50	Garnfor	Quarry	362461
Garn 1	"	"	351456
Garn 2	"	"	352457
Garn 3	"	"	352453
G1	"	"	356454
G2	"	"	362457
IC42	"	"	361459
G4	"	"	362459
PAND 1	Moel-y-Penmaen		338387
PAND 2	"		"
PAND 3	"		"
PAND 4	"		"
YFC	Yr Eifl Microgranite	Tre'r Ceiri	374446
CFAD	Carn Fadryn	Garn	280348
	Carn Bach	Pen-y-caerau	288345
CBOD	Carn Bodfearn	Tyn-y-Mynydd	317390
XXX	Carn Saethon		299339
IC30	Carreg-y-Llam	Carreg-y-Llam Quarry	337437
IC31	"	"	335438
IC33	"	"	336437
CYLL	"	"	335438
PBodH	Penrhyn Bodeilias	Tir Bach	318421
PBodX	"	"	318422
IC34	Mynydd Nefyn	Ty-Gwyn	334016
MN1	"		323415
MN2	"		335405
IC44	Pistyll	Cefnydd	331425
Moel P	Moel Penlechog		386459

Sample	Intrusion	Locality	Grid Ref.
G Ddu 1	Gurn Ddu	Quarries	399470
G Ddu 2	"	"	398469
G Goch	Gyrn Goch	Gyrn Goch	406476
YGN	Y Garn		551527
YGN	"		552527
TYM	Tal-y-Mignedd		545527
MP1	Moel Perfedd		623620
MP2	"		623621
MP3	"		623621
FF1	Foel Fras	Berra Mawr	674683
FF2	"	"	674685
FF2	"		675684
FF4	"		675687
MN1	Moel Wnion		650697
GN1	Gyrn	Summit	648688
GN2	"	"	648688
MM1	Mynydd Mawr	Afon Goch	550552
MM2	"	Cwm Planwydd	547546
MM4	"	"	547547
MM6	"	"	547548
MMA	"	Craig-y-Bera	545542
MMB	"		544542
MMD	"		542542
MME	"		541542
Llangybi	Llangybi	Carn Penyrch	424418
PYG1	Pen-y-Gwryd	Moel Berfedd	653557
PYG2	"	"	653558
CT1	Cader Idris	Llynan Crogenen	

Appendix VII

Chondrite normalising values (p.p.m.)

La	0.325
Ce	0.798
Nd	0.567
Sm	0.186
Eu	0.069
Tb	0.047
Yb	0.209
Lu	0.035
Y	1.96

Data from Kay and Gast (1973)

SAMPLE	TG11	TG12	TG13	TYG1	TG14	TG6	TG3	TG4
SIO2	71.3	68.5	73.0	76.0	72.2	74.0	74.7	74.3
TIO2	0.24	0.46	0.27	0.24	0.26	0.27	0.23	0.27
AL2O3	15.0	15.0	15.0	13.7	14.6	13.7	13.8	13.7
TFE2O3	3.69	4.27	2.44	2.79	3.16	3.01	2.90	2.80
MNO	0.25	0.31	0.23	0.21	0.17	0.13	0.14	0.13
MGO	0.39	0.63	0.32	0.38	0.38	0.22	0.18	0.20
CAO	2.70	3.87	1.51	0.03	1.78	0.32	0.02	0.05
NA2O	3.65	4.15	5.26	3.14	4.41	4.12	3.70	3.84
K2O	2.16	2.28	1.65	3.94	2.02	4.69	5.18	4.85
P2O5	0.05	0.11	0.04	0.04	0.05	0.04	0.03	0.04
TOTAL	99.27	99.38	99.64	100.32	98.90	100.34	100.74	100.06
AGPAITIC COEFF.	0.56	0.62	0.66	0.77	0.64	0.95	0.96	0.94
TRACE ELEMENTS IN PPM								
CR	0	0	0	0	0	0	0	0
NI	0	0	0	0	0	0	0	0
SR	49	47	49	68	70	36	30	33
BA	734	274	240	508	272	971	897	917
RB	69	84	57	72	61	171	164	147
Y	50	89	58	46	40	49	79	103
LA	118	24	58	36	12	35	50	35
CE	204	60	109	68	26	74	115	73
ND	86	37	51	29	14	37	54	38
ZR	174	493	222	190	192	275	285	335
NB	11	20	13	12	12	20	22	23
TH	18	14	22	21	18	20	18	17
PB	7	14	13	7	6	16	9	19
ELEMENT RATIOS								
K2O/NA2O	0.6	0.5	0.3	1.3	0.5	1.1	1.4	1.3
K/RB	260.	225.	240.	454.	275.	228.	262.	274.
(CE/Y)N	10.0	1.7	4.6	3.6	1.6	3.7	3.6	1.7
ZR/NB	15.8	24.6	17.1	15.8	16.0	13.7	13.0	14.6
ZR/Y	3.5	5.5	3.8	4.1	4.8	5.6	3.6	3.3
TH/NB	1.6	0.7	1.7	1.7	1.5	1.0	0.8	0.7
NB/Y	0.2	0.2	0.2	0.3	0.3	0.4	0.3	0.2
CIPW NORMS								
Q	34.8	26.4	32.0	41.2	34.1	30.3	32.1	32.4
C	1.9	0.0	1.9	4.3	2.1	1.4	2.2	2.2
OR	12.9	13.6	9.8	23.2	12.1	27.6	30.4	28.6
AB	31.1	35.3	44.7	26.5	37.7	34.7	31.1	32.5
AN	13.2	15.7	7.3	0.0	8.6	1.3	0.0	0.0
DI	0.0	2.6	0.0	0.0	0.0	0.0	0.0	0.0
HY	3.4	2.9	2.3	2.7	2.9	2.2	2.2	2.1
MT	2.2	2.6	1.5	1.7	1.9	1.8	1.7	1.7
ILM	0.5	0.9	0.5	0.5	0.5	0.5	0.4	0.5
AP	0.1	0.3	0.1	0.1	0.1	0.1	0.1	0.1
ACM	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

SAMPLE	BC1	BC2	BC3	BC5	BC6	BC7	BC8	BC22
SIO2	70.1	70.3	71.1	71.3	73.3	71.6	75.0	72.3
TIO2	0.69	0.41	0.45	0.40	0.37	0.37	0.40	0.43
AL2O3	14.7	14.7	16.2	16.2	15.0	15.4	14.4	14.7
TFE2O3	5.45	4.01	1.11	2.09	1.59	2.11	1.27	2.22
MNO	0.18	0.16	0.10	0.11	0.12	0.13	0.12	0.13
MGO	0.64	0.51	0.35	0.64	0.57	0.42	0.37	0.49
CAO	0.18	0.01	0.09	0.03	0.04	0.09	0.04	0.22
NA2O	4.48	3.00	6.90	4.73	4.59	3.85	5.16	4.54
K2O	4.27	5.79	3.18	5.23	5.14	6.20	4.11	4.72
P2O5	0.16	0.06	0.06	0.05	0.05	0.06	0.05	0.06
TOTAL	100.51	98.81	99.48	100.66	100.71	100.15	100.85	99.76
AGPAITIC COEFF.	0.88	0.90	0.90	0.91	0.96	0.98	0.95	0.93
TRACE ELEMENTS IN PPM								
CR	0	0	0	0	0	0	0	0
NI	0	0	0	0	0	0	0	0
SR	29	35	98	40	39	57	60	46
BA	752	788	546	706	590	590	570	687
RB	122	187	96	144	129	156	100	119
Y	54	52	38	53	59	43	41	59
LA	34	38	54	31	52	22	59	46
CE	87	79	98	56	29	43	130	93
ND	30	34	41	27	33	22	42	40
ZR	268	288	437	347	301	317	376	304
NB	20	18	19	17	17	19	19	22
TH	28	29	32	33	32	34	44	28
PB	13	8	4	6	4	7	4	3
ELEMENT RATIOS								
K2O/NA2O	1.0	1.9	0.5	1.1	1.1	1.6	0.8	1.0
K/RB	290.	257.	275.	301.	331.	330.	341.	329.
(CE/Y)N	4.0	3.7	6.3	2.6	1.2	2.5	7.8	3.9
ZR/NB	13.4	16.0	23.0	20.4	17.7	16.7	19.8	13.8
ZR/Y	5.0	5.5	11.5	6.5	5.1	7.4	9.2	5.2
TH/NB	1.4	1.6	1.7	1.9	1.9	1.8	2.3	1.3
NB/Y	0.4	0.3	0.5	0.3	0.3	0.4	0.5	0.4
CIPW NORMS								
Q	25.5	29.5	18.3	22.4	25.7	24.4	28.4	26.5
C	2.8	3.7	1.4	2.8	2.0	2.3	1.5	1.9
OR	25.1	34.6	18.9	30.7	30.2	36.6	24.1	28.0
AB	37.7	25.7	58.7	39.8	38.6	32.5	43.3	38.5
AN	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.7
DI	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
HY	4.2	3.5	1.0	2.4	2.0	2.0	1.3	2.2
MT	3.2	2.4	0.7	1.2	0.9	1.3	0.8	1.3
ILM	1.3	0.8	0.9	0.8	0.7	0.7	0.8	0.8
AP	0.4	0.1	0.1	0.1	0.1	0.1	0.1	0.1
ACM	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

SAMPLE	BC22	BC20	CAS1	CAS2	CAS3	CAS4	NGWY	COMP1
SIO2	71.9	67.2	73.2	73.2	73.2	73.0	73.2	73.3
TIO2	0.43	0.99	0.28	0.28	0.29	0.28	0.37	0.40
AL2O3	14.4	13.7	14.2	13.7	13.7	13.7	13.6	13.9
TFE2O3	2.23	5.84	1.86	2.10	2.36	2.20	3.13	2.98
MNO	0.13	0.23	0.16	0.11	0.15	0.17	0.09	0.15
MGO	0.54	1.27	1.64	1.14	1.46	1.28	1.11	0.30
CAO	0.23	1.91	0.50	0.20	0.30	0.20	0.30	0.75
NA2O	4.63	7.20	1.48	3.09	2.76	1.63	2.68	3.49
K2O	4.65	0.75	6.70	5.60	6.60	6.70	5.80	5.61
P2O5	0.07	0.26	0.03	0.03	0.03	0.03	0.05	0.06
TOTAL	99.05	98.96	99.94	99.40	100.69	99.08	100.18	100.77
AGPAITIC COEFF.	0.96	0.82	0.88	0.95	1.03	0.93	0.94	0.98
TRACE ELEMENTS IN PPM								
CR	0	0	0	0	0	0	0	0
NI	0	0	0	0	0	0	0	0
SR	47	60	57	44	80	37	78	59
BA	661	53	1159	518	981	928	935	683
RB	121	30	232	173	154	193	212	260
Y	58	50	52	60	65	56	49	68
LA	45	42	34	34	47	39	48	46
CE	92	84	64	72	96	82	90	98
ND	40	38	30	31	41	36	36	42
ZR	305	261	387	413	429	409	257	394
NB	22	21	18	20	20	17	13	21
TH	29	22	30	32	31	25	39	29
PB	6	10	5	10	6	6	21	26
ELEMENT RATIOS								
K2O/NA2O	1.0	0.1	4.5	1.8	2.4	4.1	2.2	1.6
K/RB	319.	207.	240.	269.	356.	288.	227.	179.
(CE/Y)N	3.9	4.1	3.0	2.9	3.6	3.6	4.5	3.5
ZR/NB	13.9	12.4	21.5	20.6	21.4	24.1	19.8	18.8
ZR/Y	5.3	5.2	7.4	6.9	6.6	7.3	5.2	5.8
TH/NB	1.3	1.0	1.7	1.6	1.6	1.5	3.0	1.4
NB/Y	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.3
CIPW NORMS								
Q	25.9	17.3	35.1	31.5	28.3	35.4	32.5	28.7
C	1.5	0.0	3.7	2.3	1.5	3.5	2.5	0.9
OR	27.7	4.5	39.6	33.3	38.7	40.0	34.2	32.9
AB	39.6	61.6	12.5	26.3	23.2	13.9	22.6	29.3
AN	0.7	2.9	2.3	0.8	1.3	0.8	1.2	3.3
DI	0.0	4.1	0.0	0.0	0.0	0.0	0.0	0.0
HY	2.3	3.7	5.1	3.9	4.9	4.5	4.3	2.2
MT	1.3	3.5	1.1	1.3	1.4	1.3	1.9	1.8
ILM	0.8	1.9	0.5	0.5	0.5	0.5	0.7	0.8
AP	0.2	0.6	0.1	0.1	0.1	0.1	0.1	0.1
ACM	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

```
 SAMPLE       COMP2  COMP3  COMP4  COMP5  COMP6  OG1    OG2    OG9

 SIO2        73.4   73.6   69.8   74.6   70.2   71.4   72.1   71.9
 TIO2         0.37   0.38   0.58   0.40   0.53   0.35   0.36   0.38
 AL2O3       13.8   14.1   14.4   13.8   14.7   13.8   14.2   14.4
 TFE2O3       3.07   2.76   6.01   2.72   4.70   2.50   2.57   2.53
 MNO          0.16   0.21   0.31   0.19   0.30   0.17   0.13   0.12
 MGO          0.27   0.28   0.78   0.31   0.50   0.69   0.72   0.95
 CAO          0.70   0.71   0.35   0.11   0.28   1.19   0.70   0.07
 NA2O         3.46   2.99   2.79   3.39   3.02   3.29   3.32   3.33
 K2O          5.63   5.72   4.36   5.51   5.57   5.75   5.82   5.35
 P2O5         0.05   0.05   0.12   0.05   0.11   0.05   0.05   0.05

 TOTAL      100.75 100.65  99.13 100.93  99.65  99.10  99.84  98.97
AGPAITIC      0.99   0.93   0.75   0.97   0.88   0.98   0.97   0.90
COEFF.

TRACE ELEMENTS IN PPM
 CR             0      0      0      0      0      0      0      0
 NI             0      0      0      0      0      0      0      0
 SR            56     90     42     68     49     62     59     56
 BA           695    857    805    748    961    598    644    668
 RB           263    243    156    222    190    218    225    193
 Y             69     68     71     38     68     54     53     56
 LA            46     43     44     22     59     43     44     56
 CE            94     79     81     85    112     82     84    100
 ND            40     38     38     20     52     36     37     45
 ZR           398    400    365    397    508    366    368    375
 NB            20     16     14     13     20     18     18     18
 TH            33     31     26     33     29     31     34     32
 PB            25     17     32     28     10     26     19     20

ELEMENT RATIOS
K2O/NA2O      1.6    1.9    1.6    1.6    1.8    1.7    1.8    1.6
 K/RB       178.   195.   232.   206.   243.   219.   215.   230.
 (CE/Y)N      3.3    2.9    2.8    5.5    4.0    3.7    3.9    4.4
 ZR/NB       19.9   25.0   26.1   30.5   25.4   20.3   20.4   20.8
 ZR/Y         5.8    5.9    5.1   10.4    7.5    6.8    6.9    6.7
 TH/NB        1.6    1.9    1.9    2.5    1.4    1.7    1.9    1.8
 NB/Y         0.3    0.2    0.2    0.3    0.3    0.3    0.3    0.3

CIPW NORMS
 Q           29.0   31.7   34.1   32.3   29.2   26.5   27.6   30.4
 C            0.9    1.8    4.8    2.1    3.4    0.2    1.3    3.2
 OR          33.0   33.6   26.0   32.3   33.0   34.3   34.4   31.9
 AB          29.1   25.1   23.8   28.4   25.6   28.1   28.1   28.5
 AN           3.1    3.2    1.0    0.2    0.7    5.6    3.2    0.0
 DI           0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
 HY           2.3    2.2    5.4    2.2    3.9    3.1    3.1    3.6
 MT           1.8    1.6    3.6    1.6    2.8    1.5    1.5    1.5
 ILM          0.7    0.7    1.1    0.8    1.0    0.7    0.7    0.7
 AP           0.1    0.1    0.3    0.1    0.3    0.1    0.1    0.1
 ACM          0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
```

SAMPLE	0G10	IC15	IC16	MB1	MB2	MB3	DR1	DR2
SIO2	72.7	65.3	69.0	64.9	65.3	63.6	63.9	65.3
TIO2	0.38	1.09	1.00	1.09	1.23	1.21	1.08	1.03
AL2O3	14.6	13.6	12.5	12.8	13.2	13.0	14.2	14.3
TFE2O3	2.60	6.50	5.18	6.66	7.31	7.52	6.87	6.44
MNO	0.11	0.30	0.29	0.19	0.19	0.15	0.22	0.21
MGO	1.02	1.64	1.18	1.38	1.54	1.88	1.97	1.80
CAO	0.03	4.07	4.78	3.85	2.54	3.45	3.27	3.83
NA2O	3.30	4.70	4.95	5.21	5.19	5.07	4.54	4.33
K2O	5.06	1.08	0.82	1.78	1.46	1.84	2.54	2.99
P2O5	0.05	0.28	0.27	0.29	0.28	0.30	0.28	0.28
TOTAL	99.73	98.11	99.62	97.83	97.84	97.58	98.49	100.10
AGPAITIC COEFF.	0.86	0.61	0.66	0.78	0.72	0.77	0.73	0.75
TRACE ELEMENTS IN PPM								
CR	0	0	0	0	0	0	5	5
NI	0	0	0	0	0	0	4	3
SR	55	100	109	125	96	117	170	164
BA	646	211	157	626	502	649	874	684
RB	173	32	25	71	35	41	75	132
Y	58	54	54	59	62	60	61	61
LA	61	24	26	28	30	30	29	31
CE	119	47	53	58	61	60	62	65
ND	50	26	30	31	33	32	38	36
ZR	371	299	276	293	295	305	322	325
NB	19	15	10	11	11	12	16	18
TH	31	7	8	4	8	8	11	12
PB	12	13	7	2	5	3	12	22
ELEMENT RATIOS								
K2O/NA2O	1.5	0.2	0.2	0.3	0.3	0.4	0.6	0.7
K/RB	243.	280.	272.	208.	346.	372.	281.	188.
(CE/Y)N	5.0	2.1	2.4	2.4	2.4	2.5	2.5	2.6
ZR/NB	19.5	19.9	27.6	26.6	26.8	25.4	20.1	18.1
ZR/Y	6.4	5.5	5.1	5.0	4.8	5.1	5.3	5.3
TH/NB	1.6	0.5	0.8	0.4	0.7	0.7	0.7	0.7
NB/Y	0.3	0.3	0.2	0.2	0.2	0.2	0.3	0.3
CIPW NORMS								
Q	32.2	23.8	27.6	19.8	22.2	18.5	18.4	18.7
C	3.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
OR	30.0	6.5	4.9	10.8	8.8	11.1	15.2	17.7
AB	28.0	40.5	42.0	45.1	44.9	44.0	39.0	36.6
AN	0.0	13.0	9.5	6.6	8.7	7.4	11.0	10.7
DI	0.0	4.7	10.3	9.1	1.9	6.7	3.0	5.2
HY	3.8	4.8	0.1	1.9	6.0	4.7	6.6	4.7
MT	1.6	3.9	3.1	4.1	4.5	4.6	4.2	3.8
ILM	0.7	2.1	1.9	2.1	2.4	2.4	2.1	2.0
AP	0.1	0.7	0.6	0.7	0.7	0.7	0.7	0.7
ACM	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

SAMPLE	DR3	PM1	PM2	PM3	PM4	PMA	PMB	PMC
SIO2	64.2	63.5	62.4	61.5	61.5	64.4	66.6	62.6
TIO2	1.13	0.97	0.86	0.76	0.92	0.75	0.76	0.86
AL2O3	14.1	13.5	13.7	14.0	14.1	14.1	14.3	13.8
TFE2O3	6.50	6.92	7.02	7.14	7.69	5.84	5.88	7.73
MNO	0.20	0.22	0.22	0.22	0.23	0.22	0.22	0.27
MGO	1.80	2.76	2.90	3.35	2.98	1.67	1.74	2.96
CAO	4.20	5.25	5.14	5.56	4.65	6.29	3.53	2.90
NA2O	3.20	2.84	3.39	3.41	3.36	4.33	4.07	3.43
K2O	2.75	2.80	2.59	2.46	2.87	2.86	2.83	3.30
P2O5	0.26	0.21	0.19	0.17	0.20	0.10	0.11	0.18
TOTAL	97.96	98.53	98.00	98.17	98.02	100.21	99.66	97.56
AGPAITIC COEFF.	0.62	0.62	0.64	0.62	0.65	0.74	0.71	0.72
TRACE ELEMENTS IN PPM								
CR	5	33	48	60	38	58	25	38
NI	3	18	28	30	24	16	15	24
SR	143	72	85	82	143	137	115	101
BA	721	322	390	391	423	637	482	533
RB	80	98	92	88	106	99	102	114
Y	60	53	46	46	45	50	50	48
LA	31	24	23	22	20	24	22	26
CE	66	61	56	51	58	62	61	59
ND	36	31	28	25	28	29	28	28
ZR	325	200	169	157	185	225	218	204
NB	18	11	15	13	10	22	21	9
TH	10	10	12	11	10	9	9	10
PB	0	16	16	16	15	15	18	17
ELEMENT RATIOS								
K2O/NA2O	0.9	1.0	0.8	0.7	0.9	0.7	0.7	1.0
K/RB	285.	237.	234.	232.	225.	240.	230.	240.
(CE/Y)N	2.7	2.8	3.0	2.8	3.2	3.0	3.0	3.0
ZR/NB	18.1	18.2	11.3	12.1	18.5	10.2	10.4	22.7
ZR/Y	5.4	3.8	3.7	3.6	4.1	4.5	4.4	4.2
TH/NB	0.6	0.9	0.8	0.8	1.0	0.4	0.4	1.1
NB/Y	0.3	0.2	0.3	0.3	0.2	0.4	0.4	0.2
CIPW NORMS								
Q	24.1	22.2	18.9	16.8	17.2	15.5	21.9	18.7
C	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
OR	16.6	16.8	15.6	14.8	17.3	16.9	16.8	20.0
AB	27.6	24.4	29.3	29.4	29.0	36.6	34.6	29.7
AN	16.3	16.1	14.8	15.9	15.2	10.7	12.5	12.8
DI	2.6	7.2	8.0	8.9	5.6	14.3	3.6	0.6
HY	6.0	6.7	7.0	7.9	8.7	0.0	5.5	11.3
MT	4.0	4.2	4.3	4.3	4.7	3.5	3.5	4.7
ILM	2.2	1.9	1.7	1.5	1.8	1.4	1.4	1.7
AP	0.6	0.5	0.5	0.4	0.5	0.2	0.3	0.4
ACM	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

SAMPLE	PMD	PME	PMF	PMBT1	PMBT2	PMGDL	PMDGL	NANTB
SIO2	62.5	61.8	63.0	62.6	64.0	64.0	65.3	74.0
TIO2	0.88	0.79	0.88	1.08	1.00	0.73	0.80	0.25
AL2O3	13.9	14.0	14.1	15.7	15.4	14.6	14.7	12.4
TFE2O3	7.13	7.38	7.17	7.18	6.32	6.23	6.09	4.21
MNO	0.32	0.25	0.26	0.23	0.22	0.22	0.20	0.21
MGO	3.33	3.19	2.87	1.94	1.85	1.98	2.31	0.11
CAO	5.51	4.27	4.37	6.32	4.73	2.50	4.76	0.26
NA2O	2.75	3.51	3.54	3.87	3.88	4.49	3.58	4.81
K2O	2.40	2.77	3.04	2.30	2.72	3.70	2.84	4.00
P2O5	0.19	0.17	0.18	0.22	0.20	0.31	0.15	0.02
TOTAL	98.43	97.69	99.01	101.03	99.96	98.46	100.34	100.04
AGPAITIC COEFF.	0.55	0.66	0.69	0.57	0.63	0.83	0.64	1.05
TRACE ELEMENTS IN PPM								
CR	49	54	45	47	25	41	40	0
NI	27	29	26	26	16	22	24	0
SR	97	99	68	145	133	113	131	9
BA	359	425	430	383	440	442	600	73
RB	81	99	105	78	97	110	96	141
Y	47	49	49	45	50	49	50	110
LA	23	22	22	20	22	23	22	90
CE	51	58	55	54	56	59	56	184
ND	29	27	27	28	26	27	27	78
ZR	188	186	184	171	207	198	223	826
NB	11	13	16	17	12	12	12	72
TH	9	9	11	9	10	8	9	25
PB	17	14	10	13	17	17	19	20
ELEMENT RATIOS								
K2O/NA2O	0.9	0.8	0.9	0.6	0.7	0.8	0.8	0.8
K/RB	246.	232.	240.	245.	233.	279.	245.	235.
(CE/Y)N	2.7	2.9	2.8	2.9	2.8	3.0	2.8	4.1
ZR/NB	17.1	14.3	11.5	10.1	17.2	16.5	18.6	11.5
ZR/Y	4.0	3.8	3.8	3.8	4.1	4.0	4.5	7.5
TH/NB	0.8	0.7	0.7	0.5	0.8	0.7	0.8	0.3
NB/Y	0.2	0.3	0.3	0.4	0.2	0.2	0.2	0.7
CIPW NORMS								
Q	21.4	17.3	17.7	16.3	18.6	15.5	20.5	29.0
C	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
OR	14.4	16.8	18.1	13.5	16.1	22.2	16.7	23.6
AB	23.6	30.4	30.3	32.4	32.8	38.6	30.2	40.7
AN	18.7	14.5	13.7	18.5	16.6	8.9	15.6	0.4
DI	6.3	4.9	5.7	9.1	4.5	1.3	5.7	0.6
HY	9.1	9.7	8.1	3.5	5.2	7.6	5.9	2.6
MT	4.3	4.5	4.3	4.2	3.8	3.8	3.6	2.5
ILM	1.7	1.5	1.7	2.0	1.9	1.4	1.5	0.5
AP	0.5	0.4	0.4	0.5	0.5	0.7	0.4	0.0
ACM	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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 SAMPLE       NANTB   FOELG   IC38    IC39    LBG1    IC37    IC37    YFA

 SIO2        74.2    74.6    73.8    74.4    74.0    72.9    73.0    71.7
 TIO2         0.26    0.24    0.23    0.25    0.18    0.19    0.18    0.10
 AL203       12.4    12.2    12.7    12.6    13.7    14.2    14.6    16.0
 TFE203       3.89    3.89    3.69    3.87    1.97    2.00    2.00    2.06
 MNO          0.22    0.21    0.15    0.17    0.13    0.13    0.12    0.13
 MGO          0.09    0.10    0.06    0.04    0.11    0.08    0.08    0.08
 CAO          0.27    0.39    0.16    0.19    0.60    0.01    0.01    0.22
 NA20         4.35    4.68    4.08    4.16    3.97    4.37    4.23    5.22
 K20          4.53    4.06    5.06    4.95    5.00    5.19    5.23    4.84
 P205         0.02    0.01    0.02    0.01    0.02    0.04    0.04    0.02

 TOTAL      100.01  100.16   99.74  100.40   99.56   99.01   99.27  100.23
AGPAITIC      1.06    1.05    1.08    1.07    0.98    1.00    0.97    0.93
COEFF.

TRACE ELEMENTS IN PPM
 CR              0       0       0       0       0       0       0       0
 NI              0       0       0       0       0       0       0       0
 SR              8       7      19      20      46      30      29      20
 BA             17      51      15      14     495     512     523     482
 RB            140     155     206     205     161     183     181     117
 Y             110     114     115     120      78      54      54      36
 LA             89      84      86      94      66      23      22      25
 CE            180     166     178     188     167      54      53      60
 ND             77      72      74      79      70      24      23      21
 ZR            850     833     855     911     219     211     205     232
 NB             74      74      73      74      44      48      48      46
 TH             26      27      26      27      19      20      17      17
 PB             25      19      33      29      28      25      23      12

ELEMENT RATIOS
K20/NA20       1.0     0.9     1.2     1.2     1.3     1.2     1.2     0.9
 K/RB        268.    217.    204.    200.    258.    235.    240.    343.
 (CE/Y)N       4.0     3.6     3.8     3.8     5.3     2.5     2.4     4.1
 ZR/NB        11.5    11.3    11.7    12.3     5.0     4.4     4.3     5.0
 ZR/Y          7.7     7.3     7.4     7.6     2.8     3.9     3.8     6.4
 TH/NB         0.6     0.4     0.4     0.4     0.4     0.4     0.4     0.6
 NB/Y          0.7     0.6     0.6     0.6     0.6     0.9     0.9     1.3

CIPW NORMS
 Q            29.8    30.0    29.4    29.6    30.0    27.3    28.0    21.6
 C             0.0     0.0     0.2     0.1     0.7     1.5     2.0     1.8
 OR           26.8    24.0    30.0    29.1    29.7    31.0    31.1    28.5
 AB           36.8    39.5    34.6    35.1    33.7    37.3    36.1    44.1
 AN            1.0     0.4     0.7     0.9     2.9     0.0    -0.0     1.0
 DI            0.1     1.3     0.0     0.0     0.0     0.0     0.0     0.0
 HY            2.6     2.0     2.4     2.4     1.5     1.4     1.4     1.6
 MT            2.3     2.3     2.2     2.3     1.2     1.2     1.2     1.2
 ILM           0.5     0.5     0.4     0.5     0.3     0.4     0.3     0.2
 AP            0.0     0.0     0.0     0.0     0.0     0.1     0.1     0.0
 ACM           0.0     0.0     0.0     0.0     0.0     0.0     0.0     0.0
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SAMPLE	YFB	YYF	IC46	IC50	GARN1	GARN2	GARN3	G1
SIO2	71.4	70.7	72.3	69.0	63.4	62.2	62.5	68.2
TIO2	0.11	0.14	0.10	0.51	1.37	1.58	1.43	0.54
AL2O3	16.0	15.8	15.7	15.7	15.9	15.4	15.8	15.8
TFE2O3	1.91	2.30	1.92	3.52	6.17	6.46	6.57	3.72
MNO	0.13	0.15	0.11	0.15	0.21	0.21	0.21	0.18
MGO	0.05	0.09	0.05	0.71	1.06	1.53	1.35	0.84
CAO	0.31	0.43	0.03	1.37	4.13	3.97	4.47	1.51
NA2O	5.97	5.63	5.45	5.08	5.04	4.89	5.01	5.27
K2O	4.70	4.72	4.68	4.11	3.12	3.10	3.04	4.25
P2O5	0.02	0.03	0.02	0.16	0.46	0.52	0.50	0.16
TOTAL	100.50	99.83	100.19	100.07	100.52	99.45	100.45	100.26
AGPAITIC COEFF.	0.98	0.97	0.95	0.86	0.75	0.76	0.75	0.89
TRACE ELEMENTS IN PPM								
CR	0	0	0	0	0	0	0	0
NI	0	0	0	0	0	0	0	0
SR	21	44	19	204	363	396	376	187
BA	497	1113	457	643	620	622	596	636
RB	114	102	109	98	72	67	69	99
Y	30	44	32	34	41	43	41	34
LA	30	100	24	45	45	47	48	43
CE	68	146	53	84	90	90	90	81
ND	25	61	22	34	41	43	43	32
ZR	221	285	246	531	507	479	489	519
NB	45	47	44	39	33	30	30	34
TH	15	15	15	13	8	7	7	11
PB	18	17	16	17	9	19	16	19
ELEMENT RATIOS								
K2O/NA2O	0.8	0.8	0.9	0.8	0.6	0.6	0.6	0.8
K/RB	342.	384.	356.	348.	360.	384.	366.	356.
(CE/Y)N	5.6	8.1	4.1	6.1	5.4	5.1	5.4	5.9
ZR/NB	4.9	6.1	5.6	13.6	15.4	16.0	16.3	15.3
ZR/Y	7.4	6.5	7.7	15.6	12.4	11.1	11.9	15.3
TH/NB	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.3
NB/Y	1.5	1.1	1.4	1.1	0.8	0.7	0.7	1.0
CIPW NORMS								
Q	17.4	18.3	22.0	19.4	13.3	12.9	12.1	16.4
C	0.6	0.7	1.6	0.7	0.0	0.0	0.0	0.2
OR	27.6	27.9	27.6	24.3	18.3	18.4	17.9	25.0
AB	50.3	47.7	46.0	42.9	42.4	41.6	42.2	44.5
AN	1.4	1.9	0.0	5.7	11.5	11.0	11.5	6.4
DI	0.0	0.0	0.0	0.0	4.8	4.4	6.0	0.0
HY	1.4	1.7	1.4	3.4	2.3	3.6	2.6	3.9
MT	1.1	1.4	1.1	2.1	3.7	3.9	3.9	2.2
ILM	0.2	0.3	0.2	1.0	2.6	3.0	2.7	1.0
AP	0.0	0.1	0.0	0.4	1.1	1.2	1.2	0.4
ACM	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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SAMPLE        G2      IC42      G4    PAND1   PAND2   PAND3   PAND4  LLANGYB

SIO2        63.1      68.6     66.9    57.7    55.6    56.6    56.3    67.9
TIO2         1.32      0.54     0.54    1.39    1.53    1.49    1.42    0.61
AL2O3       15.7      16.1     16.1    14.7    15.2    15.4    15.3    15.4
TFE2O3       6.11      3.95     3.75    9.62   10.74   10.75   10.56    6.36
MNO          0.20      0.17     0.17    0.26    0.25    0.24    0.24    0.23
MGO          1.21      0.62     0.78    2.78    3.87    3.99    3.50    1.87
CAO          3.86      0.52     1.43    5.00    6.16    5.30    5.10    1.09
NA2O         4.87      5.14     5.33    3.71    4.02    4.60    3.85    4.76
K2O        , 3.26      4.27     4.27    2.80    1.06    1.22    2.71    3.54
P2O5         0.50      0.14     0.16    0.74    0.72    0.69    0.71    0.11

TOTAL       99.72     99.82    99.17   98.13   98.52   99.59   99.09  101.53
AGPAITIC     0.76      0.86     0.88    0.65    0.48    0.54    0.63    0.79
COEFF.

TRACE ELEMENTS IN PPM
CR             0         0        0       0       0       0       0       0
NI             0         0        0       0       0       0       0       0
SR           364       122      188     530     528     511     517     182
BA           578       713      621     722     312     509     518     456
RB            75        84       96      42      20      41      42      94
Y             42        33       35      60      59      56      58      68
LA            47        46       43      52      55      50      52      80
CE            91        85       82      99     109     115     107     156
ND            40        36       34      61      58      60      60      81
ZR           503       531      527     546     536     531     532     584
NB            31        34       33      44      43      43      43      50
TH             8        15       12       4       5       6       5      12
PB            15        18       13      10       0       0       0       0

ELEMENT RATIOS
K2O/NA2O     0.7       0.8      0.8     0.8     0.3     0.3     0.7     0.7
K/RB        361.      422.     369.    553.    440.    247.    535.    312.
(CE/Y)N      5.3       6.3      5.8     4.1     4.5     5.0     4.5     5.6
ZR/NB       16.2      15.6     16.0    12.4    12.5    12.3    12.4    11.7
ZR/Y        12.0      16.1     15.1     9.1     9.1     9.5     9.2     8.6
TH/NB        0.3       0.4      0.4     0.1     0.1     0.1     0.1     0.2
NB/Y         0.7       1.0      0.9     0.7     0.7     0.8     0.7     0.7

CIPW NORMS
Q           13.7      19.8     15.1    11.9    10.5     8.5     8.2    20.0
C            0.0       2.5      0.5     0.0     0.0     0.0     0.0     2.0
OR          19.3      25.3     25.4    16.9     6.4     7.2    16.2    20.6
AB          41.3      43.6     45.5    32.0    34.5    39.1    32.9    39.7
AN          11.2       1.7      6.1    15.5    20.5    17.8    16.7     4.6
DI           3.8       0.0      0.0     4.0     4.7     3.3     3.4     0.0
HY           3.2       3.5      3.8     9.5    12.3    13.2    12.0     8.0
MT           3.7       2.4      2.3     5.8     6.5     6.6     6.4     3.7
ILM          2.5       1.0      1.0     2.7     2.9     2.8     2.7     1.1
AP           1.2       0.3      0.4     1.8     1.7     1.6     1.7     0.3
ACM          0.0       0.0      0.0     0.0     0.0     0.0     0.0     0.0
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SAMPLE	YFC	CFAD	CBACH	CBOD	XXX	IC30	IC31	IC33
SIO2	66.0	63.6	68.9	63.7	67.6	68.2	66.9	67.1
TIO2	0.39	0.95	0.30	0.94	0.36	0.31	0.29	0.31
AL2O3	16.3	13.4	14.9	16.1	15.5	15.6	16.1	15.8
TFE2O3	4.55	8.69	4.07	6.67	5.30	4.09	3.96	4.26
MNO	0.24	0.32	0.27	0.29	0.23	0.21	0.21	0.23
MGO	0.45	1.11	0.29	0.88	0.55	0.26	0.23	0.26
CAO	1.28	2.22	2.16	2.39	1.09	1.22	1.29	1.00
NA2O	5.66	4.65	5.11	4.24	6.26	5.77	6.07	5.93
K2O	3.94	2.96	3.17	3.60	2.29	4.13	4.03	3.99
P2O5	0.10	0.33	0.06	0.31	0.09	0.06	0.06	0.06
TOTAL	98.72	97.71	98.95	98.79	98.92	99.69	98.86	98.71
AGPAITIC COEFF.	0.86	0.83	0.81	0.72	0.80	0.93	0.92	0.92
TRACE ELEMENTS IN PPM								
CR	0	0	0	0	0	0	0	0
NI	0	0	0	0	0	0	0	0
SR	191	183	105	221	142	150	161	160
BA	704	1005	1255	1208	573	673	641	655
RB	83	79	63	72	50	93	95	89
Y	50	74	62	55	63	49	49	50
LA	60	62	60	53	62	57	60	59
CE	116	118	117	108	115	109	115	122
ND	49	61	50	52	50	48	49	50
ZR	727	535	464	811	564	619	637	637
NB	51	53	51	52	50	52	54	54
TH	11	6	8	8	11	12	12	10
PB	20	18	13	5	13	14	14	13
ELEMENT RATIOS								
K2O/NA2O	0.7	0.6	0.6	0.8	0.4	0.7	0.7	0.7
K/RB	394.	311.	418.	415.	380.	368.	352.	372.
(CE/Y)N	5.7	3.9	4.6	4.8	4.5	5.5	5.8	6.0
ZR/NB	14.3	10.1	9.1	15.6	11.3	11.9	11.8	11.8
ZR/Y	14.5	7.2	7.5	14.7	9.0	12.6	13.0	12.7
TH/NB	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2
NB/Y	1.0	0.7	0.8	0.9	0.8	1.1	1.1	1.1
CIPW NORMS								
Q	13.9	18.5	21.6	18.5	18.3	15.2	12.5	14.0
C	0.7	0.0	0.0	1.7	0.9	0.0	0.0	0.1
OR	23.6	17.9	18.9	21.5	13.7	24.5	24.1	23.9
AB	48.5	40.3	43.7	36.3	53.5	49.0	52.0	50.8
AN	5.8	7.2	8.4	10.0	4.9	4.6	4.8	4.6
DI	0.0	1.6	1.7	0.0	0.0	0.9	1.1	0.0
HY	3.9	6.7	2.4	5.5	4.6	2.6	2.4	3.3
MT	2.7	5.3	2.5	4.0	3.2	2.4	2.4	2.6
ILM	0.8	1.8	0.6	1.8	0.7	0.6	0.6	0.6
AP	0.2	0.8	0.1	0.7	0.2	0.1	0.1	0.1
ACM	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

SAMPLE	CYLL	PBODH	PBODX	IC34	MN1	MN2	IC44	MOELP
SIO2	66.9	62.4	62.0	65.3	63.9	63.4	67.0	65.4
TIO2	0.31	0.93	1.15	0.86	0.85	0.86	0.35	0.67
AL2O3	16.0	15.8	15.6	15.9	16.0	15.6	15.6	14.9
TFE2O3	4.01	6.18	6.84	5.47	5.25	5.81	4.72	5.72
MNO	0.21	0.22	0.26	0.22	0.21	0.25	0.23	0.24
MGO	0.28	1.34	1.69	1.13	1.01	1.24	0.31	0.76
CAO	1.33	2.91	3.62	2.47	2.81	2.46	1.80	2.10
NA2O	6.00	5.68	6.08	5.57	5.47	4.77	5.76	5.02
K2O	4.07	3.25	2.27	3.53	3.52	3.69	3.18	3.95
P2O5	0.06	0.36	0.52	0.32	0.33	0.30	0.08	0.23
TOTAL	98.91	98.63	99.60	100.44	99.04	98.05	98.78	98.72
AGPAITIC COEFF.	0.92	0.83	0.77	0.84	0.82	0.80	0.84	0.88
TRACE ELEMENTS IN PPM								
CR	0	0	0	0	0	0	0	0
NI	0	0	0	0	0	0	0	0
SR	157	316	399	289	314	305	192	235
BA	666	687	674	644	657	657	802	836
RB	86	62	45	65	62	78	60	109
Y	51	50	50	52	50	50	50	62
LA	56	55	59	56	56	56	60	58
CE	111	104	112	110	109	108	114	115
ND	49	48	53	48	48	48	50	53
ZR	611	784	707	771	810	780	739	581
NB	52	44	54	55	45	47	57	50
TH	11	7	5	9	8	8	10	15
PB	13	13	15	12	25	12	19	20
ELEMENT RATIOS								
K2O/NA2O	0.7	0.6	0.4	0.6	0.6	0.8	0.6	0.8
K/RB	393.	435.	419.	451.	471.	393.	440.	301.
(CE/Y)N	5.3	5.1	5.5	5.2	5.4	5.3	5.6	4.6
ZR/NB	11.7	17.8	13.1	14.0	18.0	16.6	13.0	11.6
ZR/Y	12.0	15.7	14.1	14.8	16.2	15.6	14.8	9.4
TH/NB	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.3
NB/Y	1.0	0.9	1.1	1.1	0.9	0.9	1.1	0.8
CIPW NORMS								
Q	12.7	9.4	9.2	12.7	11.7	14.3	16.4	15.5
C	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
OR	24.3	19.5	13.5	20.8	21.0	22.2	19.0	23.6
AB	51.3	48.7	51.6	46.9	46.7	41.2	49.3	43.0
AN	4.7	8.0	8.5	7.8	8.8	10.4	7.4	6.6
DI	1.4	3.5	5.0	1.9	2.6	0.0	1.0	2.0
HY	2.5	4.5	4.7	4.3	3.6	5.9	3.1	3.9
MT	2.4	3.7	4.1	3.2	3.2	3.5	2.8	3.5
ILM	0.6	1.8	2.2	1.6	1.6	1.7	0.7	1.3
AP	0.1	0.9	1.2	0.8	0.8	0.7	0.2	0.6
ACM	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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SAMPLE        GDDU1   GDDU2   GGOCH   YGN     YGN     TYM   MP1     MP2

 SIO2         64.0    63.9    70.8    65.7    66.0    66.3    67.2    66.7
 TIO2          0.79    0.85    0.45    0.76    0.67    0.74    0.79    0.76
 AL2O3        14.8    14.8    14.2    15.3    15.2    15.1    14.5    14.3
 TFE2O3        6.83    6.88    4.12    4.90    4.93    4.93    4.87    4.91
 MNO           0.28    0.28    0.19    0.17    0.17    0.17    0.19    0.24
 MGO           0.96    1.12    0.33    1.19    1.19    1.18    0.92    0.85
 CAO           2.50    2.50    0.30    2.77    3.04    3.42    2.90    3.22
 NA2O          4.49    4.56    4.82    5.11    5.11    5.10    4.33    4.25
 K2O           3.70    3.75    4.50    2.96    2.92    2.98    3.41    2.96
 P2O5          0.31    0.32    0.08    0.21    0.20    0.23    0.25    0.23

 TOTAL        98.21   98.57   99.55   98.76   99.07   99.84   99.07   98.13
AGPAITIC       0.82    0.83    0.97    0.77    0.77    0.78    0.79    0.74
COEFF.

TRACE ELEMENTS IN PPM
 CR              0       0       0       0       0       0       0       0
 NI              0       0       0       0       0       0       0       0
 SR            248     252     103     258     259     263     220     246
 BA            726     762     690     903     804     794     850     709
 RB             93      95     128      82      79      85      94      87
 Y              68      67      77      38      40      43      46      49
 LA             57      59     115      41      43      42      43      45
 CE            119     119     174      79      84      79      84      78
 ND             55      55      90      35      36      34      39      37
 ZR            607     589     507     379     374     379     388     395
 NB             46      43      52      19      17      20      20      20
 TH             13      13      13       9       9      10      11      10
 PB             23      29      23      18      18      18       0       0

ELEMENT RATIOS
K2O/NA2O       0.8     0.8     0.9     0.6     0.6     0.6     0.8     0.7
 K/RB        330.    328.    292.    300.    307.    291.    301.    282.
 (CE/Y)N       4.3     4.4     5.5     5.1     5.2     4.5     4.5     3.9
 ZR/NB        13.2    13.7     9.7    19.9    22.0    18.9    19.4    19.7
 ZR/Y          8.9     8.8     6.6    10.0     9.3     8.8     8.4     8.1
 TH/NB         0.3     0.3     0.3     0.5     0.5     0.5     0.6     0.5
 NB/Y          0.7     0.6     0.7     0.5     0.4     0.5     0.4     0.4

CIPW NORMS
 Q            16.7    15.9    23.7    17.3    17.3    17.1    21.9    23.2
 C             0.0     0.0     1.1     0.0     0.0     0.0     0.0     0.0
 OR           22.3    22.5    26.7    17.7    17.4    17.6    20.3    17.8
 AB           38.7    39.1    41.0    43.8    43.6    43.2    37.0    36.6
 AN            9.5     9.0     1.0    10.1     9.9     9.5    10.2    11.4
 DI            0.9     1.2     0.0     2.0     3.3     4.9     2.2     2.8
 HY            5.6     5.7     3.1     4.2     3.7     2.7     3.4     3.1
 MT            4.1     4.2     2.5     3.0     3.0     2.9     2.9     3.0
 ILM           1.5     1.6     0.9     1.5     1.3     1.4     1.5     1.5
 AP            0.7     0.8     0.2     0.5     0.5     0.5     0.6     0.6
 ACM           0.0     0.0     0.0     0.0     0.0     0.0     0.0     0.0
```

SAMPLE	MP3	FF1	FF2	FF2	FF4	MW1	GN1	GN2
SIO2	67.8	63.7	62.1	63.2	61.7	68.7	68.7	68.9
TIO2	0.78	1.26	1.35	1.34	1.23	0.84	0.75	0.85
AL2O3	14.4	14.1	13.3	13.7	13.6	15.2	14.4	14.4
TFE2O3	4.89	6.71	7.78	7.17	7.03	5.58	4.39	4.42
MNO	0.20	0.40	0.23	0.20	0.31	0.10	0.18	0.18
MGO	0.91	2.04	2.62	2.11	2.30	0.84	1.28	1.52
CAO	2.50	3.68	6.16	4.36	4.76	0.32	2.59	2.86
NA2O	4.70	4.61	4.16	4.20	3.90	4.84	4.11	3.80
K2O	3.14	2.92	1.52	2.76	3.10	3.62	3.71	3.67
P2O5	0.23	0.37	0.33	0.35	0.35	0.21	0.21	0.20
TOTAL	99.26	99.41	99.17	98.94	97.87	99.97	100.08	100.57
AGPAITIC COEFF.	0.80	0.78	0.61	0.75	0.76	0.82	0.80	0.77
TRACE ELEMENTS IN PPM								
CR	0	12	18	52	17	1	6	5
NI	0	8	11	34	10	1	6	6
SR	198	233	238	285	198	111	130	126
BA	766	747	531	296	509	851	628	634
RB	85	80	95	80	90	124	146	130
Y	48	46	46	47	48	49	50	51
LA	46	36	38	27	34	42	47	48
CE	80	72	68	71	70	81	97	100
ND	38	36	36	29	32	36	42	42
ZR	386	376	381	358	328	394	278	283
NB	21	12	15	14	10	22	23	22
TH	10	10	9	9	9	16	18	17
PB	0	16	20	16	0	21	17	0
ELEMENT RATIOS								
K2O/NA2O	0.7	0.6	0.4	0.7	0.8	0.7	0.9	1.0
K/RB	307.	303.	133.	286.	286.	242.	211.	234.
(CE/Y)N	4.1	3.8	3.6	3.7	3.6	4.1	4.8	4.8
ZR/NB	18.4	31.3	25.4	25.6	32.8	17.9	12.1	12.9
ZR/Y	8.0	8.2	8.3	7.6	6.8	8.0	5.6	5.5
TH/NB	0.5	0.8	0.6	0.6	0.9	0.7	0.8	0.8
NB/Y	0.4	0.3	0.3	0.3	0.2	0.4	0.5	0.4
CIPW NORMS								
Q	22.0	16.0	18.0	17.7	15.8	24.3	23.2	24.4
C	0.0	0.0	0.0	0.0	0.0	3.3	0.0	0.0
OR	18.7	17.4	9.1	16.5	18.7	21.4	21.9	21.6
AB	40.1	39.2	35.5	35.9	33.7	41.0	34.7	32.0
AN	9.0	9.3	13.3	10.4	10.7	0.2	10.0	11.3
DI	1.6	5.4	12.4	7.5	9.0	0.0	1.2	1.2
HY	3.7	5.4	3.8	4.4	4.5	4.4	4.5	4.9
MT	2.9	4.0	4.7	4.3	4.3	3.3	2.6	2.6
ILM	1.5	2.4	2.6	2.6	2.4	1.6	1.4	1.6
AP	0.5	0.9	0.8	0.8	0.8	0.5	0.5	0.5
ACM	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

SAMPLE	MM1	MM2	MM3	MM4	MM6	MMAA	MMBB	MMDD
SIO2	75.3	75.2	75.0	75.4	74.6	75.9	75.0	75.8
TIO2	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
AL2O3	13.7	13.0	13.5	13.2	13.3	13.3	13.4	13.2
TFE2O3	2.18	1.89	1.80	2.32	1.85	2.65	1.71	2.89
MNO	0.12	0.13	0.10	0.17	0.10	0.15	0.08	0.33
MGO	0.07	0.28	0.07	0.13	0.06	0.39	0.05	0.19
CAO	0.01	0.19	0.04	0.11	0.04	0.04	0.10	0.06
NA2O	5.51	5.12	5.72	5.33	5.78	4.20	5.44	4.40
K2O	3.68	3.97	3.81	3.65	3.80	4.00	4.20	3.75
P2O5	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
TOTAL	100.58	99.74	100.07	100.21	99.56	100.55	99.98	100.55
AGPAITIC COEFF.	0.98	1.03	1.03	1.00	1.05	0.91	1.06	0.91
TRACE ELEMENTS IN PPM								
CR	0	0	0	0	0	0	0	0
NI	0	0	0	0	0	0	0	0
SR	7	15	11	5	11	15	7	6
BA	45	23	16	30	21	171	11	76
RB	248	316	292	286	294	220	365	258
Y	150	177	108	179	109	118	112	224
LA	30	25	2	29	2	8	23	54
CE	72	57	12	69	10	16	58	119
ND	39	29	7	41	6	13	30	62
ZR	655	632	626	657	617	675	701	653
NB	114	116	109	121	113	115	119	110
TH	41	39	32	42	35	45	39	37
PB	47	31	61	94	65	14	43	7
ELEMENT RATIOS								
K2O/NA2O	0.7	0.8	0.7	0.7	0.7	1.0	0.8	0.9
K/RB	123.	104.	108.	106.	107.	151.	101.	121.
(CE/Y)N	1.2	0.8	0.3	0.9	0.2	0.3	1.3	1.3
ZR/NB	5.7	5.4	5.7	5.4	5.5	5.9	5.9	5.9
ZR/Y	4.4	3.6	5.8	3.7	5.7	5.7	6.3	2.9
TH/NB	0.4	0.3	0.3	0.3	0.3	0.4	0.3	0.3
NB/Y	0.8	0.7	1.0	0.7	1.0	1.0	1.1	0.5
CIPW NORMS								
Q	28.3	28.9	26.5	29.2	26.1	34.5	26.7	34.2
C	0.7	0.0	0.0	0.3	0.0	2.0	0.0	1.8
OR	21.6	23.5	22.5	21.5	22.6	23.5	24.8	22.0
AB	46.3	43.4	48.3	45.0	47.6	35.3	45.5	37.0
AN	0.0	0.8	0.0	0.5	0.0	0.1	0.0	0.2
DI	0.0	0.1	0.1	0.0	0.1	0.0	0.4	0.0
HY	1.6	1.9	1.3	2.0	1.7	2.8	1.1	2.8
MT	1.3	1.1	1.0	1.4	0.4	1.6	0.8	1.7
ILM	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
AP	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ACM	0.0	0.0	0.1	0.0	1.3	0.0	0.4	0.0

Chemical Geology, 25(1979) 175—177

ERRORS IN INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS CAUSED BY MATRIX ABSORPTION

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(Received May 10, 1978; revised and accepted October 31, 1978)

Instrumental neutron activation analysis (INAA) is widely used for the determination of trace elements in geological material (Gordon et al., 1968; Hertogen and Gijbels, 1971; Baedecker et al., 1977). This technique requires the comparison of an unknown with an international reference sample or a synthetic standard which may, for example, have been prepared by spiking the elements of interest into crushed silica.

The geochemically important rare-earth elements, together with Ta, Hf and U, have their most favourable energies below 150 keV where absorption of radiation by the sample becomes increasingly important. The extent of this energy absorption, approximately expressed by the Beer-Lambert law, is controlled by the density, thickness and total mass absorption coefficient of the sample.

Absorption effects, although well known, are apparently ignored in most published accounts where the reference and unknown samples are frequently of different chemical composition.

Determinations of the total mass absorption coefficients were made using a two-part experimental approach rather than using published data which have their uncertainties (see Heinrich, 1966). The first method used an Ortec® Ge(Li) low-energy photon detector (LEPD) to measure the intensities of gamma energies in the range 58—122 keV. The absorbers were pressed rock powders of granitic, dioritic and basaltic composition; TYG, UB69 and 105A, respectively (Fig. 1). The second method employed a Philips® 1450 AHP X-ray spectrometer to provide K_α and K_β X-ray emission energies between 33.3—82.5 keV.

Fig. 1 shows that there are clear differences in absorption for the three absorbers at a particular energy. A comparison of 500-mg samples of granite and diorite in 13-mm diameter counting vials would introduce an error, due to absorption differences, of 8% at the 63.5 keV gamma energy of ^{169}Yb. This figure would be 12% for a granite and a basalt. The errors may be lowered to reasonable proportions by reducing the sample thicknesses, corresponding to weights of 100 mg, although this would introduce a relative loss in sensitivity of approximately 40%.

There is a not uncommon practice of comparing unknowns with reference

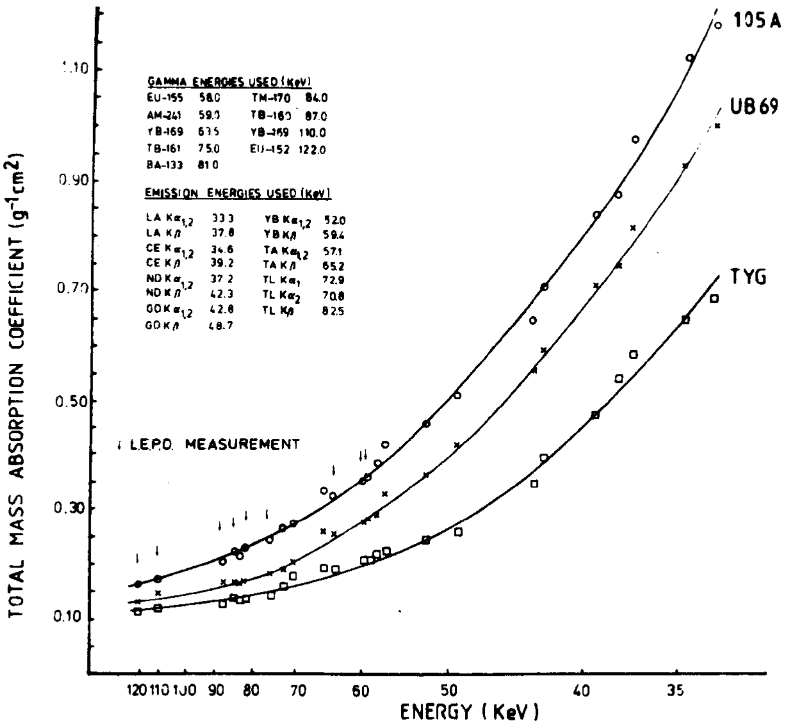

Fig. 1. Mass absorption—energy variations for three rock types.

samples of different compositions. The basalt BCR-1, for example, has been used as a reference for all rock types and also for chemical separates (Garmann et al., 1975; Grossman and Ganapathy, 1976). Thus a control must be kept on the differences in absorption between samples either by a choice of suitable references, correction for absorption or by using small sample weights. Where these precautions are ignored a bias may be introduced into determinations which will be substantially greater than the overall analytical precision.

ACKNOWLEDGEMENTS

The author acknowledges receipt of a NERC research studentship, a SRC grant for irradiation facilities and helpful advice from Dr. G.L. Hendry.

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