Petrography and geochemistry of Lower Paleozoic sandstone sequence, Girvan

by

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ABSTRACT

Detailed petrographic and geochemical investigations of the Girvan sandstones-greywackes indicate a great range in petrography and geochemistry. In terms of petrography, the dominantly basic and ultrabasic-, lava-bearing (ophiolitic) greywackes at the base of the Girvan sequence (Upper Llanvirn-Llandeilo) are replaced upwards in the Caradoc-Ashgill by sandstones characterized by acid rock fragments which include lavas and detritus probably derived from high level plutonic intrusions. During the Silurian, however, the contributions from the mafic and ultramafic source have ceased completely, acid rock fragments had become scarce and most of the contributions to the basin was quartz-rich recycled orogenic detritus.

The great heterogeneities in the greywacke composition and the systematic changes in petrography as summarized above, are in concert with the chemistry.of 212 smples were chemically and modully analysed for all major and 12 trace elements The greywackes of all ages show very large chemical variations both in their major and trace elements but they exhibit progressive changes with younging age. Particularly Si, the incompatible elements, Rb, Ba and some REE increase to their highest values in passing from Upper Llanvirn through to Llandovery. In contrast, the compatible elements such as Mg, Ni, Co and Cr are enriched in the lower sequence and decrease systematically upwards.

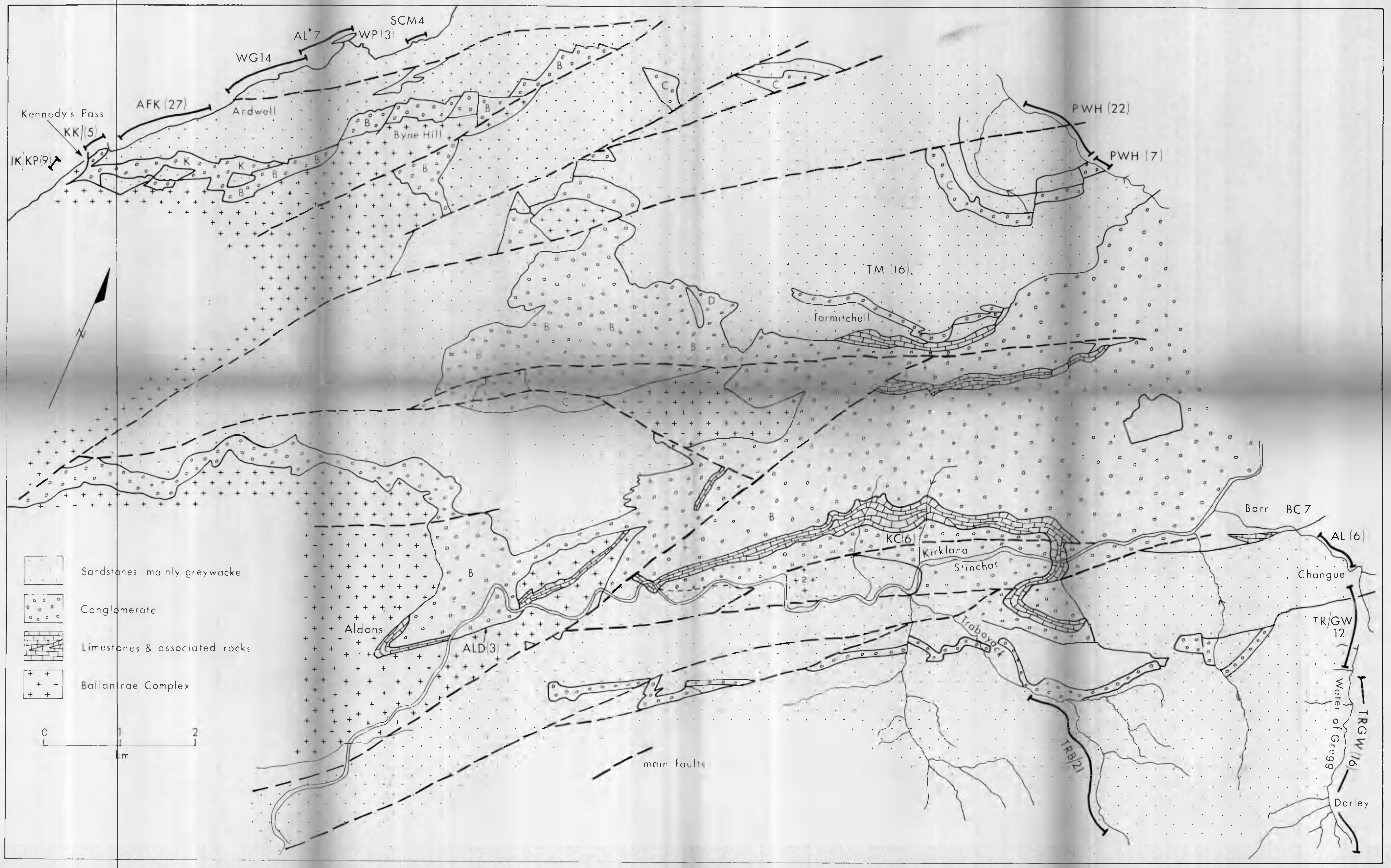
In terms of provenance areas and tectonic settings, despite some disagreements between the various models proposed, it is concluded that except for the Silurian rocks which were dominantly derived from recycled sediments, the Ordovician rocks were derived from a magmatic arc and deposited in a forearc or backarc region The chemistry also confirms a magmatic derivation of the greywackes and deposition in a forearc or backarc region

Chemical re-investigations of the Southern Uplands greywackes show that these were also deposited in a proximal arc basins. Despite some differences in composition between the two areas, a paleogeographical linkage of Girvan to Southern Uplands is suggested and the previously thought backarc or allochthonous settings for the Southern Uplands is not supported by the data presented here.

Declaration

The material presented herein is the result of independent research by the author undertaken from November 1982 to January 1989 at the Department of Geology, University of Glasgow. Any published or unpublished results of other workers have been given full acknowledgement in the text.

Fig 2.1



Kennedy's Pass
KK(5)
IK/KP(9)
AFK (27)
Ardwell
WG14
AL*7
WP(3)
SCM4
Byne Hill
K
B
C
D
PWH (22)
PWH (7)
TM (16)
Tormitchell
Barr
BC7
AL (6)
Changue
TR/GW 12
Water of Gregg
TRGW (16)
Darley
TRB(21)
Traboyack
Stinchar
Kirkland
KC6
Aldons
ALD(3)
Sandstones mainly greywacke
Conglomerate
Limestones & associated rocks
Ballantrae Complex
0
1
2
km
main faults

I dedicate this thesis to my wife and my children Ashraf, Ahmed, Eman and Aiya.

Acknowledgement

I wish to express my deep and sincere thanks to many people involved in bringing this thesis to fruition.

Above all I wish to thank Dr Brian J. Bluck for his invaluable help, advice, guidance and supervision during the course of this study..

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Above all, I wish to thank my mother and mother in law for their love, understanding and continuous support.

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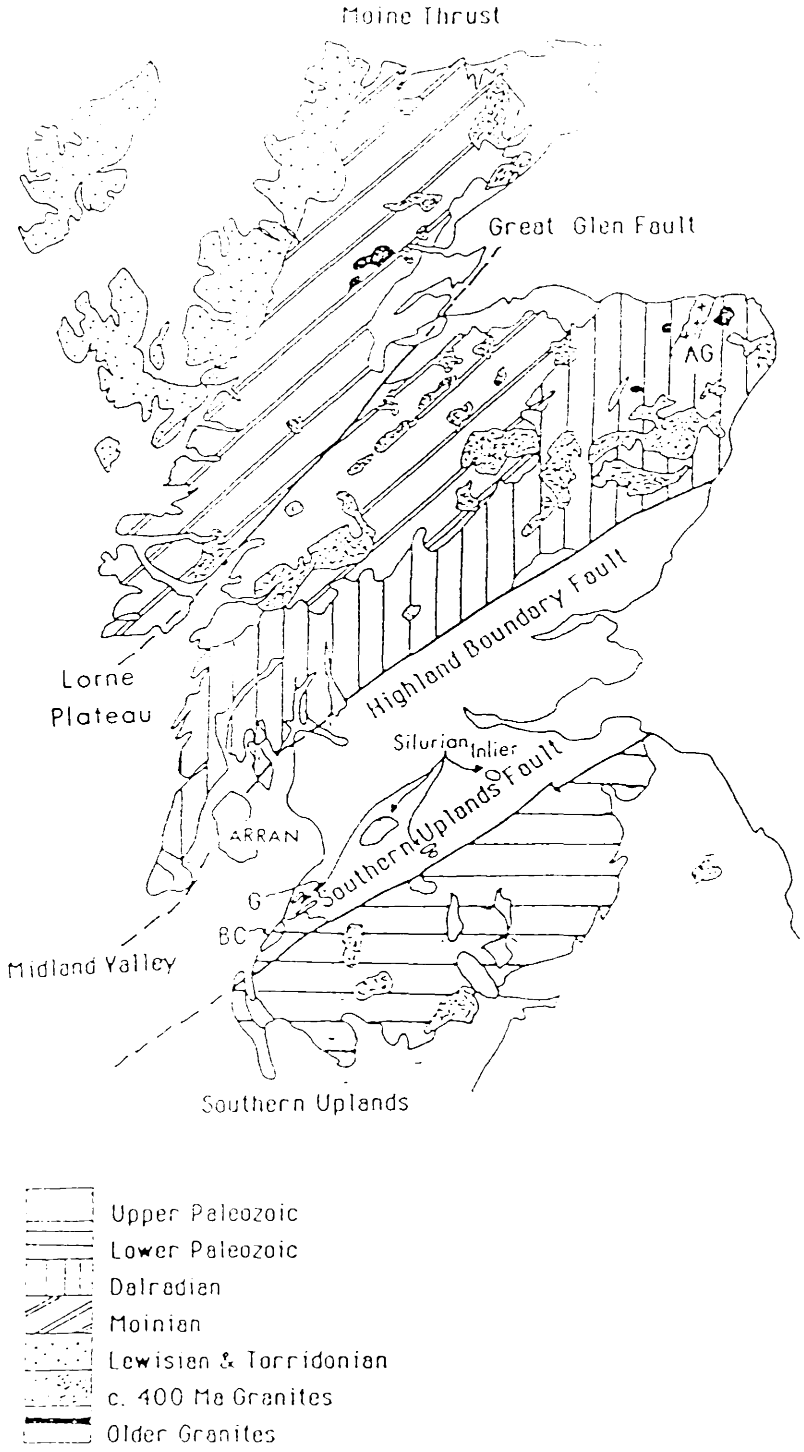
CHAPTER ONE INTRODUCTION

1.1 Geological setting

The Midland Valley of Scotland lies between two major fractures: the Highland Boundary and Southern Upland Faults (Fig 1.1). It is bounded to the N by a series of metamorphic basements, the most southerly of which is the Dalradian Block. Dalradian sediments are now known to be certainly of late Pre-Cambrian age (Rogers et al. in press) but they were folded, metamorphosed and uplifted during late Cambrian and Ordovician times. This basement was intruded by granitic plutons at c 470 Ma and between 420 and 390 Ma. The latter phase of plutonic activity was accompanied by extrusive andesitic lavas which are now preserved in some places such as the Lorne Plateau.

To the south of the Midland Valley lies a folded and thrusted sequence of Ordovician and Silurian turbidites and associated sediments belonging to the Southern Uplands. These rocks have been attributed to an accretionary prism (McKerrow et al. 1977 ; Leggett et al 1983) produced during the NW subduction of oceanic crust. The stratigraphy and structure of this region is highly suggestive of an accretionary prism origin with a major source for the sediments existing to the NW. Other workers have pointed out that volcanic detritus and some of the greywackes are of arc type affinities and appear to have been derived from the south. In a normal accretionary prism framework this provides some problems since oceanic crust is thought to have existed to the south as suggested above and as a consequence of this Stone et al. (1987). have suggested that the Southern Uplands is a back-arc basin, with a main arc to the south.



AG = Aberdeenshire Granites

BC = Ballantrae Complex

G = Girvan district (study area)

Fig 1.1 Regional geological map showing the study area.

Rocks of the Southern Uplands were intruded by a series of granites between 410 and 390 Ma. As with the Dalradian block, only in places are Devonian andesitic lavas preserved.

Lower Paleozoic rocks are not abundant in the Midland Valley, but outcrops are seen along the northern edge (The Highland Border Complex) and along the southern edge in a series of Silurian inliers and the comparatively large outcrop of Ordovician and Silurian rocks in the Girvan region. The rest of the Midland Valley is covered by Upper Paleozoic rocks particularly those of the Carboniferous.

1.2 Previous work

1.2.1 Introduction

Considerable work has been done on the rocks in the region of Girvan and this has been discussed by Williams (1962); therefore only a brief summary is needed here. The pioneer work of Lapworth (1882) and Peach and Horne (1899) on the stratigraphic succession of the Girvan district essentially established the succession and demonstrated that it was coeval with a sequence of black shales in the south at Moffat and with turbidites in the northern belt of the Southern Uplands. Henderson (1935) described some of the sedimentary structures in the Ardwell flags which he attributed to slumping thereby indicating the general tectonic regime under which the sediments at Girvan were laid down. Kuenen (1953) attempted to determine the depositional environments of the district showing that they were deposits of mass flows and turbidity currents. This early work was followed by a major step forward by the researches of Williams (1959, 1962). He discussed the structure, stratigraphy, palaeogeography and paleontology of the

Barr and Lower Ardmillan Series showing that the whole sequence was deposited in fault-bounded basins, the earliest of which formed in the SE and later ones in the NW. He also demonstrated what other palaeontologists had seen for some time that the faunas had North American affinities. The 1962 paper was a major contribution about the area as it established the stratigraphic relations and more importantly indicated -mysteriously at that time- that the fauna (brachiopods) had a more American affinity than Anglo-Welcsh 0r Baltic as put. Hubert(1969) subsequently published some work on the sedimentology and paleoenvironment of the area.

In the late 1960's, the development of the concept of sea floor spreading provided a new framework within which the Girvan sedimentary sequence could be reviewed. After Wilson (1966) envisaged a proto-Atlantic ocean separating Laurasia from a southern European continent, the faunal provinces of Williams and others became more understandable. As a result, the first plate-tectonic model was proposed by Dewey (1969) in an attempt to explain the British Caledonides in terms of destructive ocean plate margins. Subsequent work (e.g Fitton and Hughes, 1970; Dewey,1971, Phillips et al., 1976; Wright,1977; Longman et al. 1979; Longman,1980; Yardley et al. 1982; Bluck, 1983, 1984 , 1985, etc). emphasised the development of various models for the Caledonides.

These new plate tectonic models of the Caledonides drew heavily on the evidence in the Girvan-Ballantrae areas. The sequence at Girvan overlies the Ballantrae complex which is a structurally dismembered ophiolite (e.g Church and Gayer, 1973; Dewey, 1974). This complex has basalts with a chemistry resembling mid-oceanic ridge basalts, island arc and ocean island basalts (Wilkinson and Cann, 1974; Jelinek et al., 1980; Thirlwal and Bluck, 1984). The ophiolite is c 490-480 Ma and has been interpreted as a seamount (Barrett et al. 1982) or a marginal basin arc sequence (Bluck et al. 1984). It was obducted at c 480 Ma to form the basement of the Girvan Llanvirn-Ashgill sequence. It is therefore clear that since the challenging work of Dewey (1969,1971) workers attempted to view the Girvan succession as a fundamental link in ascertaining the tectonic evolution of the Midland Valley and the rest of the southern Caledonides of Scotland. In this respect Bluck (1984-85) has interpreted the sequence at Girvan as a proximal forearc basin and this basin forms the topic of the present research.

1.2.2 The general stratigraphy

The dominantly clastic sequence in Girvan rests unconformably on the Ballantrae Complex and includes rocks that range in age from Ordovician (Llanvirn-Ashgill; Ingham 1978) up to Silurian (Llandovery, Cocks et al. 1971). The Ordovician rocks are unconformably overlain by Silurian conglomerates, sandstones and limestones. The description of the stratigraphic sequence in Girvan is given below.

1.2.2.1 Ordovician rocks

The Ordovician rocks of the Girvan sequence consist broadly of a thick series of various conglomerates, sandstone turbidites, greywackes and shallow water reefal limestones

The Upper Ordovician sequence was laid down in a series of basins that had contemporaneous faults on their northern margins (Williams,

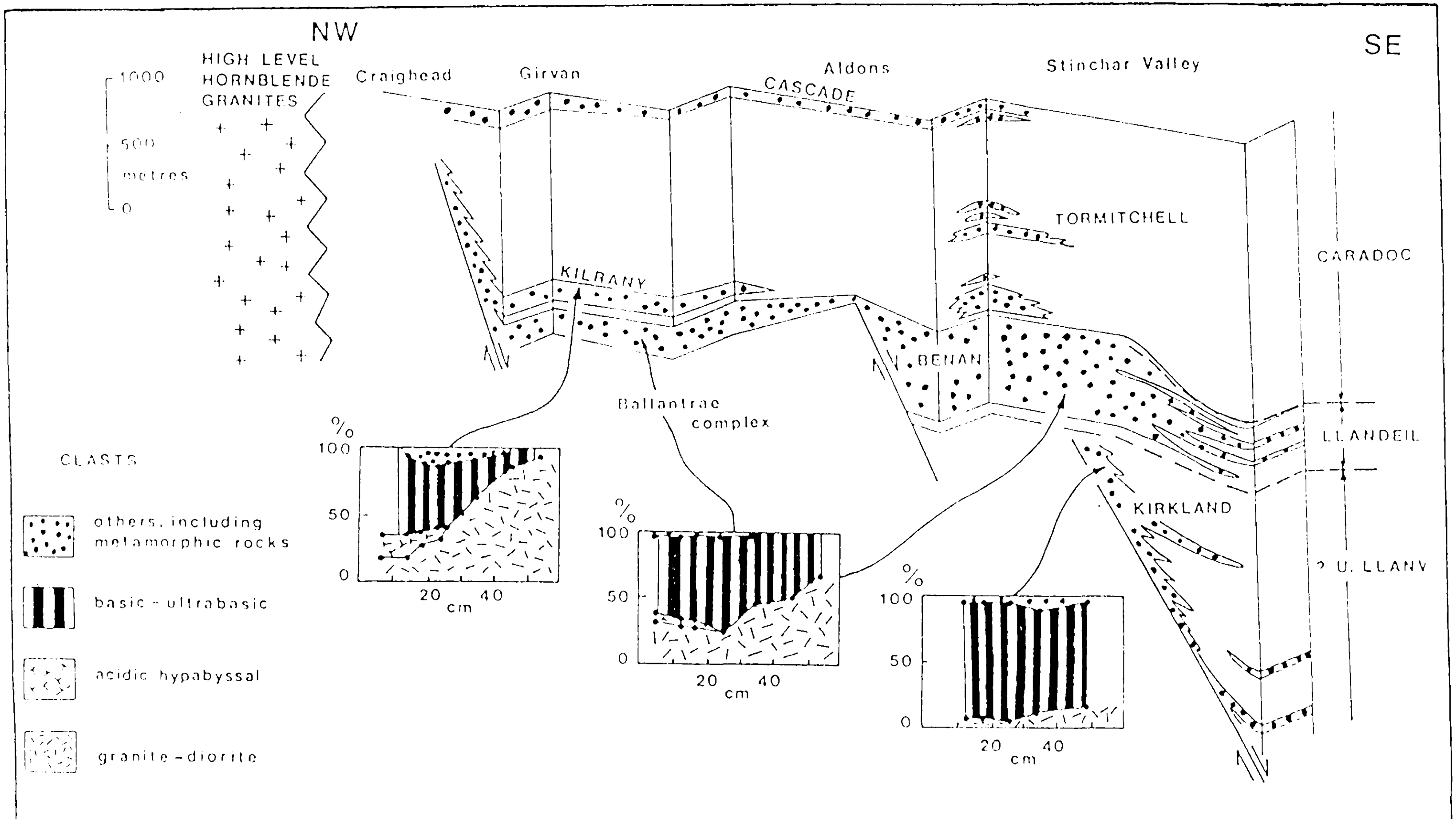


Fig 1.2 Section through the Girvan district (After Williams, 1962) with stage boundaries from Ingham (1978). The clast composition is a function of size (After Bluck, 1983)

1962, see Fig 1.2). Each basin is characterized by an assymetrical facies distribution with thick conglomerates occurring adjacent to faults and fining southeastwards into sandstone turbidites and shales.

The conglomerates have a range of textures and structures suggesting deposition in a range of water depths. Some are massive, unsorted and laterally persistent while others are very well sorted, finely layered with clasts of various shapes and sizes and well segregated into beds. This led Bluck (1983) and Ince (1984) to conclude that the conglomerate sequences were deposited in fan-deltas and submarine fans.

Most clasts are fairly well rounded in the conglomerates and range up to 3m in diameter. Although there are some variations in the conglomerate composition, the Kirkland conglomerates contain mainly basic and ultrabasic clasts with minor granitic, porphyritic and metamorphic rock fragments (Bluck, 1983). The Benan and Kilrany conglomerates have a predominance of granites in the coarser size and basic and ultrabasic fragments in the finer size. The granite-granodiorite clasts are hornblende-bearing and are accompanied by rhyolite, andesite-basalt porphyries and gabbros which suggests the unroofing of a major igneous complex. The source of these sediments probably included the Ballantrae complex, however, the presence of some clasts which are dissimilar to those now exposed at Ballantrae may have been associated with phases of granitic intrusion(s). This suggestion is supported by the age of these granitic clasts which range from 590 to 450 MA. (Longman <u>et al.</u> 1982), and are therefore both younger and older than rocks of the Ballantrae complex.

The large size of the granite clasts and associated boulders which occur throughout the conglomerates with an aggregate thickness of >5km suggest that the source batholith (s) lay immediately to the NW. Bluck (1983) envisaged a source-basin relationship where continuous uplift accompanied granite intrusion and a flanking, coeval and genetically related basin underwent complementary subsidence. It is clear therefore that the source area of the Ballantrae complex and basement was intruded by successively younger granites which may have raised the topography continuously to provide new deposits in the nearby basin. The high level , hornblende-bearing granites were rapidly eroded to supply clasts with cooling ages not significantly different from the ages of the sediments in which they occur. From the above considerations and by analogy with other forearc basins described; (e.g. Dickinson and Seely,1979;) it was concluded that in its structure and fill, the basin resembles more typically found proximal forearc settings.

The alternative view of Yardley et al (1982) which requires granite clasts metres in diameter in boulder-bearing conglomerates >5km thick to have travelled 200-250km from Aberdeenshire and to accumulate in an incidentally subsiding basin at Girvan is rejected because clasts would have to travel through a marginal basin which divided Aberdeenshire from Girvan (Bluck et al. 1980; Van Breeman and Bluck 1981; Curry et al. 1982). In any case the granite clasts in the Ordovician conglomerates of Girvan are not the same as those found in the NE Grampians. The Girvan clasts contain hornblende with biotite and have lower $^{87}Sr/^{86}Sr$ ratios (Van Breeman and Bluck 1981) whereas the Grampian granites (470-450Ma) have two micas instead. Bluck (1983) suggested a proximal forearc origin for the Girvan sequence (see subsection 1.2.2.3 below)

1.2.2.2 Silurian rocks

The succession throughout is not well exposed but substantial thicknesses of the Llandovery rocks occur at Girvan (Cocks and Toghill 1973) Lesmahagow, Hagshaw hills and North Esk in the Pentland Hills (Bluck 1983). It consists of grey marine sediments with turbidites, rare acidic ash bands

Llandovery conglomerates are rich in acidic igneous clasts and include granite, acidic to basic lavas, gabbros and dolerites. In the Girvan district there is a clear indication of a metaquartzite basement with acidic rocks exposed to the NW but this basement did not yield any of the familiar metamorphic rocks of the Dalradian Supergroup (Bluck 1983). The igneous conglomerates have mainly igneous clastics which include microperthitic granite, granite, granodiorite, diorite, rhyolite, porphyry, andesite and spilites in addition to some metaquartzite, quartz and greywacke clasts. The quartzite conglomerates are quite variable in terms of their composition but consist mainly of about 60% igneous rocks and 10% of cherts and greywackes. The greywacke conglomerates contain about 70% greywacke clasts but also have up to 25% cherts and up to 50% fine grained igneous rocks with minor amounts of quartzites.

Based on extensive field observations and data review, Bluck (1983) noted that the Silurian conglomerates of Girvan have a NW source which consisted of acidic-intermediate rocks, metaquartzites and conglomerates. Along strike, conglomerates with similar composition had a dispersal from the SE. On the basis of this evidence he concluded that upper crustal layers of similar composition existed in the Midland Valley and beneath the Southern Uplands in Silurian times. This conclusion is supported by the data on xenoliths produced by Upton et al. 1983 who suggested a similarity in crustal composition between the Midland Valley and Southern Uplands. Oliver and Leggett. (1980) have disputed this evidence suggesting that the Southern Uplands is underlain by metamorphosed greywackes belonging to the accretionary prism.

1.2.2.3 Tectonic evolution

There has been a wide variety of interpretations of the geotectonics of Scotland during the Ordovician times. The earliest plate tectonic model to explain the British Caledonides was published by Dewey (1969) (Fig 1.3 A) which was later modified by Bird and Dewey (1971, 1974). The main proposals of these early models was that the Scottish Caledonides lay on a continental edge to the north of the so called Iapetus Ocean. Dewey suggested a northward dipping subduction zone occurred to the north of the Southern Uplands with the Midland Valley as a thickening sedimentary wedge on Dalradian terranes (see fig 1.1). He also believed the Ballantrae complex to have been formed in a marginal-basin island-arc environment and suggested that the granitic detritus in the Lower Ordovician sediments was of Highland origin.

Fitton and Hughes (1970) also produced a tectonic model involving island arc development along the margins of the Iapetus ocean. This was for the Lake District on the southern side of the ocean but involved a southerly dipping subduction zone situated at Moffat in the Southern Uplands.

Church and Gayer (1973) dealt with the Ballantrae complex ophiolite but came to conclusions similar to those of Dewey with northward dipping subduction, but suggested that the additional effect of the southerly Lake District subduction would place the eventual Iapetus suture through the Solway Firth (see Fig 1.3 B).

Jeans (1973) and Gunn (1973) subsequently provided a departure from the generally proposed model to account for the work of Powell (1971). Powell used various geophysical methods to investigate the basement to the Southern Uplands and concluded that it was underlain by a Lewisian type basement. This cast doubt the Dewey type model which implied a paleo-oceanic floor to the Southern Uplands. The essence of both Jeans' and Gunn's models is siting the Iapetus ocean in the Midland Valley and having subduction to the north at the Highland Boundary Fault and to the south at Girvan/Ballantrae (see Fig 1.3 C) This model, however, could not explain the faunal province evidence of Williams (1962). More recent structural and other evidence (Bluck, 1983, 1984, 1985; Longman _et al._ 1979; Longman ,1981) does not support this proposed model.

Mitchell and McKerrow (1975) compared the pattern found in the Scottish Caledonides to the modern situation in the Burma orogen and as such proposed the concept of oblique rather than parallel subduction and ocean closure (see Fig.1.3 D)

Lambert and McKerrow (1976) developed this oblique closure, migration of subduction zones as far north as the Highland Boundary Fault and subduction of a spreading ridge to enhance metamorphism and magma generation (see Fig 1.3 E)

Bamford et al. (1976, 1977, 1979) used various geophysical parameters on a longitudinal profile through Britain (LISPB) to further define the basement under central and southern Scotland. Their work showed that the Midland Valley is floored by a fairly typical continental crust section but that the Southern Uplands basement is somewhat anomalous. Mosley (1977) used the better evidence from the LISPB profile and Powell's (1971) geophysical interpretation to imply the absence of large oceanic remnants under Scotland. He suggested marginal basin development and closure to give the ophiolite slivers at Ballantrae and the Highland Boundary Fault with the eventual ocean suture along the Solway Firth (Fig 1.3 F). McKerrow et al. (1977) investigated the stratigraphy of the Southern Uplands and concluded that it matched that of an accretionary prism as recorded from modern continental margins. This provided a substantial refinement of the subduction zone site suggesting its early position near the Southern Uplands.

Mitchell and McKerrow (1975) also used the analogies with the Burma Orogen and the Himalayas to propose an arc and marginal basin situation but with early southeasterly subduction behind the arc and later northwesterly subduction (Fig 1.3 G). The next refinements to the Caledonide plate-tectonic models were those of Longman et al. (1979); van Breeman and Bluck (1981); Yardley et al. (1982); Leggett (1980); Leggett et al. (1983); Bluck (1983, 1984, 1985). Bluck (1984,1985) re-read the evidence and produced additional data to suggest that the tectonic elements in Scotland were not realated to each other (i.e. did not form a continuous destructive margin). He noted that each tectonic unit was fault bounded and had been accreted to the Caledonides as terranes. he also recognized at least seven terranes in the Caledonides of Scotland.

And so the concept of terrane tectonics, first established for western North America was applied to the Caledonides.

Leggett (1980), Leeder (1982), Yardley et al. (1982) (Fig 1.3 H), and to some extent Leggett et al. (1982-83) believed that the Midland Valley was a forearc region dividing the Southern Highlands (arc basement) from the Southern Uplands (trench-accretionary prism) in Ordovician and Silurian times (Fig 1.1). It was flanked by the Southern Highlands to the NW and a rising upper trench slope break (Cockburnland) to the SE.

The alternative view is that of Longman et al. (1979); Van Breeman and Bluck (1981); Bluck (1983, 1984, 1985) (Fig 1.3 I) who envisage the Midland Valley as an arc-inter-arc terrane during the Ordovician and Silurian times (Fig 1.1) with the arc flanked to the N by a marginal basin in which rocks of the Highland Border Complex formed (Bluck et al. 1984) and to the S in the Llanvirn-Ashgill sequence at Girvan, by a proximal forearc in which boulders of granitic and volcanic detritus accumulated.

Bluck (1983) argued that the presence of a proximal forearc sequence in the southwestern margin of the Midland Valley demands an arc to the immediate N of it in the Midland Valley and a forearc to the south of it in the position of the Southern Uplands. He suggested that a trench sequence and coeval proximal forearc basin sequence lie adjacent to each other in southern Scotland and a complete forearc basin is missing. The Southern Uplands accretionary prism is thought to have been thrust over this basin as well as the continental crust of the Midland Valley. To a large extent the tectonic setting of the Midland Valley in general and the Girvan area in particular is of some importance in deciding which of the models have any validity.

1.3 Use of petrography and geochemistry in forearc basins

The composition of sandstones and greywackes is strongly controlled by the source areas, the dispersal paths linking source to basin and the sedimentary processes within the depositional basins all of which are governed by plate tectonics. Since the early proposals of Krynine (1911-1948) and subsequently Pettijohn (1943-1957), there has been substantial contribution to sedimentary petrography. Dickinson (1970, 1974), Dickinson and Suczek (1979), Dickinson et al. (1983), Ingersoll (1983) and others have improved our ability to deduce the provenance areas and tectonic settings from modal analyses of some framework modes.

Dickinson and Suczek (1979) and Dickinson et al. (1983) noted that the average compositions of sandstone suites derived from different sources and controlled by plate tectonics tend to plot within three major tectonic fields on the QFL and QmFLt diagrams. These fields which represent the continental blocks, recycled orogens and magmatic arcs are discussed in more detail in Chapter 4 Refinements of these tectonic fields were presented by Ingersoll and Suczek (1979) based on QpLvmLsm and LmLvLs frameworks and Dorsey (1988) based on LsLm1Lm2 frameworks (see chapter four for more detail and Table 4.1 for definition of terms.

During the last decade, there has also been some interest in applying whole rock chemistry to solve tectonic problems. For instance, Schwab (1974), Maynard et al. (1982), Bhatia (1983), Roser and Korsch

(1986) and van de Kamp and Leake (1985) have attempted to characterize the geochemistry of some sandstones from known provenance areas and tectonic settings. Based on extensive major and trace element determinations, Maynard et al. (1982) distinguished sands from forearc basins and passive margins from sands derived from other tectonic settings. Bhatia (1983) and Roser and Korsch (1986) used some discriminating factors to broadly group sands from various tectonic settings. These tectonic fields and other details are well discussed in chapter five.

1.4 Aims of the work

1°- Using the Girvan sequence as an example to examine the petrographic and geochemical vertical variabilities as a clue to evolution within the arc and its environs

2°- Assess whether the Girvan sequence is a forearc basin

3°- characterize the petrographical and geochemical aspects of sandstones in the arc-related environments

4°- Show how both chemistry and petrography may be integrated into assessing the nature of tectonic setting of sandstones in the arc-related environments

5°- Compare Girvan with Southern Uplands

6°- Investigate the tectonic significance at Girvan on the evolution of the Caledonides

Fig 1.3 Sketches of plate-tectonic models for the Scottish paratectonic zones

Key to Figure 1.3

Continental crust

Oceanic crust

Arc basement

Volcanic arc

Sediments

Ophiolites

BC = Ballantrae Complex

HBF = Highland Boundary Fault

LD = Lake District

MV = Midland Valley

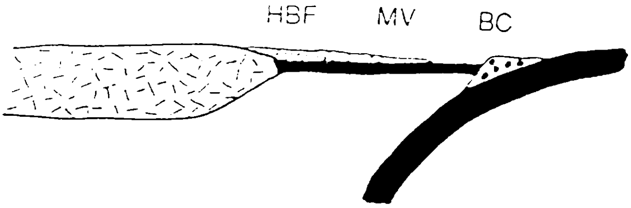
SU = Southern Uplands

SUF = Southern Uplands Fault

Fig 1.3

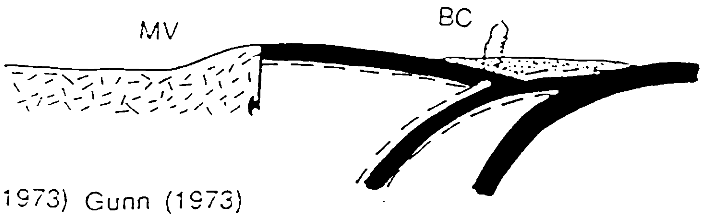
Dewey (1969+1971)

A



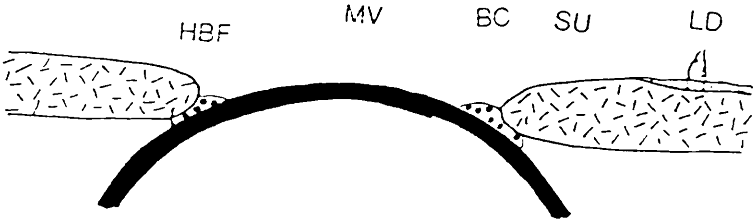
Church + Gayer (1973)

B



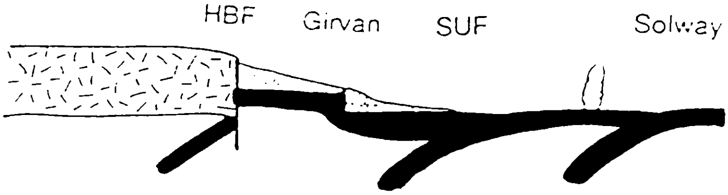
Jeans (1973) Gunn (1973)

C



Mitchell + McKerrow (1975)

D



Lambert + McKerrow (1976)

E

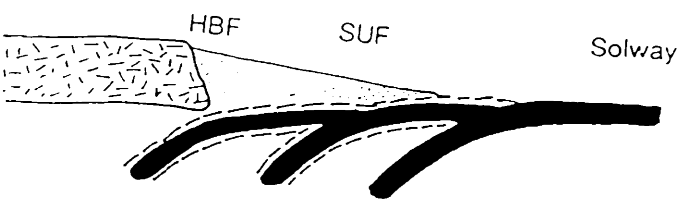
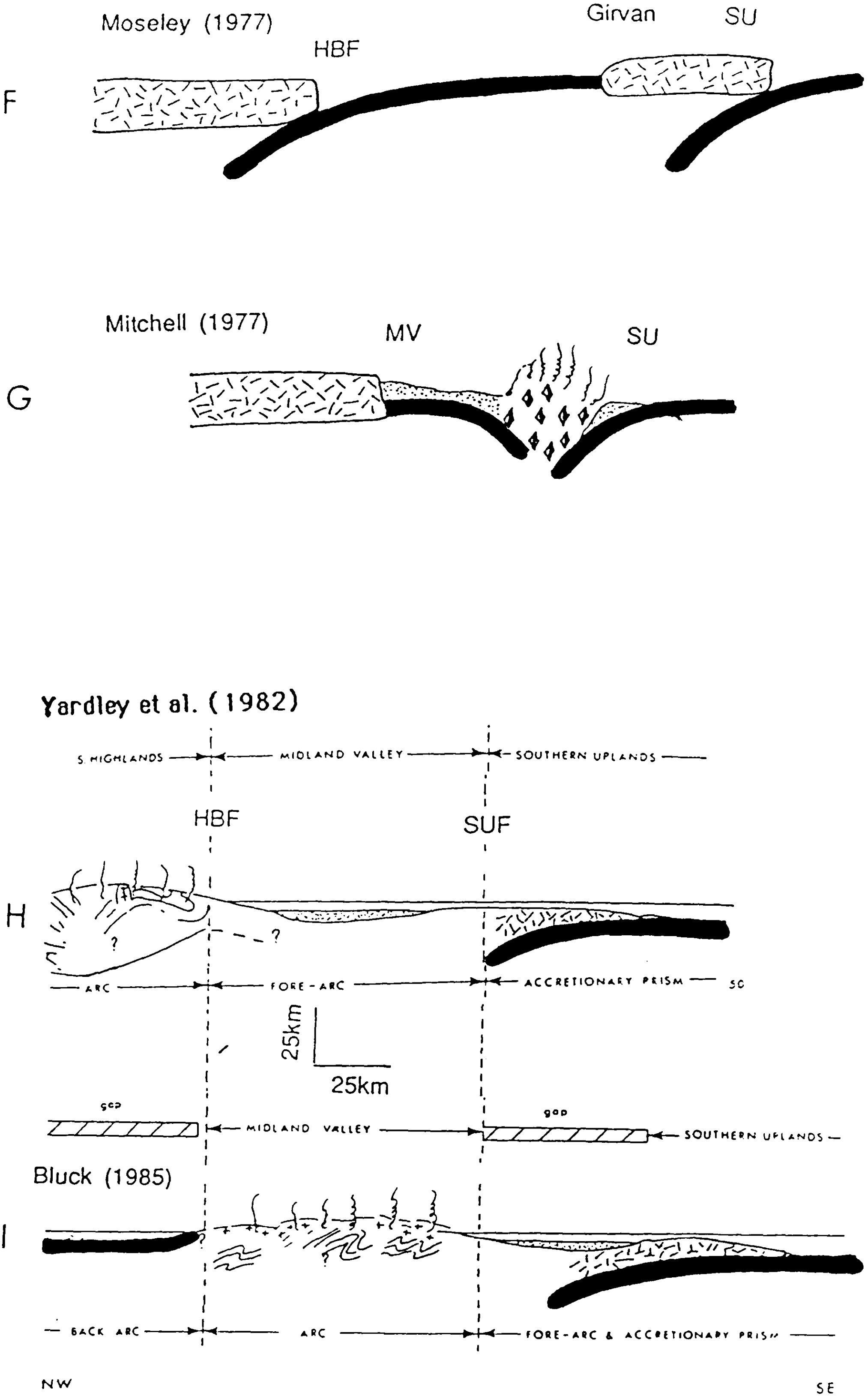


Fig 1.3


Moseley (1977)
HBF
Girvan
SU
F
Mitchell (1977)
MV
SU
G
Yardley et al. (1982)
S. HIGHLANDS
MIDLAND VALLEY
SOUTHERN UPLANDS
HBF
SUF
H
?
?
ARC
FORE-ARC
ACCRETIONARY PRISM
SC
25km
25km
gcp
god
MIDLAND VALLEY
SOUTHERN UPLANDS
Bluck (1985)
I
?
?
BACK ARC
ARC
FORE-ARC & ACCRETIONARY PRISM
NW
SE

CHAPTER TWO SAMPLING PATTERN AND ANALYTICAL METHODS

2.1 Introduction

The ultimate goal of the present study is to reconstruct the original sandstone compositions in order to deduce the source terranes and interpret these compositions in terms of tectonic models. Therefore, diagenetic and metamorphic influences must be removed wherever possible because as pointed out by Dickinson et al. (1969) point counting and compositional reconstruction of deeply buried sandstones is rather difficult. For instance in the Great Valley sequence (USA) it is found that deep burial has resulted in albitization of plagioclase and chloritization of biotite. Post depositional processes (e.g crushing of lithic grains and phylosilicates, alteration of characteristic heavy minerals and feldspars, calcite replacement and cementation) are also complicating factors.

Bearing in mind any possible contamination, large samples were initially trimmed to remove weathered surfaces using a hydraulic press. The samples were then crushed into small pieces depending on the number of the required test specimens which were subsequently used to make thin and microprobe sections, chemical and heavy mineral analyses.

2.2 Sampling pattern

Sampling involved collection of fresh unweathered specimens from various localities in the Girvan area. Sample locations are shown in Figure

2.1 and 2.1 at the end of thesis with the list of sample location, formation and age being given in Table 2.1. Two geologic sections through the Girvan area are also shown in Figure 2.2. Particular care was taken to ensure that the samples were clean. Samples were collected as widely as possible but at each locality at least two samples were collected near to each other so that any small scale variations in composition would be seen and could be accounted for during interpretations. Samples were collected wherever practicable from massive sandstones and greywackes lacking visible calcite replacement.

Fairly uniform stratigraphic and geographic distribution of sites was achieved by sampling along river valleys, coastal sections and areas of fairly extensive exposure (see Figure 2.1,2.1,2.3). Sandstones with a range of grain sizes were sampled and large specimens (± 1 kg) were collected so that both the chemistry and point counting of the same samples could be achieved.

2.3 Analytical methods

2.3.1 Petrographic methods

Thin sections have been analyzed for composition, proportions of matrix and grain size distributions. For the grain size investigation, the microscope had a calibarated eye-piece micrometer. Grain size was estimated from measurements of the largest axis of the grains in thin sections and the maximum visible grain diameter of 0.01 mm was defined as matrix (Dott, 1964).

Table 2.1 showing sample formation, location and age. See Figure 2.1 ,2.1 for the exact location of the samples on the geological map.

Samples number	Formation	Location	Age
Silurian			
SWP(9)	Scart Grit	[167 953] Black Neuk	Llandovery
HA/Q(4)	Quartz Conglomerate	[179 962] The Haven	Llandovery
HA/COW(3)	Craigskelly	[178 961] The Haven	Llandovery
Upper sequence			
AL*(7)	Shalloch Fm	[168-949] to [168-952] Ardmillan Lodge-Woodlands Point	L. Ashgill
WP(3)	Shalloch Fm	[168 952] Woodlands Point	L. Ashgill
SCM(4)	Shalloch Fm	[177 955] Shalloch Mill	L. Ashgill
WG(14)	Whitehouse Group	[159 943] to 168-949] Ardwell Bay to Ardmillan Lodge	U. Caradoc-L. Ashgill
Middle sequence			
PWH(22)	Whitehouse Group	[249 970] to [237 973] Penwhapple Burn	Caradoc-L.Ashgill
PWH(7)	Cascade Grits	[252 969] Penwhapple Burn	Caradoc
TM(16)	Ardwell Group & Cascade Grits	[235 943] Tormitchell Quarry	Caradoc
AF/K(27)	Ardwell Flags	[NX149 933] to [NX158 942] Kenndy's Pass to Ardwell Bay	Caradoc

Table 2.1: Continued

Lower sequence

IK-KP(9)	Infrakilrany Greywackes	[146 928] S of Kennedy's Pass	[Llandeilo-Caradoc?]
K/K(5)	Kilrany Conglomerate	[NX149 933] At shore Kennedy's pass	[Llandeilo-L. Caradoc?]
ALD(3)	Benan Conglomerate	[203 899] Road, B734 over R. Stinchar	Llandeilo
TR/GW(12)	Changue Fm	[290 939] to 295 923] Water of Gregg	U. Llanvirn
TR/GW(16)	Darley Fm	[295 923] to [299-912] Water of Gregg	U. Llanvirn
AL(6)	Craigmalloch Fm	[288 942] to [280-940] Water of Gregg	U. Llanvirn
TRB(21)	Changue Fm	[285 918] to [273 905] Traboyack Burn	U. Llanvirn
KC(6)	Kirkland Conglomerate	[245 926] Burn N of Kirkland farm	U Llanvirn
TAP(17)	Changue Fm	[332 947] to [334-937] Forestiry track above Balloch Burn	U Llanvirn
BC(7)	Craigmalloch	Water of Craig	U Llanvirn

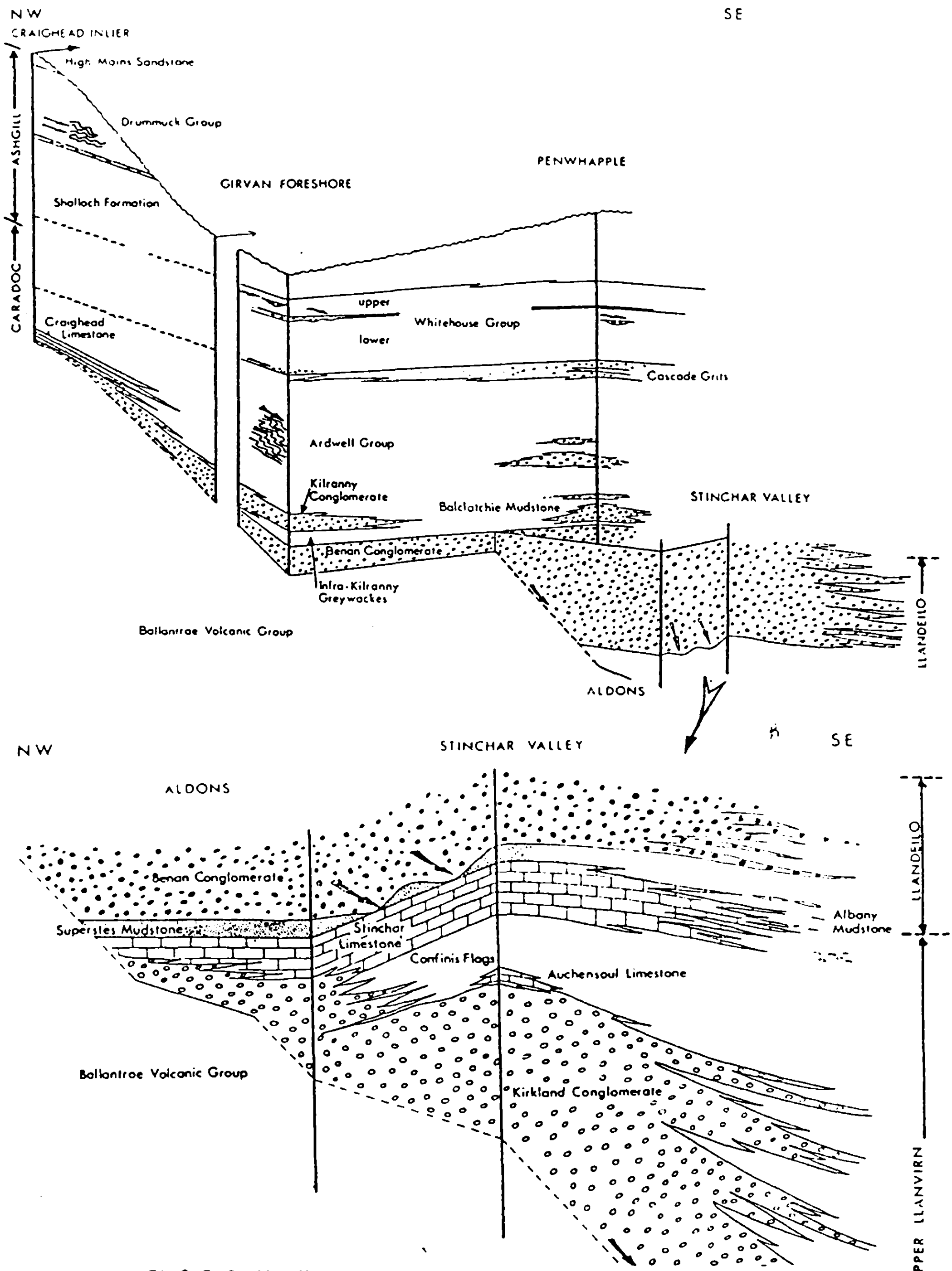


Fig 2.2 Section through the Girvan district (After Williams, 1962) with stage boundaries from Ingham (1978).
)

Throughout the present study , modal analyses were made using a polarizing microscope with a Swift automatic point counter unit attached to its stage. Because of the relatively large number of samples point counted (200 samples), the number of counts per slide was limited to 500 with the results being presented in appendix one. The standard deviations for 500 counts at 95% confidence are about ±4.5%, ±4%, ±3% and ±2% for volume percentages of 50%, 28%, 12% and 5% respectively (Van Der PLas and Tobi, 1965).

The accuracy of the results depends largely on the number of minerals to be counted, grain size of the mineral constituents and the degree of alteration and sorting of the minerals . In this study it is believed to be less than 10%. The point distance choosen throughout the whole study was slightly greater than the largest grain fraction found (Van der Plas, 1959).

Cobaltonitrate staining techniques were used to ease the identification of untwinned plagioclase and K-feldspar. In this method, uncovered thin sections are etched by placing their faces down in HF fumes for 10 ,seconds or 30 seconds when weaker acids are used. Then the slides are quickly immersed in saturated sodium cobaltonitrate solution for 15 seconds. The K-feldspar stains light yellow. After that the slides are rinsed briefly under running tap water to remove excess reagent. Then the sections are dipped quickly in and out of barium chloride solution, rinsed briefly in running tap water and then distilled water and covered with rhodizonate reagent from a dropping bottle. Plagioclase becomes pink in colour and the slides are then left to dry, rinsed and covered in the conventional way.

2.3.2 Heavy mineral separation technique

This method consists of two main steps namely: crushing and heavy liquid separation. the 50-200# fraction is taken and washed under running tap water in a 200 ml beaker to remove the unwanted light particles. After drying in an oven at 80-100^{o}C, the powders are then separated using bromoform liquid (specific gravity=2.89). The heavy fraction is then washed in acetone, properly labelled and stored in vials ready for investigation.

Representative fractions were subsequently examined under a binocular microscope for mineral identification and surface examinations. Those minerals intended for microprobe analysis, were hand picked and mounted on microprobe slides (4.7 x 2.1 cm) using thin drops of epoxy resin. The grain mounts were then uncovered using self adhesive silicon carbide paper discs (400 and 600 grits) and polished by machine (6μ and 1μ diamond paste respectively) and coated with carbon ready for analysis.

2.3.3 X-ray fluorescence

The principles and practice of X-ray fluorescence are well documented (e.g Norich and Chappell, 1967; Jenkins and De Vries, 1967) and the application to the determination of major and trace elements in geological samples have been discussed (Leake et al. 1969; Harvey et al. 1973). This technique has been used in the present work to quantify the major and trace element contents in the samples.

2.3.3.1 Principles

On bombarding a sample with a source of X-rays, the atoms present in the sample will scatter some and absorb the remaining photons. Photons absorbed by an atom in the sample will give rise to characteristic X-ray emission of that element. The characteristic X-ray photons produced by this X-ray bombardement of an element is known as X-ray fluorescence. The intensity of the charateristic fluorescent radiation for a given intensity of source X-rays is not completely linear in relation to the element concentration due to various absorbance effects by the sample matrix. These effects which depend essentially on the thickness on the substance, its density and its absorption coefficient are corrected for and the concentration of elements can be estimated.

The detection of an element in X-ray fluorescence emerges from the application of Braggs equation ($n=2d \sin\theta$). For a given value of the angle, θ may be predicted if a crystal having a known atomic spacing (d) is used. Since the X-ray radiation for every element has known fixed wavelengths then the value of θ can be calculated for any given element. Thus, the fluorescent radiation emitted by a rock sample may be investigated to find whether an element is present and if so in what concentration.

The detection limits of X-ray fluorescence for major and some trace elements are given below:

Table 2.2 Detection limits of XRF

Major elements			Trace elements	
detectionaccuracy			detection	
limits(wt%)			(wt%)limits(ppm)	
SiO_2	0.086	0.46	Cr	1.9
TiO_2	0.018	0.11	Ni	4.8
Al_2O_3	0.087	0.36	Co	3.2
Fe_2O_3	0.045	0.10	Ga	2.4
MnO	0.012	0.008	Sr	1.5
MgO	0.165	0.13	Zr	2.7
CaO	0.006	0.17	Rb	1.7
Na_2O	0.155	0.26	Zn	1.8
K_2O	0.002	0.09	Cu	4.4
P_2O_5	0.018	0.02	Pb	11.6

2.3.3.2 Methodology

Chemical analyses in conjunction with petrography are important means of examining compositional variation in rock samples . Therefore 212 samples were subjected to XRF analysis for both major and trace elements.

The first step consists of reducing the size of the samples into small, typically 0.8 x 0.5 cm chips and then crushing down to 100# and 250# respectively. The former size is suitable major element analyses and the latter for the trace elements. The methods of analyses are those described by Leake et al. 1969 and Harvey et al.

1973 for trace and major elements repectively.

2.3.4 Wet chemistry

Conventional wet chemical analysis is necessary to determine the H_2O and CO_2 values which are not suitable for XRF methods. They were determined simultaneously using the method of Riley (1958)

2.3.5 Microprobe analysis

In this method individual mineral analyses were possible using a Cambridge Instrument Microscan 5 machine. This uses X-ray radiation generated by an electron beam striking a finely polished and carbon coated thin probe sections (90μ thick). Each element produces a characeristic X-ray energy spectrum which is measured by a solid state detector for a counting time of 100 second. The total spectrum is processed by on-line Data General Corporation Nova 2 microcomputer using a program written by Colin M. Farrow and which produces the analysis in weight % oxides.

CHAPTER THREE CHARACTERISTICS OF FOREARC AREAS

3.1 Introduction

The purpose of this chapter is to briefly outline the characteristics of forearc regions and examine the diversity of petrologic composition of sandstone now being laid down within the recent forearc areas. By comparison with this information it is possible to locate more precisely the setting of the Girvan sequence and understand the way in which the sedimentary pile there has evolved.

The classification of plate tectonic regimes have been extensively discussed by Dickinson (1974), Dickinson and Seely (1979) and others. These are shown in Figures 3.1(A-C) and 3.2-3 which show two major divisions namely: passive and active settings each of which can be further subdivided into different parts (see Fig 3.1-3).

3.2 General characteristics

It has already been pointed out that during Ordovician and Silurian times Scotland is considered to have been part of a destructive margin of the Laurentian continent, so this chapter emphasis the tectonic elements which characterize zones of plate convergence.

3.2.1 Plate convergence

Convergence, where the surface of one plate is continental and the other is oceanic, is maintained by subduction of the oceanic plate beneath the continental plate; the oceanic lithosphere is consumed deep in the mantle below the continental margin. This type of convergence is often referred to as "Andean-type" (see Figure 3.1 (A & C). Where convergence takes place between two oceanic plates and an intra-oceanic island arc subduction zone develops and is sometimes referred to as "intra-oceanic convergence" (see Figure 3.1 A & B). Due to the development of this type of plate convergence in Marianas, it is usually referred to as "Marianas-type" (Uyeda 1981). Convergence between two continental plates leads to orogenic mountain belts and is some times called "Himalayan" or Continental collision.

3.2.2 Sedimentation in plate convergence.

The rock records in regions of plate convergence are characterized by (i) a great deal of volcanic eruption and high volumes of pyroclastic rocks and (ii) island arc magmas which are dominantly mafic, most commonly basalt to andesite. In the case of magmas which are mafic to highly silicic such as that of the "Andean-type", there is some tendency for magmas derived from deeper levels and higher temperature to be rich in K2O and SiO2. In this case lavas further away from the subduction zone may be richer in K2O and SiO2.

Sedimentation along convergent margins is poorly understood as it reflects complex interaction between tectonics and depositional processes (Dickinson and Seely 1979; Underwood et al. 1980). Usually sedimentation takes place seaward of the trench, in the trench axis, on the inner trench-slope and in the forearc basin (see Figures 3.1-3). These depositional environments are continuously modified as the accretionary prism grows. Provenance and dispersal of sediments in these environments are very complicated. Terrigenous detritus may be derived directly from a nearby arc terrane, can be either transported for long distances along the trench axis or carried into the trench on the subducting oceanic plate.

Models of convergent plate margins commonly assume that much of the arc and forearc in particular, is underlain by oceanic crust (Dewey and Bird 1970; Mitchell and Reading 1971). A major reason for this assumption is that the initial crustal fracture which leads to trench formation occurs within the oceanic crust.

3.2.3 Intra-oceanic convergence

Early in their history, intra-oceanic convergences produce quartz-free and mafic volcanics components that constitute the basement sequence of volcanic or accretionary terranes. In these basal sequences pillow basalts are abundant but pyroclastics are rare Today's active arcs are predominantly situated on the west side of the Pacific from the Aleutian in the north to the Kermadec-Tonga Kermadec arc in the south. Most arcs are intra oceanic (e.g Marianas, Tonga, Solomons, New Hebrides etc), some are separated from sialic continents by narrow semi-ocean basins (Japan, Kuril, Banda etc), some pass laterally into Cordillerran-type fold belt (Aleutian), some are built against continental crust (Sumatra, Java). It is clear therefore that there are transitional types between intra-oceanic arcs and Andean-type continental margin in which the volcanic belt is an integral part of the continental land mass (see Figure 3.1 B for small details).

3.2.4 Andean-type convergence

This type of convergence generates complex rock assemblages and is more likely to be preserved in the continental rock record (Figure 3.1 C). The sedimentary environments present and the tectonic regimes which accompany an oceanic-continental convergence differs from an intra-oceanic arc convergence setting in many respects. The interaction with the continental block may involve two different models: (i) an arc offshore with a marginal sea between the arc and the continent and (ii) the true Andean-type with the arc being located on the continent itself. The latter has both forearc and backarc regions on the continent and only a strip of marine forearc between the trench and the onshore forearc basin. In Andean-type convergence, the trench may lie close to the shore as does the Peru-Chile trench of the coast of South America or somewhat further offshore, as the Aleutian trench off Alaska. The accretionary prism and forearc basins become a part of the continental block converging with the oceanic plate. The arc is in land, the magmas rising through thick continental crust to form a continental volcanic mountain chain.

Volcaniclastic (mafic to highly silicic) sediments of Andean-type convergences are very variable in terms of rock type and petrographic composition (Miyashiro 1975). The zone along the west coast of South America is often considered the classical continental arc of this type and it displays all structure and tectonic elements (subduction zone, arc massif, forearc basin and volcanic arc) that indeed characterize Andean-type convergence (Seely 1979).

3.3 Arcs

3.3.1 Structures of arcs

Broadly there are systematic variations in the structural zones in passing across the strike of island arcs. They normally include a trench, a forearc, an arc, backarc basin and an inter-arc or marginal oceanic basin (see Figures 3.2-3).

The trench, which is typically 50-100 km wide and may be up to 11 km deep (e.g Marianas), is the site of the deep-sea pelagic sedimentation. It is mixed in some places with turbidites and slumped material derived from the arc side of the trench and perhaps mixed with detritus derived from the seaward side. The turbidites usually include plenty of volcaniclastic material derived from the arc itself and sometimes shallow-shelf carbonate material and slumped sediments are included.

The forearc basin region (50-400 km wide) may be one of subsidence between two positive areas, the arc region being elevated by magmatic activity and the accretionary prism being thrust up. The sediments in this region contain volcaniclastic material, turbidites, subaqueous ash flow and welded tuffs (e.g Fiske and Matsuda 1964; Bond 1973; Howells et al. 1979).

The arc region itself (50-100 km wide) is the site of extensive high level volcanics and deeper-seated magmatic intrusions. Sands related to this region are particularly rich in volcaniclastic components typically of andesitic and other intermediate composition. Sediments of the arc contain eroded older extrusives, fragments of older continental terranes and occasionally even metamorphosed rock fragments. In terms of rock types, volcanic arcs are characterized by a high proportion of pyroclastic rocks (83-93 volume percent) interbedded with thick deposits of greywackes and mudstones and by overprinting of the sedimentary signatures by high temperature low pressure metamorphism (Garcia 1978).

The backarc region (15-30 km thickness), which is often a marginal sea between the arc and a continent, is a subsidiary spreading region of oceanic plate whose motions may force migration of the arc complex and subduction zone in the direction of the advancing lithosphere on the far side of the subduction zone. The sediments in this region are normally pelagic sediments and tubidites ,both of which are rich in volcaniclastic components derived from the arc.

The marginal basins (Interarc basins) lie behind island arc systems and are underlain by oceanic crust and situated between the main magmatic arc and the corresponding continental margin (e.g Japan Basin) or another island arc-trench system (e.g. Philippine Basin). This type of basins is thought to have formed by extensional rifting (Karig 1970) or spreading of the ocean floor (Packham and Falvey (1971). Re-investigation of paleomagnetic data led Windley (1984) to conclude that the latter process is most likely.

3.3.2 Sedimentation in arcs

The relation of sedimentary basins and sedimentation to plate tectonics was explored in a ground breaking paper by Bird and Dewey (1970) and Dickinson together with his co-workers (e.g Dickinson 1970, 1971, 1974; Dickinson and Seely 1979; Dickinson et al.

1979; Dickinson and Valloni 1980, Maynard 1984 and many others). Within the plate tectonic framework, sediments are deposited in the trench-subduction complex and hence the trench should contain pelagic oceanic sediments and thrusted slices of ophiolites off scraped into the continent-edge of the subduction zone. However, most trenches especially those in the intra-oceanic arcs of the western and north Pacific contain less than 300m pelagic sediments and hardly any terrigenous sediments. Scholl et al (1977) concluded that deep-sea sediments that have been subducted and that off scraping of terrigenous deposits into a trench are only possible where thick (greater than 500-1000m) sequence is swept against island arc.

The trench-slope break (Fig 3.2) marks the inner edge of the subduction complex which was formed by tectonic accretion and which comprises a thrust stack of off-scraped sediments from the trench and it emerges as Barbados island in the lesser Antilles (Westbrook 1982). In this particular instance there is an abundant sediment supply. In contrast Lundberg (1983) emphasized that intra-oceanic arcs like the Marianas and Costa Rica lack thick clastic deposits and melange complexes because of low terrigenous sediment input and thus they lack high grade exotic components such as blue schists and eclogites.

Forearc basins lying between the trench slope break and the arc often contain flat lying undeformed sediments that may reach 5km in thickness. These sediments may reflect the progressive shoaling as the basin fills up with turbidites and shallowing marine sediments and fluviatile-deltaic shoreline complexes (Dickinson 1982). Some of the forearcs that are already fairly well characterized were defined as submarine (Central Aleutian, Marians, Tonga Kermadec) and some are partly submarine and partly sub-aerial (Japan and Costa Rica). The sediments deposited in forearcs are mostly derived from the adjacent arc volcanoes (volcaniclastics) by erosion of uplifted basement of metamorphic-plutonic rocks as is the case of the Sunda arc of Sumatra (Moore et al. 1982) or recycled orogenic material such as pre-existing sedimentary basins.

3.3.3 Arc-trench

Modern arc-trench gaps widen with time as a result of the prograde accretion of subducted material above and behind the trench and by the retograde migration of the volcanic arc away from the trench (Dickinson 1973). Karig and Sharman (1975) and Dickinson (1975) discussed in some length the nature of the tectono-stratigraphic contact between the subduction complex and the undeformed sediments of the forearc basin. As the accretionary prism builds upward and outward, the forearc basin sediments onlap the tectonically stable flank of the subduction complex near the trench slope break. Periodic re-activation of thrusts within this area causes deformation of the base of the onlapping sediments so that the contact between the subduction complex and the forearc basin sediments have both depositional and tectonic charateristics (Dickinson 1975).

Forearc basins of modern arc-trench systems tend to evolve from steep-sloped, narrow zones with little sediment accumulation to wider and shallower basins within which great sedimentary thicknesses accumulate (Karig and Sharman 1975). As the forearc basin widens, most sediments that were derived from the arc are deposited within the arc trench gap with only little sediment reaching the trench and eventually the forearc basin may be filled to near sea-level and arc-derived sediments again may be deposited primarily within the trench or within the trench-slope basin (Moore and Karig,1976). This latter situation is likely to occur within margin of arc-trench systems with higher rates of sediment supply than in island-arc systems with low rates of sediment supply.

3.4 Forearcs

3.4.1 Different types of forearc basins

Distinction between the various and often complex types of forearc basins depend primarily on the structural evolution of the subduction complex and the history of accompanying sedimentation. Based on the nature of the substratum beneath the basin, Dickinson and Seely (1979) recognized five types: (1) arc massif, (2) residual, (3) accretionary (4) constructed and (5) composite basins (see Figure 3.4 A-C)). Arc massif basins are characterized by block faulting and marine or non-marine arc or backarc derived sediments. The accretionary basins are commonly structured by compressional folds and listric thrust faults are filled with marine sediments derived from uplifted subduction complex or arc terranes. The residual and constructed basins are structurally and stratigraphically transitional between the arc massif and accretionary types. Residual basins also include abyssal sequence of abyssal-plain sediments. Both the arc massif and the structural high are belts of uplifted areas and hence prvide potential source material for basins within them or proximal to them (Dickinson and Seely 1979).

3.4.2 Forearc evolution

The quantity of sediment delivered to the forearc regions is a prime factor governing forearc evolution. An initial residual forearc basin may later become a composite of sedimentary forearc basins. Also large scale lateral accretions can occur only if there are large quatities of trench fill, abyssal plain and slope sediments. Sedimentation, metamorphism, and volcanism are always linked in fore arc regions and arc trench systems (Dickinson 1979).

The position of the axis of magmatism in respect to the trench governs the extent of forearc regions. Slow retrograde migration of the magmatic axis away from the forearc is common and occurs at a rate of roughly 1km/Ma (Dickinson (1973). Where the crust is thick in the arc massif, there is usually a potential for isostatic uplift which is ultimately followed by erosion. Sediments derived from the plutonic roots of the arc massif may there fore join volcanic debris which is being deposited in the forearc basins. Thus the amount of the uplift is likely to increase with time. Accordingly, the ratio of plutonic to volcanic detritus is likely to increase upward in the stratigraphic section within the forearc basin. The petrological character of the volcanogenic materials produced along an arc tend to evolve from relatively mafic rock types early in the history of the arc through to more felsic rock types during later stages of igneous activity (Dickinson, 1979). Dickinson (1970) related the evolution of magmatic composition to the provenance of volcanic and plutonic detritus in sandstones derived from erosion of arc terranes.

Dickinson and Suczek (1979) classified all provenances and derivatives of sandstone suites into three main super groups: continental, magmatic and recycled. Those sandstones and greywackes derived from the continental block were attributed to shields, platforms and faulted basement blocks. The source of the magmatic arc material is likely to be within the active arc orogens of island arcs or active continental margins. The recycled orogenic material on the other hand is derived mainly from uplifted stratal sequences in subduction zones, along collision orogens or within foreland fold-thrust belts.

The authors further divided each super group into several smaller categories and indicated the nature of common kinds of transitional sandstone suites. For instance they divided arc-derived suites into those eroded from: (1) undissected arcs in which the continuous volcanic cover is present and where largely volcaniclastic debris are shed from volcanogenic highlands along active island arcs. In addition there are some continental margins where arc volcanic chains have undergone only limited erosion. The sites of deposition include trenches and forearc basins on the frontal side of the arc. The characteristic mineral constituents of undissected arcs are abundant plagioclase feldspar and volcanic lithic fragments. (2) Dissected arcs in which the material is derived from more mature magmatic arcs especially those along the continental margins. Detritus derived from mixed plutonic and volcanic origin shed into both forearc and backarc basins. In these types of sediments, the sandstone compositions are more complex but generally contain less lithic rock fragments than volcaniclastic debris. Both feldspars are commonly present in significant proportions and non-volcanic lithic fragments predominate in varying degrees. The third provenance is transitional arcs with the material being a mixture of both recycled orogens and magmatic arcs.

Potter (1978), Valloni and Maynard (1979) made studies of selected modern sand samples and their results confirm those of Dickinson and Suczek as discussed above.

3.4.3 Petrographical characteristics

Sand from orogenic settings is consistently less quartzose than from non-orogenic settings and also varies markedly in detail. The sand off coastal transform orogens is more quartzose, contains fewer lithic fragments and has a lower ratio of plagioclase to K-feldpsar than sand of continental-margin arc orogens (Dickinson and Valloni 1980). The sand surrounding island arcs within ocean basins is even less quartzose, contains more lithic fragments and has still more plagioclase in relation to K-feldspar. Volcanic rock fragments are the dominant lithic fragments in both arc-related sand suites whether deposited off continental margins or island arcs. The proportion of poly crystalline to monocrystalline quartz grains tend to be higher in all orogenic suites than for the rifted margin settings (Dickinson and Valloni 1980). Sand derived from the intra-plate oceanic sources on the other hand generally lacks quartz but contains plagioclase as the only feldspar and volcanic rock fragments as the only lithic grains except for carbonate clasts.

From detailed studies of mean framework (the proportions of detrital grains which make up the framework of the sandstone, because the character and amount of interstial cement and matrix are both largely a function of diagenesis, and of no significance in provenance studies.) modes of sandstones from circum-Pacific suites, Dickinson (1982) suggested that sandstone compositions, provenance and tectonic settings can be brought out by the use of primary parameters (QFL, QmFLt) and supplementary parameters (QmPK, QpLvLs) plots which are partial modes of mineral grains and polycrystalline lithic fragments respectively (see Table 4.1 for the definition of the mentioned abbreviations).

In California, both the Franciscan suites (subduction complex) and Great Valley Sequence suites (forearc basin) are characterized by turbidites with similar distributions of mean framework modes mentioned above. However, the subduction complex sediments are slightly more feldspathic and less lithic compared to those deposited in forearcs but both have comparable quartzose grains. Lithic-rich sediments in both terranes where present are inferred to have been derived from relatively undissected segments of magmatic arcs, whereas the lithic-poor sediments are inferred to have been derived from fairly dissected magmatic arcs. These results are interpreted to mean that the sources of the subduction complex sediments lay preferentially in more dissected segments of the magmatic arc than did sources for turbidites of the adjacent forearc basin (Dickinson 1982).

The framework modes QFL and QmFLt of rocks from the subduction complex in Alaska have been studied in detail by Dickinson (1982). The authors showed that data from the abyssal-plain turbidites, for several Cook Inlet suites, and for most of the

Pacific NW suites, fall within the field for the Alaskan subduction complex except three framework modes. These are (1) more quartzose and less feldspathic rocks from slope basins and this trend probably reflect re-working of sediments partly derived from arc terranes and partly from uplifted subduction complex; (2) less lithic and more quartzo-feldspathic rocks within the Cook Inlet forearc basin which probably reflect derivation mainly from adissected batholiths where the amount of volcanic cover in the arc terrane was temporarily or locally minor; and (3) quartz-poor rock in Ataka basin of Aleutian terrane which reflect exclusive derivation from the volcanic island arc of the Aleutian ridge. Also based on the framework modes QFL and QmFLt, both the Shimanto (subduction) and Median Zone (forearc) of the SW Japan fall within the fields of Alaska subduction complex, and within the combined Franciscan and Great Valley suites in California. In both places the subduction complexes apparently contain slightly more feldspathic and less lithic rocks than the coeval strata of forearc basins so that they lay wholly within the arc trench gap during the time span of their deposition (Dickinson 1982).

From the framework modes ,QmPk means for all suites from the Circum-Pacific subduction complexes fall between 33% and 50% monocrystalline quartz (Qm). Mean ratios of total feldspar to quartz are uniformly between 1:1 and 2:1 and the mean values of suites from slope basins and other types of forearc basins lie mostly within the same field but with more quartzose compositions which extend toward 67% Qm, representing a quartz to total feldspar ratio of 2:1. The composition of these more quartzose rocks probably reflect extensive sedimentary re-working of arc-derived detritus within the forearc region. A few suites of quartz-poor volcaniclastic rocks from analogous forearc basins in New Zealand and Aleutian plot within 33%Qm.

From the QpLvLs framework modes of the California, Pacific NW and Alaskan suites, more than a half of the lithic fragments are of igneous origin (Lv) and that the rest are believed to represent a mixture of volcanic and metavolcanic grains, with varying proportions of lithic fragments having non igneous origin (Qp and Ls) (Dickinson 1982). When represented on a QpLvLs triangular diagram, it was found by the same authors that the median mixture of added non igneous grains contains cherty detritus (Qp) and argillite to slaty detritus (Ls) in the proportion of 1:2 in all suites. The wide distribution of the data shows, however,that neither the proportions nor the amount of the non-igneous admixture are constant. The general interpretation given by the authors is that sandstones exposed within forearc regions of the Circum-Pacific orogenic belt have similar compositions everywhere (Dickinson 1982). Dickinson and Suczek (1979) observed that variations in detrital modes mainly reflect varying degrees of dissection of the volcano-plutonic complex from the bulk of the arc massif.

The most typical rocks of the Circum-Pacific greywacke suites have feldspatholithic and framework components with intermediate quartz contents. Compositional variations mostly mark variations in the proportions of lithic fragments, where total feldspar to quartz ratios are most commonly semi-constant with values between 1:1 and 2:1. Plagioclase is always dominant over K-feldspar and the volcanic rock fragments as the most abundant lithics (Dickinson 1982).

By combining their own data of 80 modern deep sea sand and other data from the literature, Valloni and Maynard (1981) noted that the amount and type of lithic fragments and the type of feldspar are particularly important discriminating factors. They also assigned sands to five plate tectonic categories each of which has a distinct average petrologic composition. These are summarized in Table 3.1:

Table .3.1: QFL modes of some tectonic elements

Tectonic setting	Q	F	L
Basin associated with passive continental margin	62	26	12
Basin associated with active continental margin			
a) Subduction	16	53	31
b) Strike-slip	34	39	27
c) Backarc	20	29	51
d) Forearc	8	17	75

Yerinc and Maynard (1984) assembled a set of samples from the Peru-Chile trench and adjacent areas. They divided the area into three main regions: (1) the framework components for the Peru-Chile trench have a mean falling close to that reported by Maynard et al. (1982) for sands from the forearc region of continental margin arcs. (2) The Strait of Megellan sands are also similiar and (3) Central-America trench samples have a distribution more typical of the forearc of island arcs. In all three cases, the sum of feldspar and lithic fragments greatly predominate over quartz which is consistent with other active tectonic settings. The results of analyses from the three regions discussed above are summarized below in Table 3.2 which clearly shows that feldspars are almost exclusively plagioclase and the lithic fragments are mostly volcanic.

Table 3.2: Summary of some framework data of the Peru-Chile trench and adjacent areas.

Area	No of sample	Q	F	L	C/Q	P/F	Lv/L	Q	F	R
1	46	18	44	38	0.16	0.97	0.82	16	26	58
2	7	3	21	76	-	1.0	0.99	3	7	90
3	6	22	45	33	0.29	0.97	0.75	19	24	57

1= Peru-Chile trench: The average framework composition is similar to the ocean side of the continental margin volcanic arc

2= Central America trench: Has a composition typical of sands from the forearcs of island arcs

3= Strait of Megellan: Has a composition which seems to reflect the transition from the forearc to backarc side of the continental-margin arc

From the studies of the grain populations of the Great Valley Sequence, Dickinson and Rich (1972) inferred that the source rocks were mainly cogenetic suites of volcanic, hypabyssal and plutonic igneous rocks with which were associated in adjoining metamorphic terranes of low grade metasedimentary and metavolcanic rocks. They also recognized five petrofacies and discussed the petrographic characteristics of each petrofacies with reference to a series of figures showing various aspects of the composition of sandstones using the framework QFL. In the lower sequence, there is a combination of low Q and high L, high P/F, high V/L and low mica. They deduced that there is an upward trend from the most lithic rocks in the base to least lithic rocks at the top of the section in passing from the Stony Creek feldspatholithic sandstones to Rumsey litho feldspathic sandstone.

Rocks in Nias island (Indonesia) consist of two main units: trench deposits (tecto-melange) and trench slope deposits (Moore 1979). Modal analyses from the two settings revealed that the sediments are particularly rich in quartz and sedimentary/metasedimentary lithic fragments and both cluster on the QFL diagram. The trench deposits (tecto melange) consist of small amounts of Qp cemented together by phyllosilicate minerals and have framework modes Lv, Lm and Ls of 37, 17 and 46 respectively. In contrast, the trench slope deposits contain abundant K-feldspar, polycrystalline quartz, glauconite and carbonate grains and cement. The average framework modes Lv21Lm53Ls26. It is clear therefore that sediments from melange have very high P/F, high Lm and low Ls and Lv but those from the slope basin have low P/F, Lm and Lv and high Ls and glauconite.

Sediments derived from the Himalaya which average Q57F28L14 are well documented and are micaceous, highly quartzose and the lithic types are dominated by metamorphic rock fragments, (Lm87Lv4Ls29) (Ingesoll and Suczek 1979). Other petrological studies of Himalayan sediments all confirm their enrichment in quartz and metamorphic rock fragments (e.g Raju 1967; Thompson 1974; Mallik 1976&1978),

Sedimentation in the Sunda forearc region varies both spatially and temporally. Transport of Himalayan detritus along the trench axis dominates in the north but hemi-pelagic sediments become more important components in the trench wedge to the south. Off south Sumatra, quartzose turbidites derived from the Himalayas are deposited in the trench whereas volcanic rich turbidites derived from Sumatra are deposited in the forearc basin. Off Java, hemi-pelagic sediments dominate both in the trench and on the lower trench slope.

From the petrography of Plio-Pleistocene sandstone, eastern Taiwan, Dorsey (1988) noticed that the changes in relative abundance of sedimentary and metasedimentary lithic fragments through time can be used to interpret an unroofing sequence from the collision fold and thrust belt where during earliest stages of arc-continent collision, sandstones are rich in sedimentary lithic fragments (Ls) which are shed from the accretionary wedge. From early Pliocene to early Pleistocene time, sandstones became progressively depleted in sedimentary lithic fragments and enriched in both low (Lm1) and medium (Lm2) grade metamorphic ones. The progressive decrease through time in the sedimentary lithic fragments but increase of Lm1 and Lm2 respectively provide an evidence for uplift and unroofing for accretionary prism wedge (Dorsey 1988).

The continental margin orogenic belts have a long complicated history of igneous activity. Broadly, the igneous products are of two types; volcanic and plutonic. Many of the volcanic rocks formed in the arc zone are eroded and the underlying granitic rocks in the arc core are therefore exposed and subsequently progressively eroded.

In western North and South America both magmatic types are found. The intrusive and extrusive arc rocks are predominantly mantle-derived and represent new additions to the continental crust which is correspondingly growing at a rate close to 0..5 km3 yr -1 (Brown 1982).

From the existing data produced for present-day forearc regions, it is clear that there are some important factors governing the composition of sediments laid there:

1. The nature of the forearc setting. Intra-oceanic forearcs (e.g Tonga-Kermadec, Marianas, Aleutians, etc) tend to have high lithics, high volcanics dominated by mafic most commonly basalt to andesite but low in detritus derived from the basement. The sediments are dominatly marine and usually include pelagites and hemi-pelagites. In contrast, continental forearcs (e.g Andean type, Java etc) can be rich in non-marine sediments. variable lithics (volcanics to granophyre), volcaniclastics, turbidites, shallowing marine sediments. Fluviatile-deltaic shoreline complexes are also characteristics of this type of forearcs.
2. The evolutionary trend in either of these arcs greatly control the nature of the sedimentary record there. Mature arcs are characterized by progression from tholeiitic to calc-alkali and alkali series from oceanic to continental side. Also there is a thick subarc crust (30-35 km) and usually lie close to the continental margins (e.g Japan). In contrast, immature arcs lack thick clastic deposits and high grade exotic components and are charaterized by thin subarc crust (15-25 km) (e.g. Marianas, Tonga Kermadec arcs). Tholeiitic basalts are typical of this type of arc.

3. There are similarities between the petrography of trench and forearc regions. For instance the Great Valley forearc region has similar QFL and QpLvLs to the Alaskan arc trench system Dickinson (1982). However, where the trench is fed by a river system which deposits sediments along its axis, then there can be significant differences in the type of sediment found in the trench and forearc basins as is the case of sand of Sumatra

3.4.4 Geochemical characteristics

The First stages of island arcs with crustal thicknesses less than 20 km are characterized by tholeiitic series possessing low abundances of incompatible elements (e.g K, Rb, Ba, U, REE) (Perfit et al 1980). More evolved stages of volcanism are characterized by calc-alkali series with higher abundances of incompatible elements for a given SiO2 value and with more fractionated REE patterns (Coulon and Thorpe 1981). In less mature island arcs (e.g. Indonesia and Kuril islands), the most characteristic variation is an increase in the content of alkali elements towards the continent in island arc tholeiites and calc-alkaline suites (i.e. for rocks with a similar SiO2 content there is an increase in K2O and Na2O + K2O). In mature island arcs such as Japan, however, there is a progression from tholeiitic to calc-alkali and alkali series from the oceanic to continental side (LeBas 1982).

There is also a close correlation between the three chemical series and the degree of tectonic activity of different types of arcs. The youngest(i.e. least mature) have the deepest earthquakes and highest rates of uplift of plate convergence, with typically tholeiitic basalt series In more mature arcs, the calc-alkali series is typical, the alkali series is present but not important and the tholeiitic volcanics are uncommon. It should be noted that in arcs with the slowest rate of plate convergence and shallowest earthquakes, alkali volcanics are common.

In the true Andean type convergence, the arc is located on the continent and it has both forearc and backarc regions, so detritus derived from mixed plutonic and volcanic origin is shed into both forearc and back basins

Sediments in these basins cannot be distinguished from each other on the basis of petrography and bulck composition.

Key to Figures 3.1-2

Figure3.1: Spatial relations of the various plate tectonic elements (after Dickinson and Seely, 1979). A= a general view showing the key tectonic elements discussed in the text above; B=tectonics, volcaniclastic deposits and sedimetary environments of intra-oceanic island arcs; C=Andean-type continental arcs ;

Figure 3.2: Schematic diagram of continental- margin arc-trench system (after Windley 1984) showing the main arc tectonic elements (magmatic arc, trench basin, forearc basin, backarc basin, foreland basin and subduction complex)

Figure 3.3: Shematic diagram of intra-oceanic arc (after Windley 1984) showing the key tectonic elements mentioned above in addition to the presence of intra-oceanic basin.

Figure 3.4: Various types of forearc basins after Dickinson and Seely (1979). Note that unlike in figure A, the oceanic crustal element was not trapped beneath forearc in figure B and hence the basin rests only on arc massif and subduction complex. In figure C the residual basin evolves into a composite basin due to accretion.

1=Intra-massif basin

2=Residual basin

3=Accretionary basin

4=Constructed basin

5=Composite basin

Fig 3.1

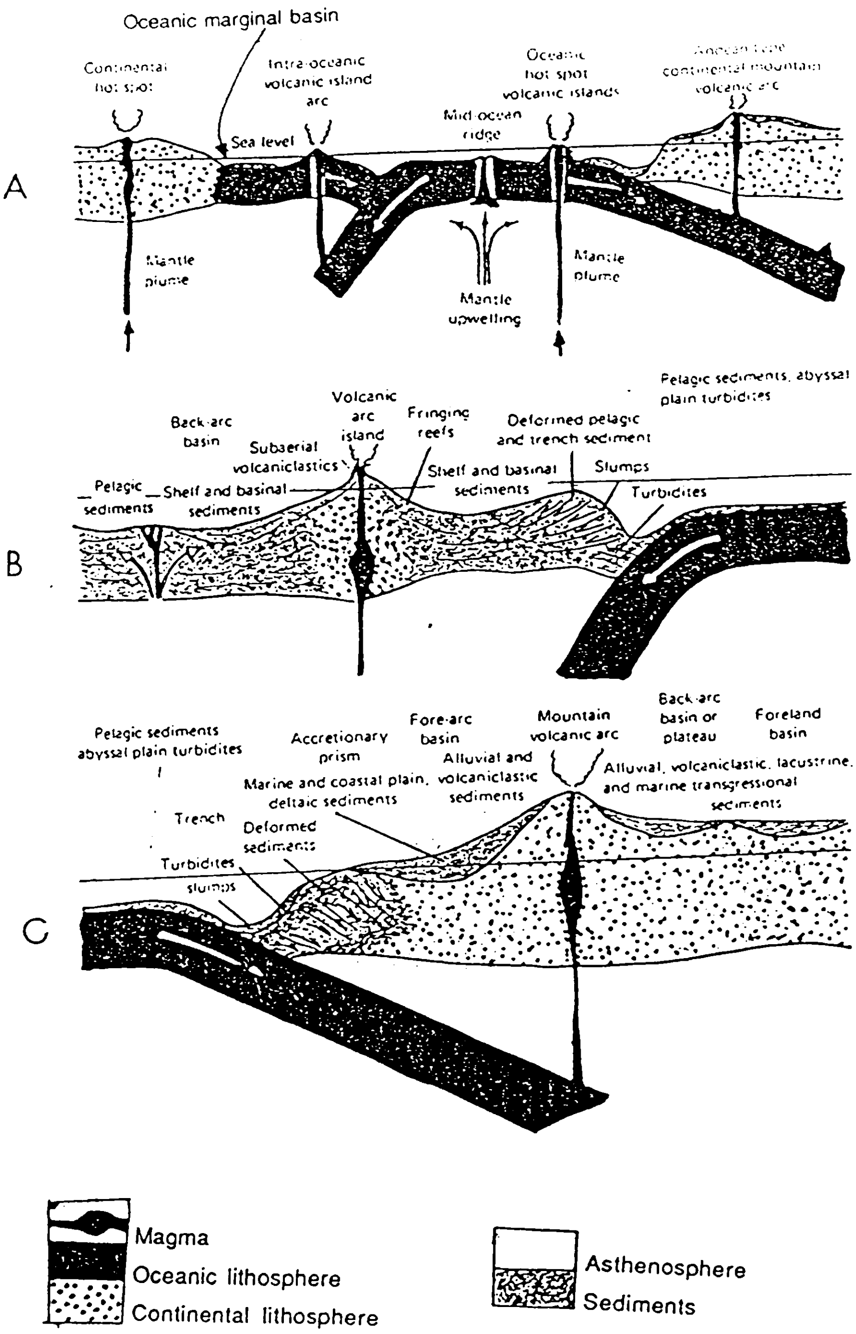

A
Oceanic marginal basin
Continental hot spot
Intra-oceanic volcanic island arc
Oceanic hot spot volcanic islands
Andean-type continental mountain volcanic arc
Sea level
Mid-ocean ridge
Mantle plume
Mantle upwelling
Mantle plume
B
Pelagic sediments, abyssal plain turbidites
Volcanic arc island
Back-arc basin
Fringing reefs
Deformed pelagic and trench sediment
Subaerial volcaniclastics
Shelf and basinal sediments
Slumps
Pelagic sediments
Shelf and basinal sediments
Turbidites
C
Back-arc basin or plateau
Fore-arc basin
Mountain volcanic arc
Foreland basin
Pelagic sediments abyssal plain turbidites
Accretionary prism
Alluvial and volcaniclastic sediments
Alluvial, volcaniclastic, lacustrine, and marine transgressional sediments
Marine and coastal plain, deltaic sediments
Trench
Deformed sediments
Turbidites
slumps
Magma
Oceanic lithosphere
Continental lithosphere
Asthenosphere
Sediments

Fig 3.2

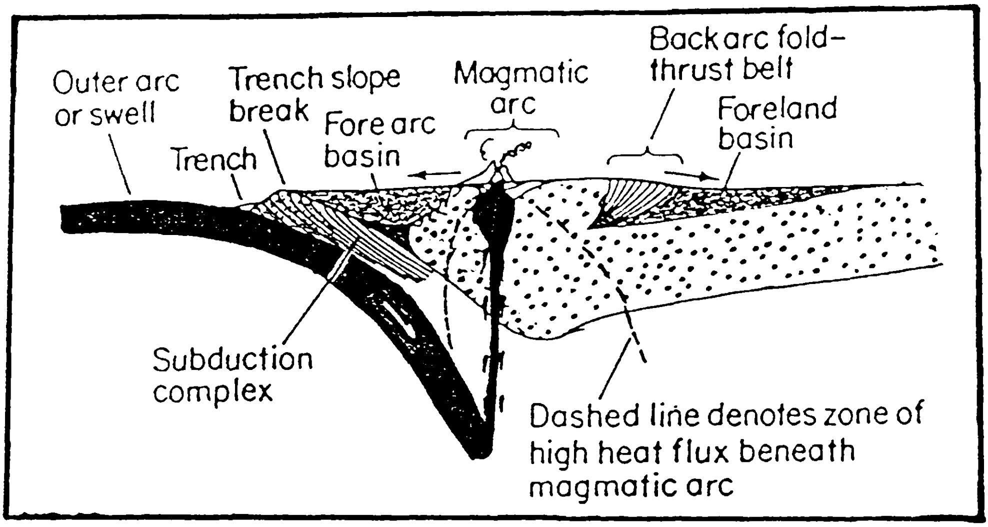

Outer arc or swell
Trench slope break
Magmatic arc
Back arc fold-thrust belt
Foreland basin
Trench
Fore arc basin
Subduction complex
Dashed line denotes zone of high heat flux beneath magmatic arc

Fig 3.3

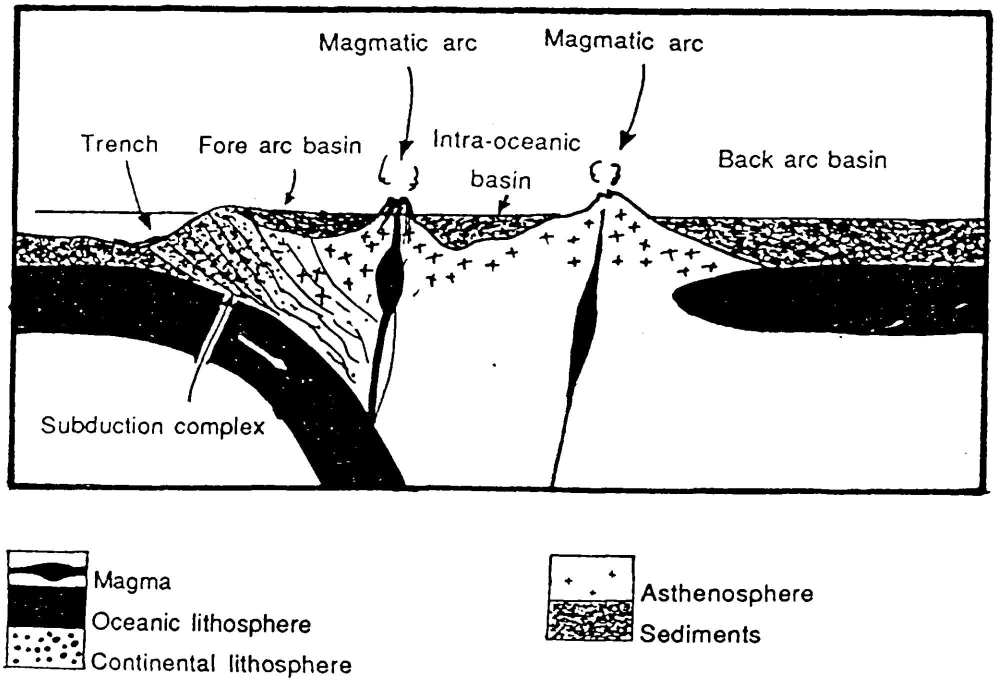
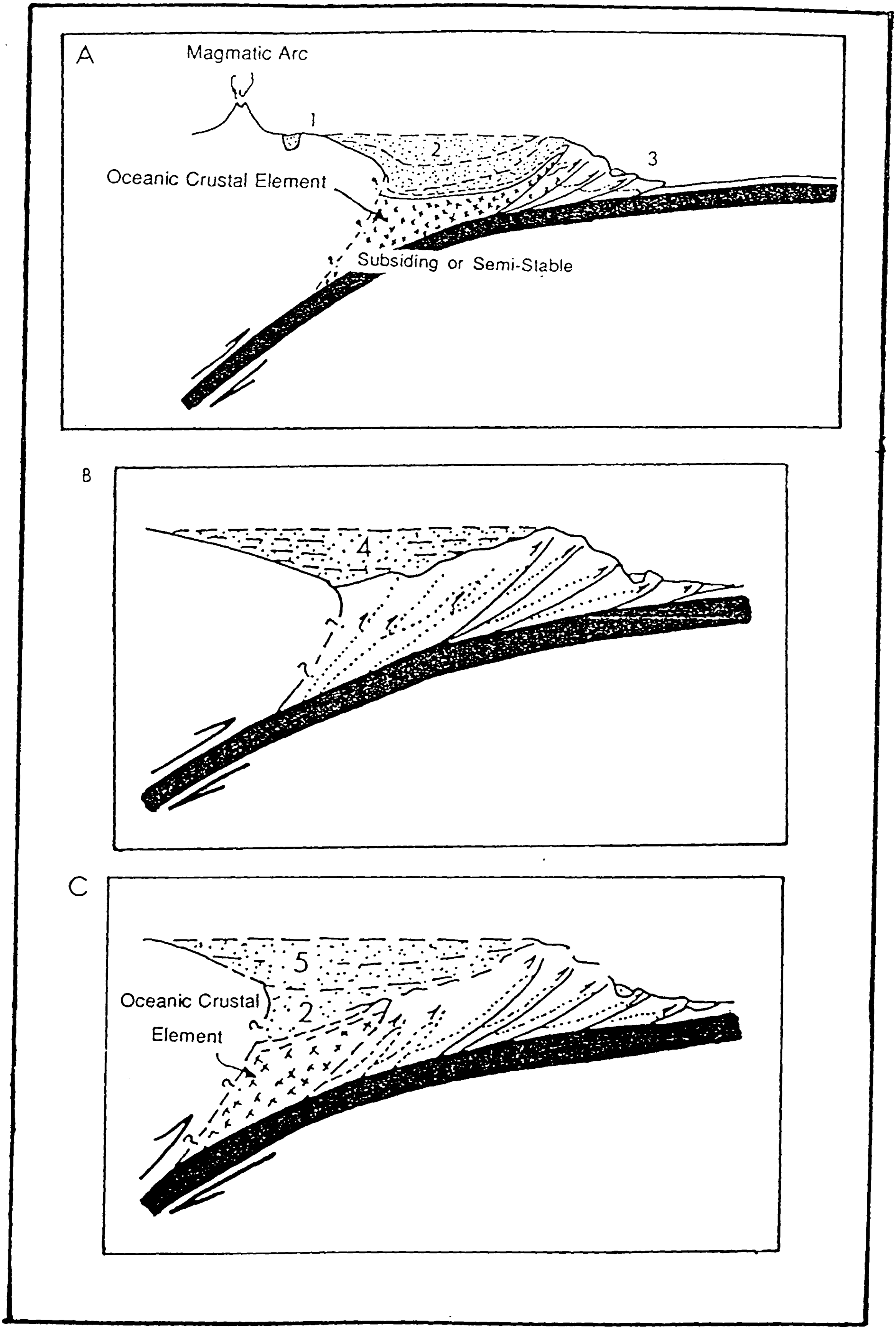

Magmatic arc
Magmatic arc
Trench
Fore arc basin
Intra-oceanic basin
Back arc basin
Subduction complex
Magma
Oceanic lithosphere
Continental lithosphere
Asthenosphere
Sediments

Fig 3.4


A
Magmatic Arc
1
2
3
Oceanic Crustal Element
Subsiding or Semi-Stable
B
4
C
5
Oceanic Crustal
Element
2

CHAPTER FOUR PETROGRAPHY

4.1 INTRODUCTION

Sedimentary petrography, defined as the systematic description of both composition and texture of sediments, has been used to greatly expand our understanding of the geological evolution of sedimentary basins (e.g Dickinson and Seely 1979; Dickinson et al. 1983). Sandstones and greywackes in particular were extensively investigated in this respect in an attempt to deduce their provenance areas, tectonic settings and economic potentials.

The major impetus to sandstone classification comes from the early proposals of Krynine from 1911 to 1948 and Pettijohn from 1943 to 1957. During this early period, both authors recognized the importance of mineralogy as a clue to source-rock compositions and source area tectonism but they placed different emphasis on the role of texture. The most important concept used was the composition triangles for representing modal analyses and defining fields of importance within these triangles.

Krynine (1948) produced a sandstone composition triangle which considered only detrital fractions and divided the rocks into classes based on the three component system; Quartz (+ chert), feldspar (+ kaolin) and phyllosilicates (mica + chlorite). However, a different emphasis was given by Pettijohn to the classification of the rock fragments -mica + chlorite + clay and matrix complex- that Krynine has treated as only a mineralogical component. Pettijohn (1954) recognized a four component system in which the matrix was a separate component. Folk (1954-1956) refined Krynine's classification by introducing grain size end members with all gradations between gravel, sand, silt, and mud as well as the abundance of clay components as an index of a "textural maturity".

Williams et al. (1954) used textural criteria; the degree of sorting and detrital matrix to divide all sandstones into suites: wackes and arenites.

Using these concepts Dott (1964) produced a widely accepted classification of terrigenous sandstones.

4.2 Sandstone compositions and plate tectonics.

Sandstone compositions are strongly influenced by the character of the sedimentary provenance, the nature of the sedimentary processes within the depositional basin and the kind of dispersal paths which link provenance to basin (Suttner, 1974). The key relation between provenance and basin is usually governed by plate tectonics which ultimately control the distribution of different types of sandstones. Important papers by Dickinson and Suczek (1979), Ingersoll and Suczek (1979), Dickinson and Valloni (1980), Valloni and Mezzadri (1985), Dorsey (1988) and others have contributed substantially to our ability to predict the tectonic settings of a source terrane from framework compositional modes. Data from modern marine and terrestrial sands taken from known tectonic settings provide standards against which to evaluate the effects of tectonic settings on sandstone composition. By direct analogy with such modern sands and by inference for older sandstone suites, broad categories of sandstone can be correlated with specific types of source terranes and basins associated with diverse plate tectonic regimes. However there is a number of limitations to this approach such as temporal changes in tectonic settings (e.g Mark, 1984), compositional variations related to depositional environment and climate (e.g. Suttner, 1974; Mark, 1984), large scale lateral transport of sand from regions tectonically unrelated to the basin of deposition (e.g. Velbel, 1985) and later substantial secondary alterations (e.g. Dickinson 1969, 1970; Ingersoll 1978b).

Criteria for distinguishing components and problems in removing diagenetic alterations to reconstruct original compositions are further complicating factors and have been discussed by many authors among others Dickinson (1970), Graham et al. (1976), Ingersoll (1978b), Suczek and Ingersoll (1985). However, despite the above mentioned complications and the fact that the amount of interstitial cement and matrix is largely a function of diagenesis, recent workers (e.g. Crook, 1974; Schwab, 1975, Dickinson and Suczek, 1979; Lash, 1987; Dorsey, 1988, Saccani, 1988) have been able to document the relationships between the mineralogy of sandstone provenance types and the tectonic setting of sedimentary basins and recognize lithic fragment detrital modes in sands and sandstones which are derived from uplifted zones of continental collision or suture belts (Dickinson and Suczek, 1979; Suczek and Ingersoll, 1985). Crook (1974) and Schwab (1975) have shown that quartz-rich rocks (>65%) are associated typically with passive continental margins, that quartz-poor rocks (<15%) are mostly of volcanogenic derivation from island arcs and that rocks of intermediate quartz (65-15%) are associated mainly with active continental margins or other orogenic belts. Graham et al (1976) also discussed how sandstones derived from magmatic arcs are usually distinguishable from suture belt-derived sandstone based on lithic populations.

Dickinson and Suczek (1979), Dickinson et al. (1983) showed that the mean composition of sandstone suites derived from different kind of provenance terranes controlled by plate tectonics tend to lie within three main fields on QFL and QmFLt diagrams (see Fig 4.1-2 for representation and Table 4.1 for definition of terms). The three categories of provenance terranes are(1) continental blocks for which sediment sources are on shields and platforms or in faulted basement blocks;(2) magmatic arcs for which the sources are within active arc orogens of island arc or active continental margins; and(3) recycled orogens for which the sources are deformed and uplifted stratal sequences in subduction zones, along collision orogens or within foreland fold-thrust belts. The authors also defined the tectonic settings from sandstone compositions using QmPK and QpLvLs triangles (see Fig 4.3-4) which were further developed by Dickinson (1982). In the meantime , Ingersoll and Suczek (1979) introduced QpLvmLsm and LmLvLs triangles (see Fig 4.5-6) as important plots for more detailed distinction between different tectonic settings. Dorsey (1988) also attempted to introduce LsLm1Lm2 based on the degree of metamorphism experienced by the different metamorphic lithic fragments but this diagram needs more refinement and is still of little use in sedimentary petrology.

The results of the above mentioned investigations form the basis for comparison with the results obtained in the present research. In this thesis an attempt is made to deduce the provenance source(s) of the rocks of the Girvan sequence and investigate its tectonic evolution. In addition a brief comparison is made between the petrographic and geochemical charateristics of the sandstones in Girvan with those in the Southern Uplands. In the sections that follow, the petrography of the sequence studied is first discussed, then the data obtained are compared to the published results from other tectonic regimes in other areas. The vertical variability is then investigated and related to tectonic evolution of the source area and finally general conclusions are attempted.

Table 4.1 Definition of petrographic framework modes

Q=Qm + Qp	Q = total quartzose grains
	Qm = monocrystalline quartz grains
	Qp= polycrystalline quartz grains
F = P + K	F = total feldspar grains
	P = plagioclase feldspar grains
	K = potassium feldspar grains
Lt = L + Qp	Lt = total aphanitic lithic grains
	L = total unstable lithic grains
L = Lm + Lv + Ls	Lm = metamorphic lithic grains
	Lv = volcanic lithic grains
	Ls = sedimentary lithic grains

Table 4.1: Continued

L = Lvm + Lsm	Lvm = volcanic and metavolcanic lithic grains Lsm = sedimentary and meta-sedimentary lithic grains

4.3 Petrography

Detailed petrographic investigations of sandstones and greywackes of Upper Llanvirn through to Llandovery from the Girvan area were undertaken. As a petrographic and geochemical frameworks, the samples of Ordovician age will be referred to as lower, middle and upper sequence to denote Upper Llanvirn to Llandeilo; Caradoc; and Upper Caradoc to Lower Ashgill respectively.

4.3.1 Mineralogy

4.3.1.1 Lower sequence

These rocks, Upper Llanvirn-Llandeilo, were collected mainly from the Kirkland and Benan conglomerates, and the Changue, Craigmulloch and Darley formations (see Figure 2.1 ,2.1 and Table 2.1 for the exact location of the samples and plates 1-6 for photomicrographs showing some rock fragments and minerals). Broadly, the rocks consist mainly of lithic greywackes rich in basic rock fragments but with significant proportions of angular quartz. The rock fragments, which range in size from 0.5 to 2 mm, are made up essentially of often angular spilitic volcanics, tuffaceous material, basic and ultrabasic fragments, cherts of various types, granitoides and abundant plagioclase feldspars. Epidote, perthitic K-feldspar and radiolarian cherts are common minerals but serpentinite and brown spinel are found only as a trace or are absent.

Sandstones-greywackes interstratified with the Kirkland Conglomerate, contain angular quartz (0.10 to 0.35 mm), microcline, micrographic rock fragments and fine-grained tuffaceous components with some chlorite and serpentinite set in a matrix of carbonate cement.

The greywackes from Benan Conglomerate have the mineralogical composition described above but the rock fragments tend to be larger in size

Those from Changue Formation contain abundant rock fragments (1.5 mm average diameter) which are dominantly of lava type. Chlorite including the deep green variety was also seen as a common mineral in these rocks together with brown spinel. In the Changue Formation greywackes at Traboyack Burn, feldspar, which is highly altered to white mica and sericite, is particularly abundant and forms up to 15% of the rock constituents. The common rock fragments are lava cherts and porphyritic granitoids. Opaque minerals are often present together with chlorite and carbonate but epidote has not been seen.

At Balloch Burn, the mineralogy is quite similar to those already described but at Water of Gregg, microgranite, rhyolite and granophyre fragments are present and small crystals of garnet are also occasionally present.

The rocks from Kilrany conglomerate and InfraKilrany greywackes, are transitional to the middle sequence (Llandeilo-Lower Caradoc) and are particularly epidote-rich and contain strongly chloritized lavas.

From the above descriptions, it is clear that there are substantial variations in petrography. These variations are related both to formations and probably also to some changes in the source areas, diagenesis and secondary alterations.

4.3.1.2 Middle sequence

The middle sequence rocks have been studied from Ardwell Flags, Cascade Grits and Whitehouse Group (see Figure 2.1 ,2.1 and Table 2.1 for the exact location of the samples and also plates 7-13 for photomicrographs showing some rock fragments and minerals). The rocks contain medium (0.6 mm average grain size) angular fragments and chips of quartz, albitic plagioclase and other various rock fragment types but with minor amounts of epidote. Those from Ardwell Flags, Cascade Grits and Whitehouse Group are poorly sorted angular fragments of usually strained quartz (0.8 to 1.0 mm in diameter) and turbidite feldspar. Serpentinites, spilite lavas, tuffaceous material and metaquartzites have also been noted in almost all formations.

4.3.1.3 Upper sequence

Two main formations have been sampled; Whitehouse and Shalloch. Those sandstones collected from the Whitehouse Group consist of quartz, often partly sericitized plagioclase and rock fragments set in a matrix of carbonates.The rock fragments found contain mainly siltstone, metaquartzite and cherts. Those from the Shalloch Formation contain in addition to the components just cited abundant biotite, some muscovite, chlorite and zoisite inclusions in quartz. Accessory small grains of garnet and rounded zircons are also occasionally present (see plates 14-18 for photomicrographs showing some rock fragments and minerals from this sequence).

4.3.1.4 Silurian (Llandovery)

The Silurian rocks have been collected from Craigskelly Formation and quartz conglomerates at the Haven and Scart grit.at Black Neuk. Sandstones from Craigskelly at the Haven contain plentiful subangular quartz (0.65 to 0.80 mm), microcline, perthite and rock fragments which are composed mainly of granitic material. Detrital zircon, zoisite inclusion in quartz and traces of tourmaline are also sometimes present. In the greywackes from the Quartz and Scart Grit Conglomerates at both the Haven and Black Neuk, quartz is subangular-angular. Feldspar is also present but rocks fragments which are dominantly of sedimentary and metasedimentary types are scarce. Zoisite inclusions in quartz are also occasionally present (see plates 19-21 for photomicrographs showing some

4.3.2 Description of the framework modes

The more abundant frameworks modes are described below and include quartz, feldspar and rocks fragments. A brief summary of the matrix minerals is also given.

Quartz

In the lower and middle sequence, quartz (0.2 to 1.2mm in diameter) occurs as angular chips or rarely as veins or aggregates with many quartz grains displaying undulose extinction and sutured crystal interfaces. The veins of quartz are believed to represent secondary re-mobilization of silica.

In the upper sequence and Silurian rocks, quartz which is present as both mono and polycrystalline, is clearly more abundant, (0.4-0.8 mm in diameter), almost unstrained and contains zoisite inclusions.

Feldspar

Both plagioclase and K-feldspar are present in the whole sequence. Plagioclase which is albite-rich in both the rock fragments and matrix (but generally more calcic in the former compared to the latter (Fig 4.7 and appendix one)) is by far the most common mineral. The K-feldspar shows optical variations from orthoclase to microcline but the main features is the abundance of microperthite which is occasionally developed into perthite. Granophyric intergrowths of K-feldspar and quartz are also present in several sections particularly in those rocks from Lower Ashgill and Llandovery. This texture indicates rapid cooling at low water pressures from near eutectic compositions and hence are typical of high level intrusions (Ahmed-Said, 1988). It is therefore concluded that the granitic material present in the sandstones was derived from high level plutonic intrusions. Mineral alterations and weathering are ubiquitous throughout the whole sequence but the main effects are sericitization and/or saussuratization of the plagiocalse components producing white micas mainly in the form of sericite.

Lithic fragments.

These are composed of igneous, metamorphic and sedimentary types. In the Llanvirn-Llandeilo rocks (lower sequence), the igneous fragments are by far the most abundant of all and include mainly basaltic, spilitic and other lava fragments together with porphyritic fragments. The spilites rock fragments (1.2 mm average diameter) are composed mainly of sodic plagioclase laths set in a ground mass of interstial chlorite. The andesite fragments seen (0.7 to 1.0 mm) have both porphyritic and non-pophyritic texture and usually contain small microlites and phenocryst of plagioclase. Serpentinite (0.5 to 1.0 mm) often appears as fibrous pale-green fragments.

The plutonic suites which are more abundant in the upper sequence are dominated by granitic fragments that contain graphic and granophyric-myrmekitic intergrowths. The granites (0.50 to 2.0 mm) are almost invariably composed of similar proportions of quartz, plagioclase and K-feldspar. The granophyres, which are of similar size to the granite clasts, show the intimate quartz-K-feldspar intergrowths in a graphic texture (see plates 11 &15).

The metamorphic fragments (0.25 to 0.90 mm) are dominantly metaquartzite with only minor amounts of mica schist and slate clasts. The sedimentary fragments (0.80 to1.2 mm), are represented in decreasing abundance by crypto-crystalline silica, radiolaria, jasper, silt and mudstone. In the Whitehouse Group of the Upper Caradoc-Lower Ashgill and the Silurian rocks, carbonates are additionally present.

Matrix

The matrix constituents, which usually range from 15 to 20% of the whole rocks, contain very small unstable fragments and mineral constituents particularly feldspar, mica schist, chlorite and quartz. In the lower sequence, where there are many unstable volcanic rock fragments and there is also an increase in the matrix. The opposite is true for the upper sequence where there are more mature sediments, less matrix and more cement .In the Silurian rocks, calcareous cement in the matrix is more common and has probably replaced the small detrital grains of the matrix. This is consistent with previous findings where the amount of matrix in greywacke sandstones was lower at the time of deposition but increased during diagenesis and the matrix may be absent from the greywackes because it has been replaced by calcite (Cummins 1962).

4.4.Implications of sandstone and greywacke compositions for the provenance areas and tectonic settings of the Girvan sequence.

The results of framework modal analyses of the Girvan greywackes are given in Appendix one, summarized in Table 4.2 and plotted in ternary diagrams in Figures 4.8-36.

Below, the overall provenance areas and tectonic setting trends based on all data are first briefly discussed then the results are interpreted individually in geochronological order based on the framework mode triangles QFL, QmFLt, QmPK, QpLvmLsm, and LmLvLs respectively. The vertical variability of certain framework modes are illustrated and discussed and finally conclusions are reached.

Table 4.2 Results of framework modal analyses and some calculated ratios.

	l. seq.		m. seq.		u. seq.		Sil.	
values given in percentages								
	X	σ	X	σ	X	σ	X	σ
Q	45.41	11.6	60.58	15	64	12.6	77.27	4.3
L	23.33	11.5	14.42	9.9	20.6	10.5	9.55	3
F	29.66	10	25	11.4	15.13	9.4	13.72	2.8
Qm	33.4	10	47	16.1	60.8	14.6	66	7.1
Lt	35.23	15	28	12.8	24.46	8.6	20.27	6.3
Qp	39.87	16.8	54.7	18	49.03	19.4	75.85	9
Lv	56.81	16.6	37.2	18.9	39.28	16.7	15.85	9.8
Ls	3.3	3.6	8.1	6	11.67	10.6	8.28	4.8
Qm	50.07	13.4	64.85	18	70.07	12.3	83.78	10.8
P	42.15	16.8	26.7	17.7	23.89	11.4	12.14	11.29
K	7.35	6.4	8.65	5.5	6.03	4.6	4.07	2
values given as ratios in fractions of one								
P/F	0.83	0.15	0.71	0.15	0.78	0.14	0.67	0.17
Lv/L	0.94	0.06	0.79	0.13	0.78	0.16	0.63	0.18
Qp/Q	0.43	0.12	0.45	0.07	0.40	0.11	0.47	0.03

Key to Table 4.2

Q + F + L = 100

Qm + F + Lt = 100

Qp + Lv + Ls = 100

Qm + P + K = 100

4.4.1 General provenance areas and tectonic settings of the Girvan greywackes.

All framework mode analyses are shown together in Figures 4.8-13. The provenance areas and tectonic setting fields of Dickinson and Suczek (1979), Ingersoll and Suczek (1979) Dickinson et al. (1983) are also shown in each diagram for easy comparison with the published results.

Figure 4.8 shows that the samples fall within two main fields on the QFL diagram namely: recycled orogens and magmatic arcs with very few samples falling within the continental block field. The QmFLt diagram (Fig. 4.9) is clearly more selective and indicates that almost all the lower sequence rocks fall within the magmatic arc fields (transitional and dissected) with some samples -as would be expected-falling within the mixed field but also within the recycled orogens and to much lesser extent the continental block. The Caradoc rocks of middle sequence also cover the above mentioned range but extend further to mostly fall within the mixed field but within the recycled orogen field as well. The Upper Caradoc-Lower Ashgill of upper sequence samples clearly do not plot within the magmatic field but plot within both mixed and recycled orogens only. The Silurian rocks plot almost exclusively in the quartz-rich recycled orogens field. Again, Fig 4.9 suggests only minor contributions -if any-from the continental block to the district. It is therefore very interesting to note that the contribution to the

Girvan area is continuous and progressive from almost pure magmatic arc material during Upper Llanvirn-Llandeilo through to almost pure recycled quartzoses during Llandovery times.

The poor nature of the Girvan sequence ln Ls but somewhat enrichment in Lv and Qp components respectively made the provenance fields of Dickinson and Suczek (1979) much less applicable; although it is very interesting to note that none of the samples plot within the collision orogen sources thus excluding this possible source for the Girvan rocks (Fig 4.10).

Figures 4.11-2 are clearly a further support to the interpretations given above but Fig 4.13 is less reliable for reasons discussed below in subsection 4.4.2.

4.4.2 Evolution of the provenance areas and tectonic settings of the Girvan rocks.

QFL diagrams

The QFL diagrams show substantial and systematic changes in passing from Upper Llanvirn to Llandovery times. The most important of these changes is the progressive and continuous enrichment in the total quartz, but impoverishment in the total feldspar and to much lesser extent in total lithics.

Figure 4.14 shows that the lower sequence samples fall almost equally between recycled orogens and active magmatic arc provenances suggesting roughly similar contributions from these sources. Only one sample falls within the basement uplift field which suggests that the basement was stable during these times; consistent with previous findings (e.g. Bluck 1983-85) where contributions from the basement were scarce or absent. It should also be noted that there was no contribution-or if any only insignificantly- from the continental block.

During Caradoc more recycled orogenic material was introduced to the area compared to that derived from active magmatic arcs (Fig 4.15). During these times and up to Llandovery there was still no noticeable contributions from the continental block.

During Lower Ashgill and Llandovery times, unroofing of the magmatic arc has ceased and only more quartz-rich material derived from recycled orogens was still being introduced to the basin (Figs 4.16-17). This therefore indicates that uplifting and erosion of the magmatic arc has stopped before the end of the Lower Ashgill.

QmFLt diagrams

The progressive changes described above are more enhanced on the QmFLt. The magmatic arc material was clearly unroofed mainly from transitional and dissected arcs during Upper Llanvirn-Llandeilo times but there was less and less contribution from the transitional and then dissected arcs during the Caradoc and Lower Ashgill times respectively (Figs 4.18-19). Figures 4.20-21 suggest that almost pure quartz grains were recycled into the Girvan basin during Lower Ashgill and Llandovery times, a suggestion in excellent agreement with deduction from the geochemistry (see chapter five).

QmPK diagrams

In terms of QmPK (Figures 4.22-5) all the samples lie on the QmP leg of the diagram indicating relative impoverishment in K of the rocks at all times. There seems to be no clear explanation for the poor nature in K-feldspar of the sediments but the presence of some white mica and sericite suggests that K-feldspar was unstable and was secondarily converted into these mineral during diagenesis. Definite proof is lacking as no transitional phases from feldspar to white mica and sericite have been observed.

Dickinson and Suczek (1979) showed that sandstones derived from different provenance areas due to different tectonic settings plot on distinct areas on QmPK diagrams. The two field of active magmatic arc and that of continental block and recycled orogens are shown on all QmPK diagrams presented (see Figure 4.3). It is clear that the conclusions reached earlier regarding the evolution in composition of the sediments are strongly confirmed. The source of the sediments became less arc-like through time and in Silurian times was replaced by material which was derived almost exclusively from recycled quartz-rich provenance. At the same time the ratio of plutonic/volcanic material increased with decreasing age.

Korsch (1985) noted that when sandstones do not plot within the magmatic arc of Dickinson and Suczek (1979) but fall in the Qm apex, it is an indication of deeper levels of erosion in the continental blocks. If this deduction is true, then it can be inferred that the original quartz-rich material which was subsequently included within the recycled orogens was derived from the continental block (i.e. extraneous). However, with the present views that the Caledonides grew by accretion of displaced terranes, then it is possible that sources or basins may move laterally into different provenance areas.

QpLvLs diagrams

The QpLvLs are even more selective and all indicate that the Girvan greywackes, which are poor in terms of sedimentary lithics, was not derived from collision orogen sources but contribution from the magmatic arc and recycled orogens were very significant (Figs 4.26-9).

From Upper Llanvirn through to Llandovery times, there was a progressive and continuous enrichment in Qp relative to Lv but contributions from sedimentary lithics do not show any significant changes through time. Dickinson et al. (1982) argued that Qp and Ls are more resistant to diagenetic reactions than the volcanic lithic fragments (Lv) which contain unstable components including igneous minerals and even glass. This explanation does not hold for the Girvan greywackes for the rocks are poor in Ls not Lv. The only tenable explanation is that less and less volcanic material was available but more and more recycled quartz-rich material was being introduced to the area. This is in excellent agreement with conclusions reached from the QFL, QmFLt and the geochemistry (see chapter five).

It should also be noted that Figures 4.26-29 show that there was no contribution-or only very little if any-, during Upper Llanvirn-Llandeilo times from the subduction complex. The melange now seen in the Ballantrae Complex was thought by Hamilton et al. (1984) to be part of a more extensive (possibly subduction related) Cambrian unit. The petrography discussed here does not support the views that this was a widespread unit in the provenance area at least.

QpLvmLsm diagrams

These diagrams (Figs 30-33) are far more selective and show that the majority of the lower sequence samples fall within the mixed magmatic arcs and rifted continental margins with many samples falling within the magmatic arcs and forearc areas. This therefore indicates substantial contributions from magmatic arc, forearc and rifted continental margin materials to the Girvan. During Lower Caradoc times there was still contribution from mixed magmatic arcs and rifted continental margins but by Caradoc-Ashgill through to Llandovery times, a large number of samples do not plot within any of the fields previously studied from known tectonic settings. These samples possibly represent recycled particularly quartz-rich material.

There are few lower sequence samples which plot in the Lvm-rich corner of the triangle thus plotting outside the field of magmatic arcs, forearcs and mixed magmatic arcs and continental margins. Plio-Pleistocene sandstones from eastern Taiwan which were deposited in forearc basins adjacent to the Luzon volcanic arc (Chi et al. 1981) were found to plot within this area (see also Dorsey, 1988) which suggests by inference that Lv-rich samples from Girvan were derived from a magmatic arc and then deposited in an adjacent forearc basin, a conclusion supported by the large size and angular shape of the rocks fragments.

LmLvLs diagram

These diagrams are much less reliable compared to those already described on account that the samples are poor in Lm and Ls and often, due to the low degree of metamorphism of the metamorphic rock fragments present, distinction between sedimentary and metasedimentary lithics is almost impossible and therefore all samples are shown together on one diagram only (Fig4.13). However the available evidence suggests a mixed magmatic arc, continental margins and forearc sources, although some samples do not plot in any of the published fields probably due to the quartz-rich nature of the recycled sediments.

4.5 Vertical variability of some framework modes and rock fragments

This aim was achieved through detailed studies of nine parameters. The parameters investigated were in part those suggested by Ingersoll (1978) and include P/F, Lv/L, Qp/Q, QFL% Q, QFL% F, QFL% L, QmPK K, QmPK% P, QmPK% Qm. Once the petrofacies had been established, means and standard deviations are calculated, presented and shown diagrammatically in Figures 4.34-36.

The P/F ratio which was found to be the most important discriminating parameter in the Great Valley sequence, is clearly not an important discriminating parameter in the Girvan area; although there is a general tendency for the P/F ratio to decrease with time but only if the standard deviations are not considered. The Lv/L ratio is clearly the most important discriminating parameter.

The Lv/L of both the middle and upper sequence rocks overlap over a large part with each other as well as with the lower sequence and Silurian but these latter two do not overlap with each other.(Fig 4.34). The Qp/Q parameter is not very significant because the four sequences overlap with each other although it is very interesting to note that the Silurian rocks have a relatively homogeneous Qp/Q (very small standard deviation) possibly suggesting a very similar source for these quartz-rich rocks.

In terms of QFL% Q, F, L parameters, Figure 4.35 shows that there is a progressive enrichment in the total quartz but impoverishment in total F and lithics. Again, the Silurian rocks do not overlap with the Low Ordovician sequence which suggests a significantly different source areas for the former compared to the latter.

The QmPK% diagrams (Figs 4.36) show that the four petrofacies cannot be discriminated in terms of QmPK% K but the Silurian rocks can easily be differentiated from those of Upper Llanvirn-Llandeilo by being poor in P and richer in Qm.

In summary therefore, the lower sequence combines low Q, Qm and K but to much lesser extent F and L , medium P and Qp/Q and high P/F and Lv/L. This is consistent with the mineralogy where the lower sequence greywackes are often poor in quartz and acidic fragments but rich in volcanic lavas, spilites, basalts and andesites. These trends again confirm the possibility of a magmatic arc origin for these rocks. The Silurian rocks on the other hand combine high Q and Qm, medium Qp/Q, P/F, Lv/L and low K, F, L and P. This is also consistent with the mineralogy for these rocks are particularly rich in quartz. Both the middle and upper sequence rocks span the range between the lower sequence and Silurian rocks suggesting a range of composition between those of the Upper Llanvirn-Llandeilo and Llandovery source areas.

4.6 Discussion and conclusions

In the previous sections, it has been shown that there was progressive and continuous changes in the composition of the Girvan sandstones and greywackes during Ordovician and Silurian times.

Williams (1962) and Ingham (1978) showed that the Ballantrae ophiolites provided the floor and partly the source of the Ordovician conglomerates and turbidites. These early findings are confirmed by the present results in that the lower sequence rocks are rich in basic and ultrabasic rock fragments and plot within two source areas namely; magmatic arcs and recycled orogens. It is probable that at least some of these recycled orogen material were partly derived from the obducted Ballantrae Complex. However, the present results show that the substantial contribution came from dominantly dissected and to a lesser extent transitional magmatic arcs. Again this is in excellent agreement with previous findings reached from conglomerate studies.(e.g Longman et al. 1979; Longman, 1980; Longman et al. 1982; Bluck 1983). The composition of these conglomerates shows that there is a range of types. Apart from the basic and ultrabasic rock clasts, assumed to have been derived from the Ballantrae Complex, there are fine grained acidic to intermediate clasts along with granites. These granitic clasts have Rb/Sr age determinations which range in age from 593 ± 28 Ma to 451 ± 8 Ma and have chemical affinities of plutonic arc granites (Longman, 1980), Longman et al.(1979). Bluck,(1983) suggested they were deposited in a proximal forearc settings and represent material derived from a fairly dissected plutonic arc. It can therefore be concluded that both the conglomerate clasts previously studied and the composition of the sandstones and greywackes presently studied indicate original contributions from transitional and dissected magmatic arc regimes and that they were deposited in a forearc or backarc basin. However the large size of the conglomerate clasts (over one metre) and the angular shape of the sandstone and greywacke rock fragments suggest very near source areas which therefore confirm the possibility of deposition in a proximal forearc basin.

The description given above for the lower sequence is also tenable for the middle sequence but not for the upper sequence rocks. The rocks from the latter sequence tend to be richer in acidic fragments and quartzitic material and plot mostly within the recycled orogen fields. These trends can be either the result of evolution in the composition of the magmatic arc or else introduction of particularly quartz-rich recycled orogenic material from different source(s) or both.

The evolution in the composition of the magmatic arc material with time cannot be fully ruled out and indeed the progressive evolution in the composition of rocks from basic and ultrabasic-and lava-rich greywackes through to acidic-rich sandstones(i.e increasing plutonic/volcanic ratio with time, (Fig 4.3) suggest a regular evolution in the composition of the source areas which are probably the magmatic arc regions. The geochemistry also strongly support this conclusion (see chapter five). However, if this explanation is the only possibility then many of the samples would be relatively quartz-poor and still plot within at least one magmatic field on Dickinson and Suczek (1979); Ingersoll and Suczek (1979) or Dickinson et al. (1983) diagrams. Indeed Figures 4.8-13 suggest that most of the middle sequence rocks were probably derived from a more evolved magmatic arc but the upper sequence rocks must have included "extraneous material" as do the Silurian rocks. This therefore indicates that the uplifting and unroofing of the magmatic arc had ceased by Lower Ashgill times. These changes in the provenance sources are shown diagrammatically in Figure 4.3 7.

The case of the Silurian rocks is more complex since they are particularly quartz-rich so that they plot entirely within the recycled orogen (recycled quartzoses) field but do not plot in any well defined tectonic field. This significant change in the composition of the Silurian rocks is expected because there is an Unconformity at the base of the Silurian suggesting that a new tectonict regime may have been established. The source area of these Silurian rocks is still problematic but can be inferred from the composition of the conglomerates which were intensively investigated (e.g Rolfe, 1961; McGiven, 1967; Cocks and Toghill, 1973; Ingham, 1978). Most conglomerates were derived from a source area south of the contemporary Wenlock trench to the Solway and possibly beyond (Bluck, 1983). Bluck (1984) showed that the rocks that gave the composition of the conglomerates do not exist in the Southern Uplands and derivation from older conglomerates of the type characterizing the present Southern Uplands is improbable. Bluck (1983) therefore suggested that an igneous basement underlies the Southern Uplands block and that this basement was the source of the Silurian conglomerates in the southern Midland Valley.

In tectonic terms the Silurian rocks do not plot in any field such as magmatic arc and forearc areas or continental block. The figures studied earlier also exclude the possibility of subduction complex source or a rising Ordovician trench-slope break. Bluck (1983) noted that the Silurian conglomerates which have a source in acidic-intermediate igneous rocks, metaquartzite rocks and conglomerates with a N, NW or W derivation, share this type of provenance with the Llandovery and Wenlock conglomerates which have dispersed the from S or SE. He therefore concluded that the upper crustal layers of the Midland Valley extended beneath the Southern Uplands in Silurian times. This therefore, according to Bluck (1985), indicated a deposition in an inter-arc basin. However, on the basis of the petrography presented here there is no support for an inter-arc setting.

Key to Figure 4.1-36

Figures 4.1-2: QFL and QmFLt diagrams (after Dickinson et al, 1983) to decipher the provenance.

Figures 4.3-4: QmPK and QpLvLs diagrams (after Dickinson and Suczek, 1979) to decipher the provenance areas and tectonic settings

Figure 4.5-6: QpLvmLsm and LmLvLs diagrams (after Ingersoll and Suczek, 1979) to decipher the provenance areas and tectonic settings.

Figure 4.7: CaO-Na_2O-K_2O diagrams showing the composition of plagioclase and K-feldspar from the upper and lower sequences. The composition of these two minerals from the matrix is also shown (all determined by microprobe analysis).

Figures 4.8-13: QFL, QmFLt, QpLvLs, QmPK, QpLvmLsm and LmLvLs diagrams respectively of all the studied samples to decipher the provenance areas and tectonic settings of the Girvan area.

Figures 4.14-7: QFL diagrams of the four sequences from the Girvan area to decipher the evolution of the sequences with time.

Figures 4.18-21: QmFLt diagrams of the four sequences from the Girvan area to deduce the provenance sources and tectonic evolution with time.

Figures 4.22-25: QmPK diagrams of the four sequences of the Girvan area to deduce the provenance sources and tectonic evolution with time.

Figures 4.26-9: QpLvLs diagrams of the four sequences of the Girvan area to deduce the provenance sources and tectonic evolution with time.

Figures 4.30-3: QpLvmLsm diagrams of the four sequences of the Girvan area to deduce the provenance sources and tectonic evolution with time.

Figures 4.34-6: Means and standard deviations of nine parameters (P/F, Lv/L, Qp/Q; QFL% Q, F, and L; QmPK% K, P and Qm) for the four sequences of the Girvan area (bars=1σ).

Figure 4.37: Possible changes in the arc-source from Upper Llanvirn to Llandovery.

1- Dominantly basic and ultrabasic rocks and lavas with only minor amounts of plutonic components.

2- Dominantly acidic rock fragments and lavas with decreasing amounts of basic and ultrabasic components.

3- Comparable proportions of acidic rock fragments and recycled Orogen materials.

4- Almost pure recycled orogen quartz-rich material with insignificant amounts of acidic rocks.

Fig 4.1

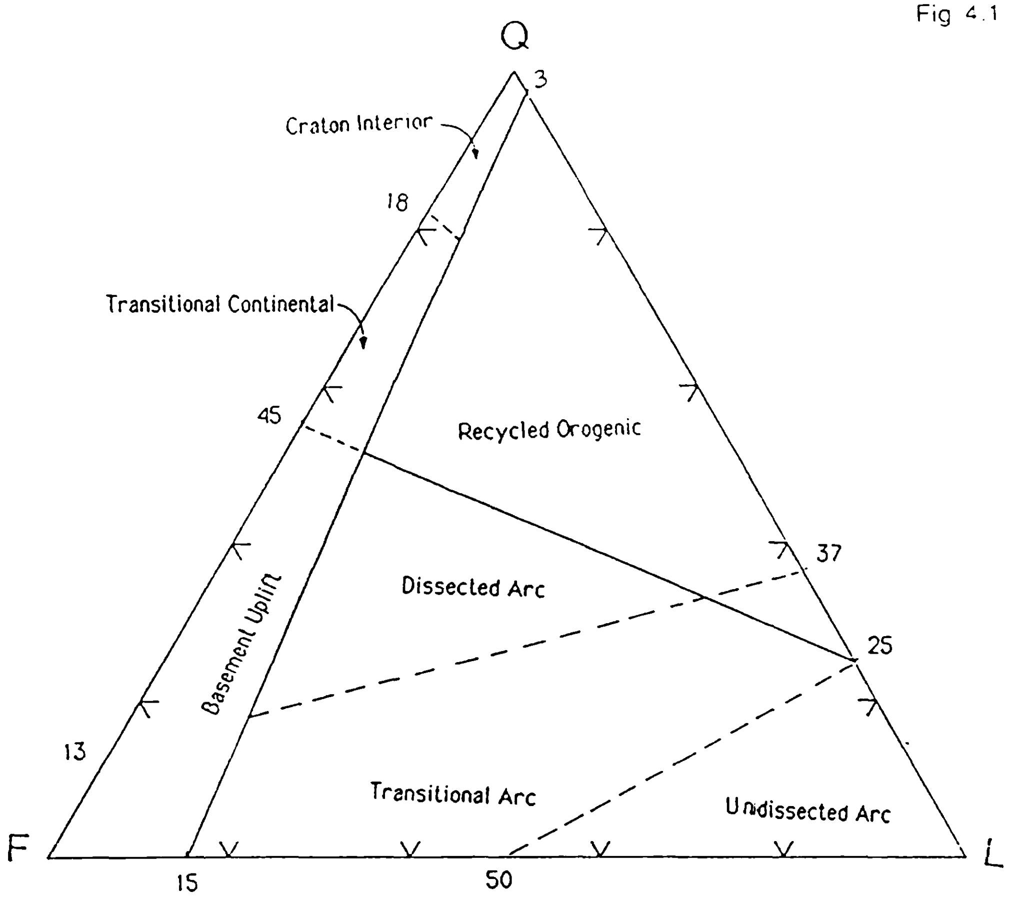

Q
3
Craton Interior
18
Transitional Continental
45
Recycled Orogenic
Basement Uplift
Dissected Arc
37
25
13
Transitional Arc
Undissected Arc
F
L
15
50

Fig 4.2

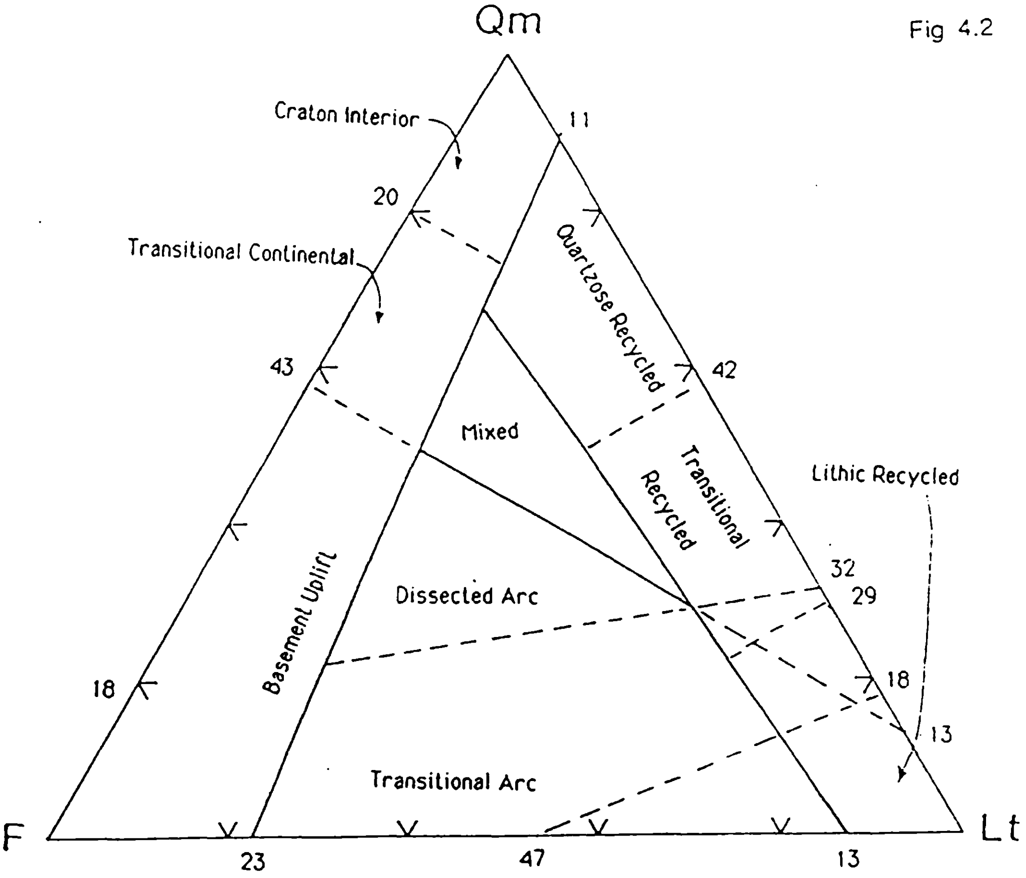

Qm
Craton Interior
11
20
Transitional Continental
Quartzose Recycled
43
42
Mixed
Transitional Recycled
Lithic Recycled
Basement Uplift
32
29
Dissected Arc
18
18
13
Transitional Arc
F
Lt
23
47
13

Fig 4.3

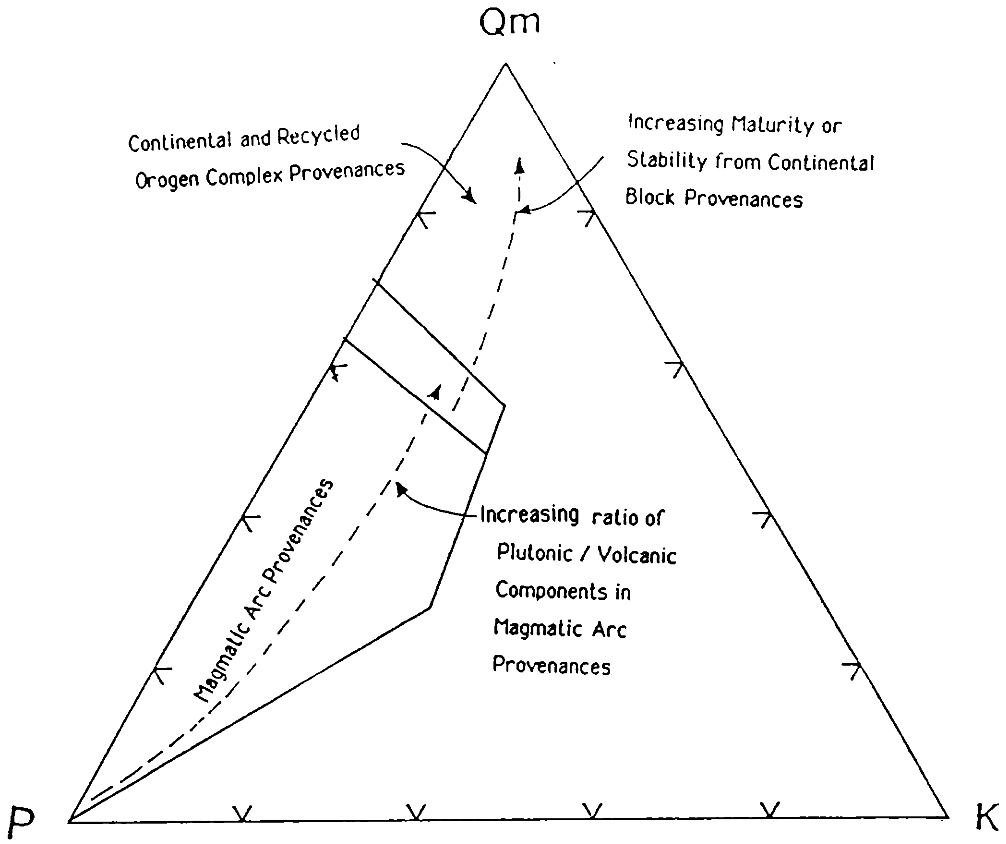
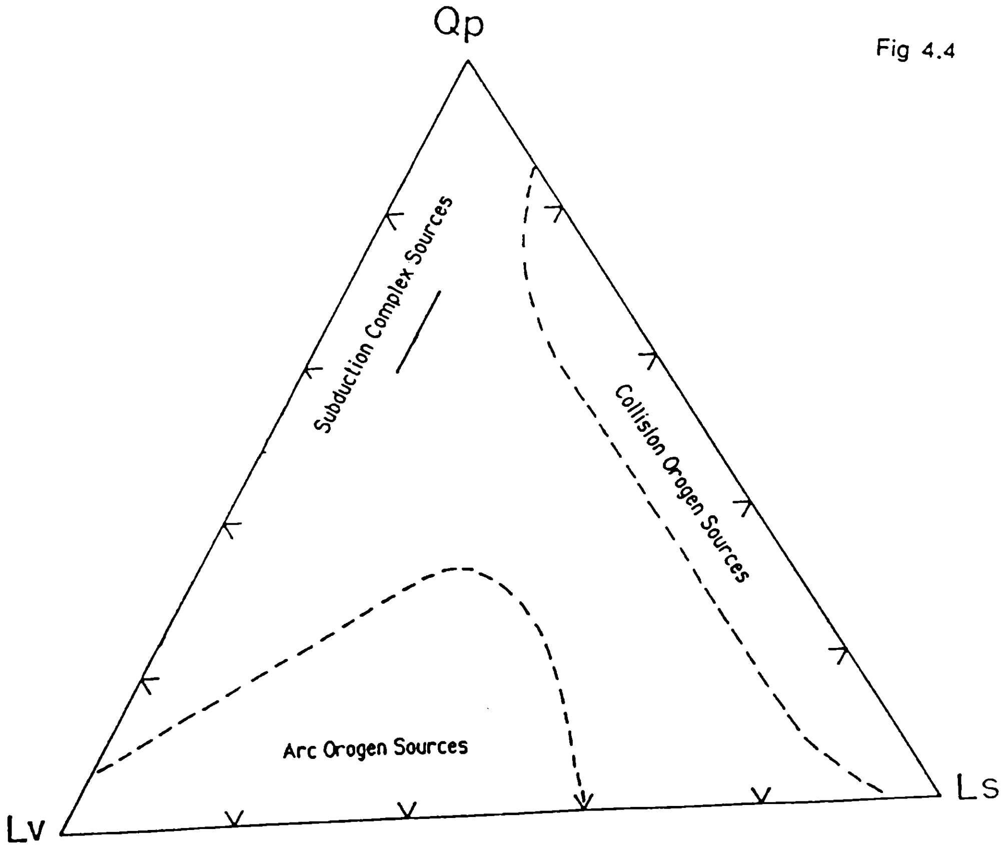

Qm
Continental and Recycled Orogen Complex Provenances
Increasing Maturity or Stability from Continental Block Provenances
Magmatic Arc Provenances
Increasing ratio of Plutonic / Volcanic Components in Magmatic Arc Provenances
P
K

Fig 4.4


Qp
Subduction Complex Sources
Collision Orogen Sources
Arc Orogen Sources
Lv
Ls

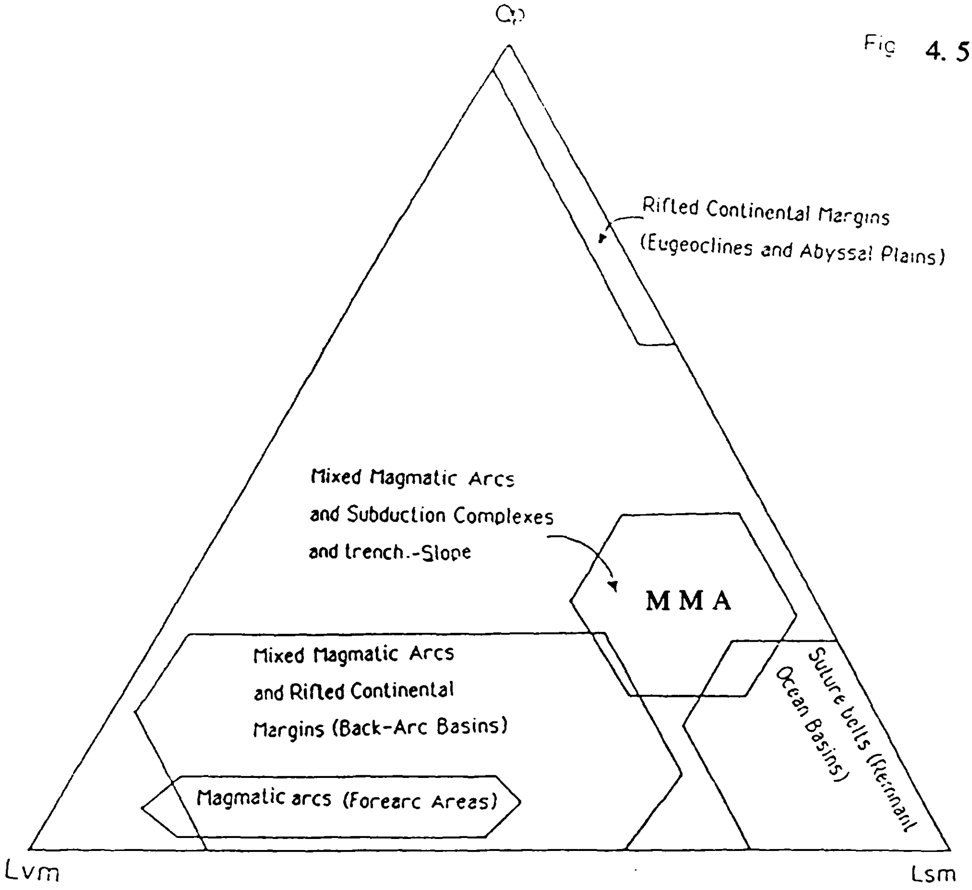

Qp
Rifled Continental Margins (Eugeoclines and Abyssal Plains)
Mixed Magmatic Arcs and Subduction Complexes and trench.-Slope
MMA
Mixed Magmatic Arcs and Rifled Continental Margins (Back-Arc Basins)
Suture belts (Remnant Ocean Basins)
Magmatic arcs (Forearc Areas)
Lvm
Lsm

Fig 4.5

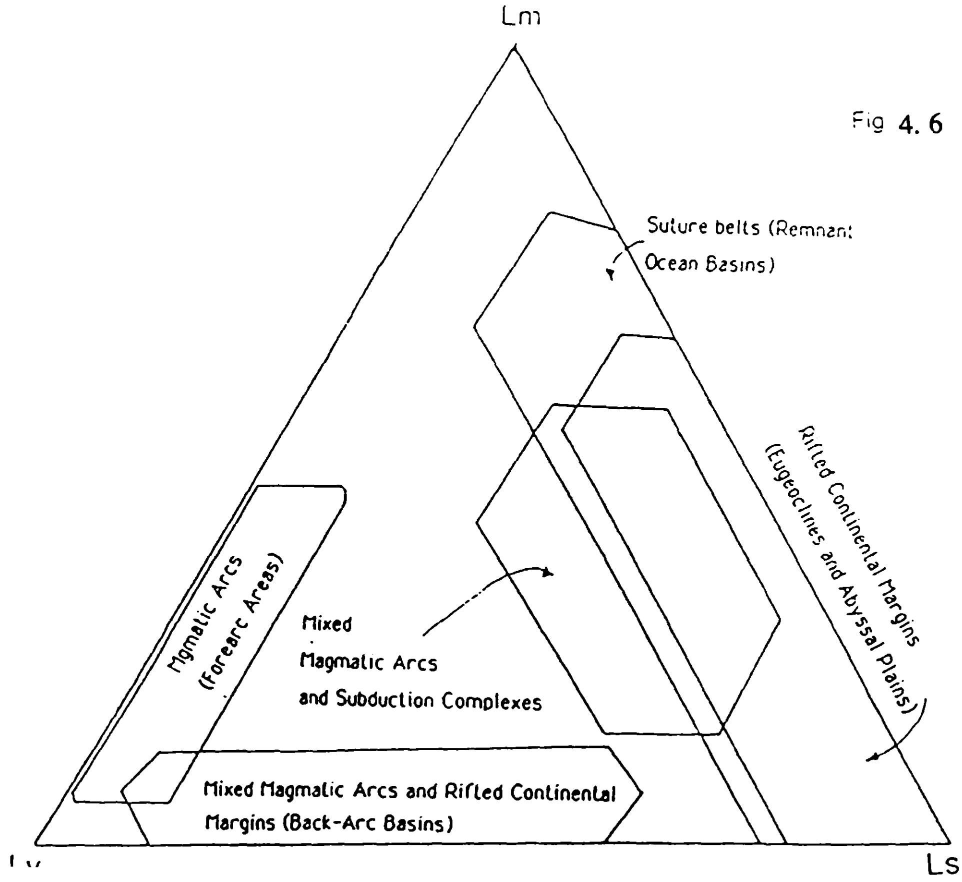
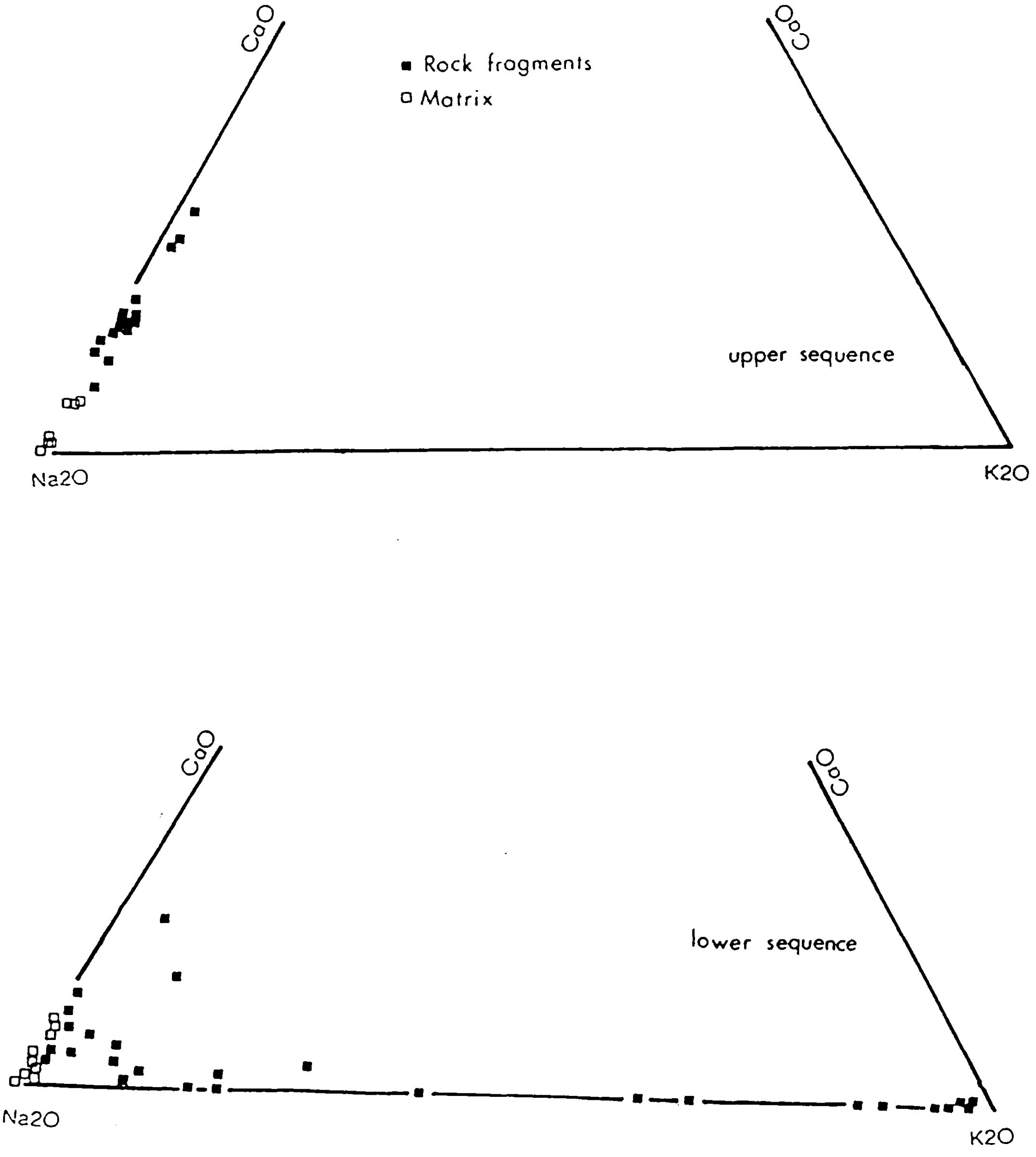
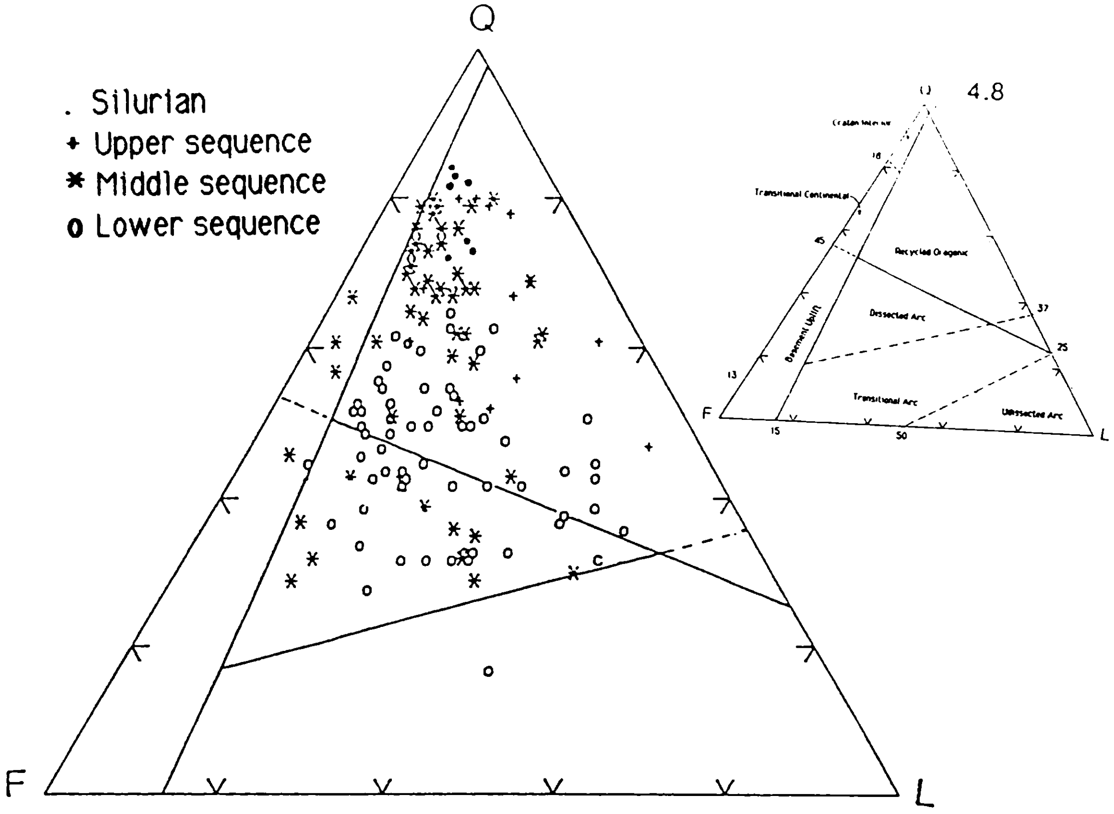

Lm
Suture belts (Remnant Ocean Basins)
Rifled Continental Margins (Eugeoclines and Abyssal Plains)
Magmatic Arcs (Forearc Areas)
Mixed Magmatic Arcs and Subduction Complexes
Mixed Magmatic Arcs and Rifled Continental Margins (Back-Arc Basins)
Lv
Ls

Fig 4.6

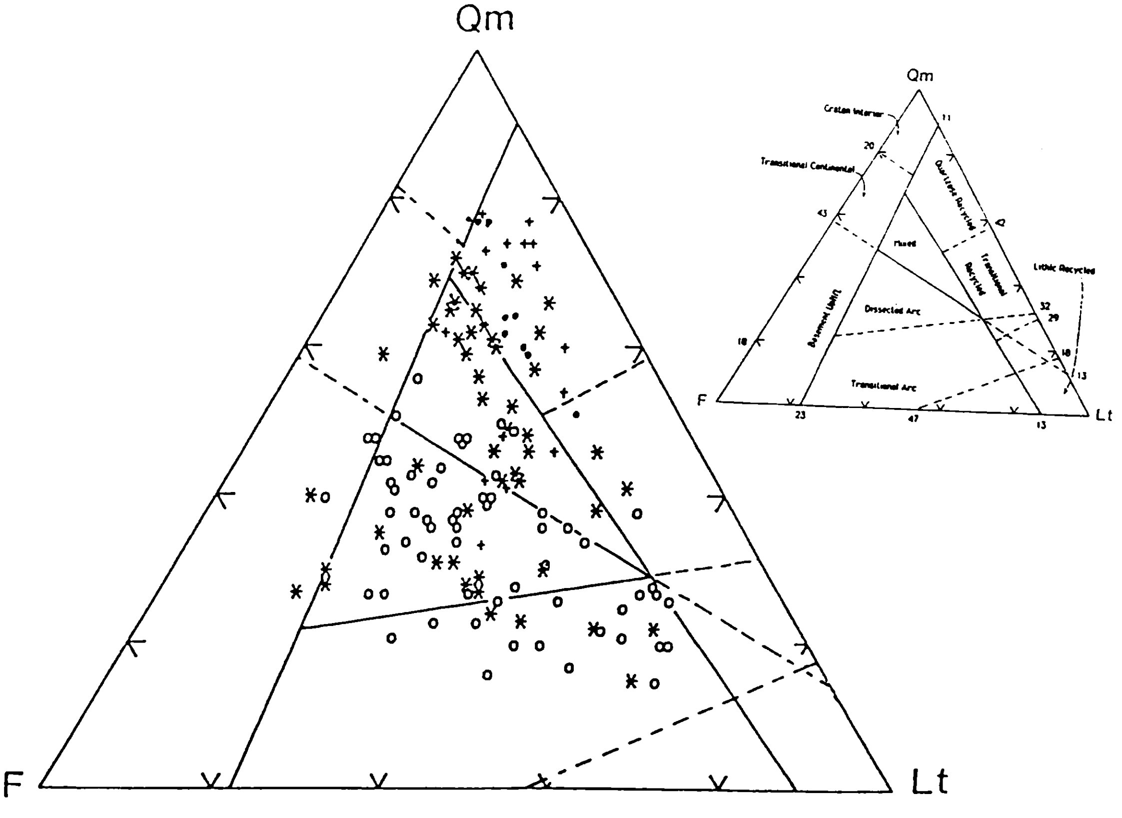
Fig 4. 7


CaO
CaO
■ Rock fragments
□ Matrix
upper sequence
Na2O
K2O
CaO
CaO
lower sequence
Na2O
K2O


Q
. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
F
L
Q
Craton Interior
16
Transitional Continental
45
Recycled Orogenic
Dissected Arc
Basement Uplift
37
25
13
Transitional Arc
Undissected Arc
F
15
50
L

4.8

Fig 4.9


Qm
F
Lt
Qm
Craton Interior
11
20
Transitional Continental
Quartzose Recycled
43
42
Mixed
Transitional Recycled
Lithic Recycled
Basement Uplift
Dissected Arc
32
29
18
18
13
Transitional Arc
F
23
47
13
Lt

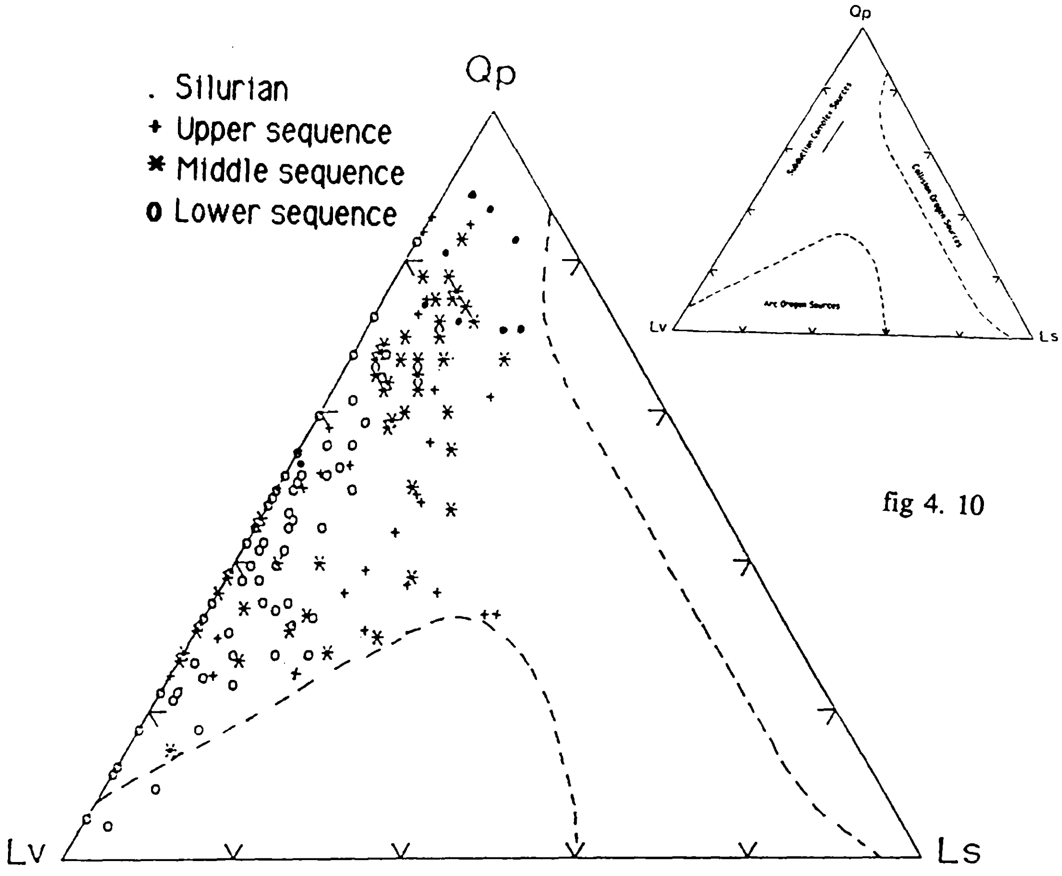


fig 4. 10

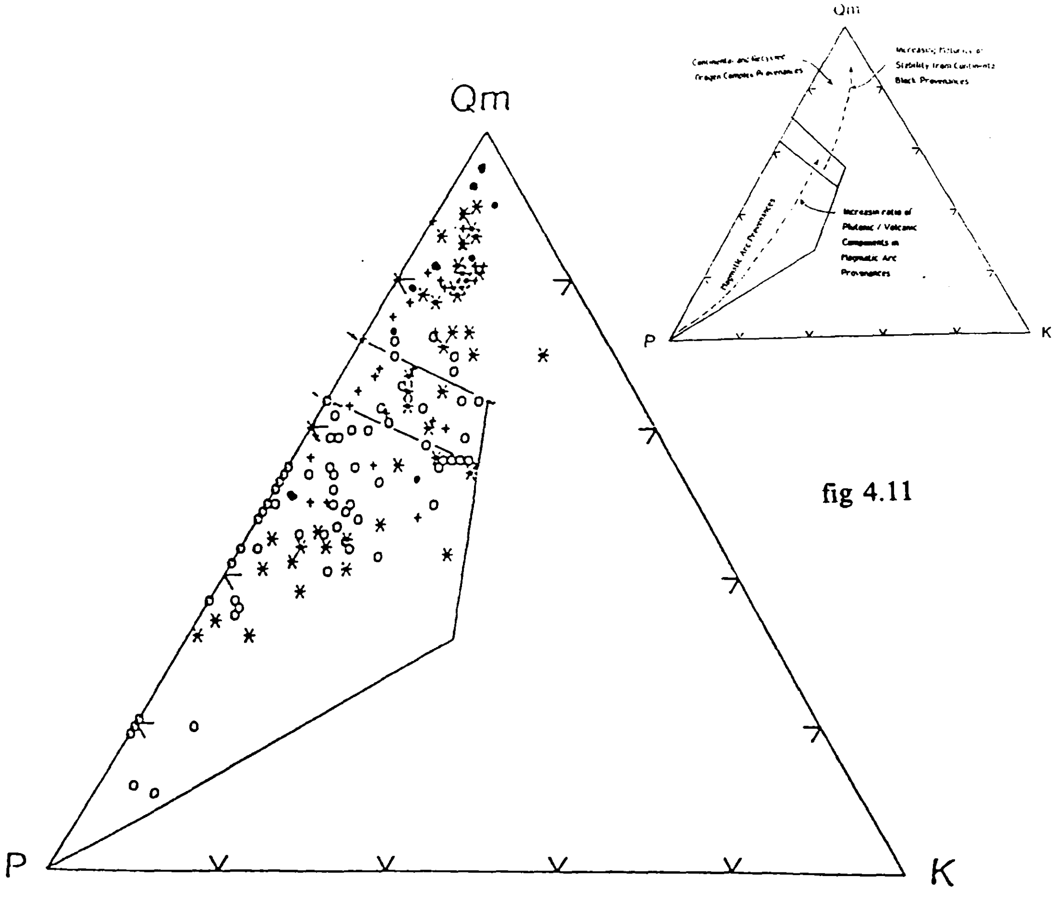


fig 4.11

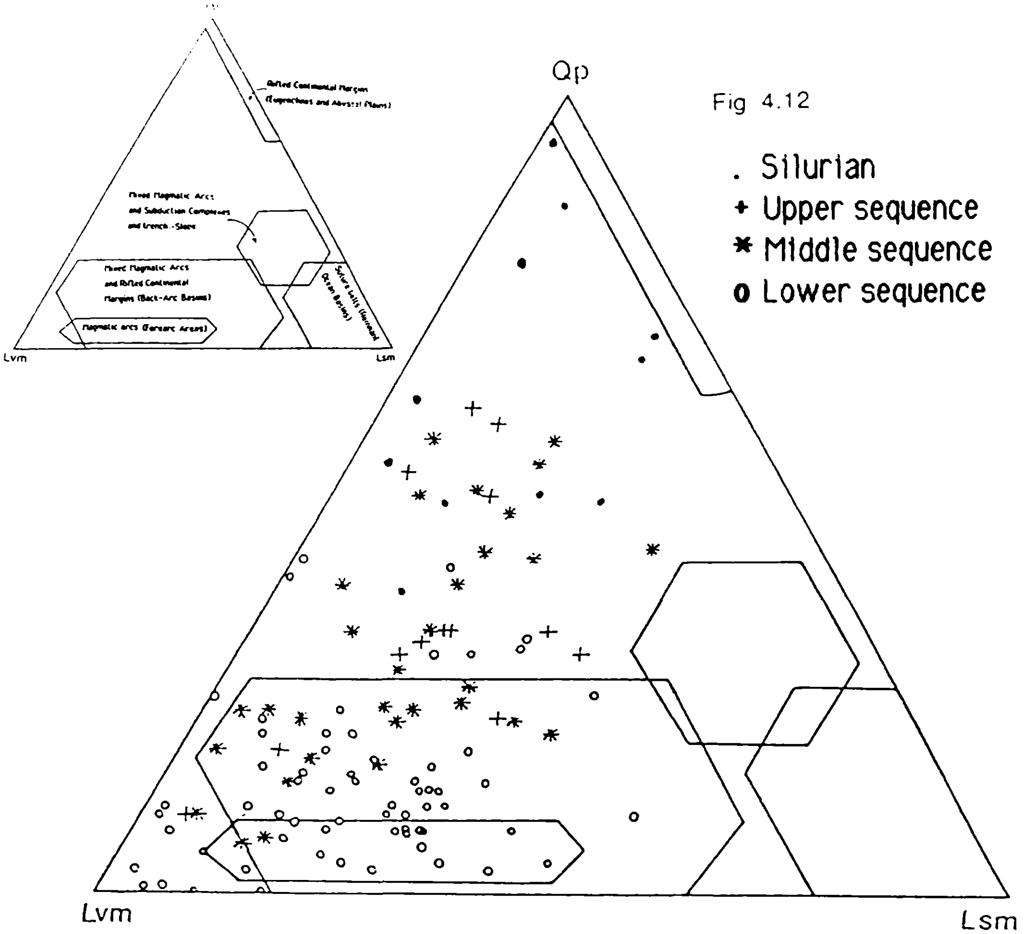


Fig 4.12

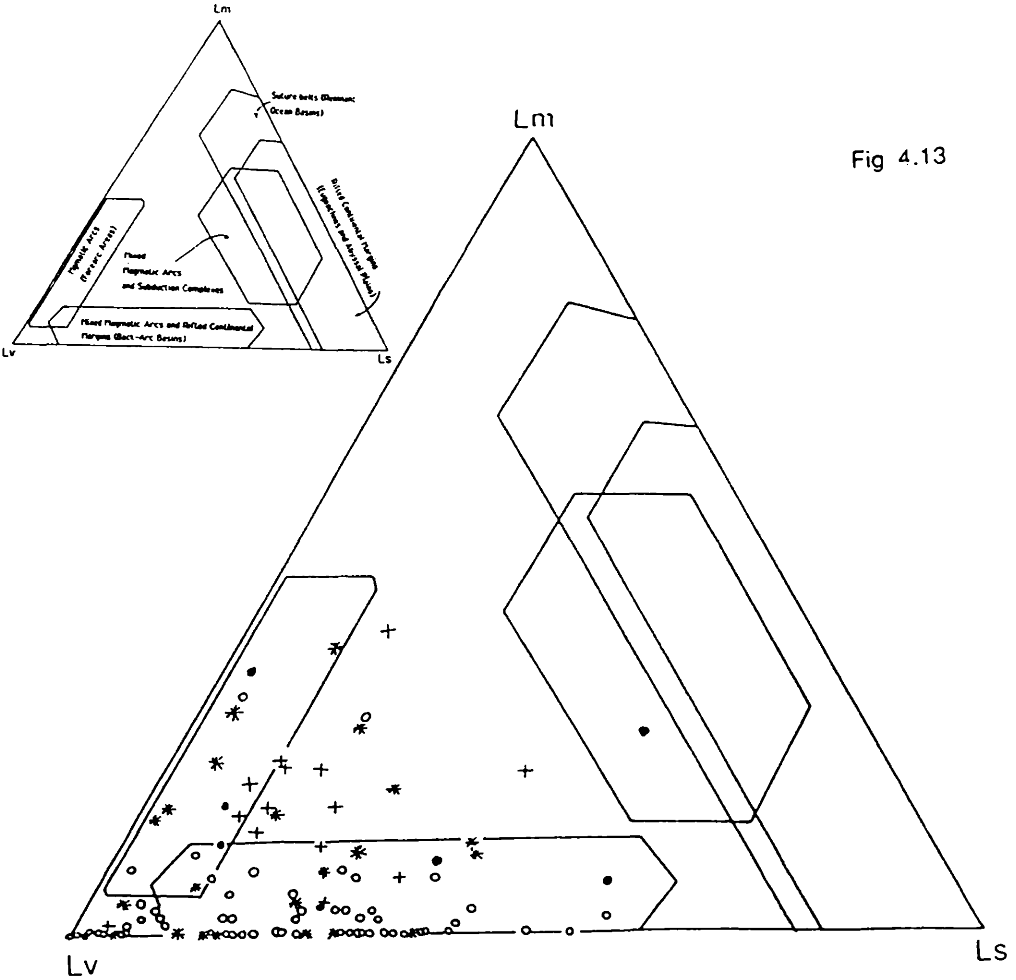


Fig 4.13

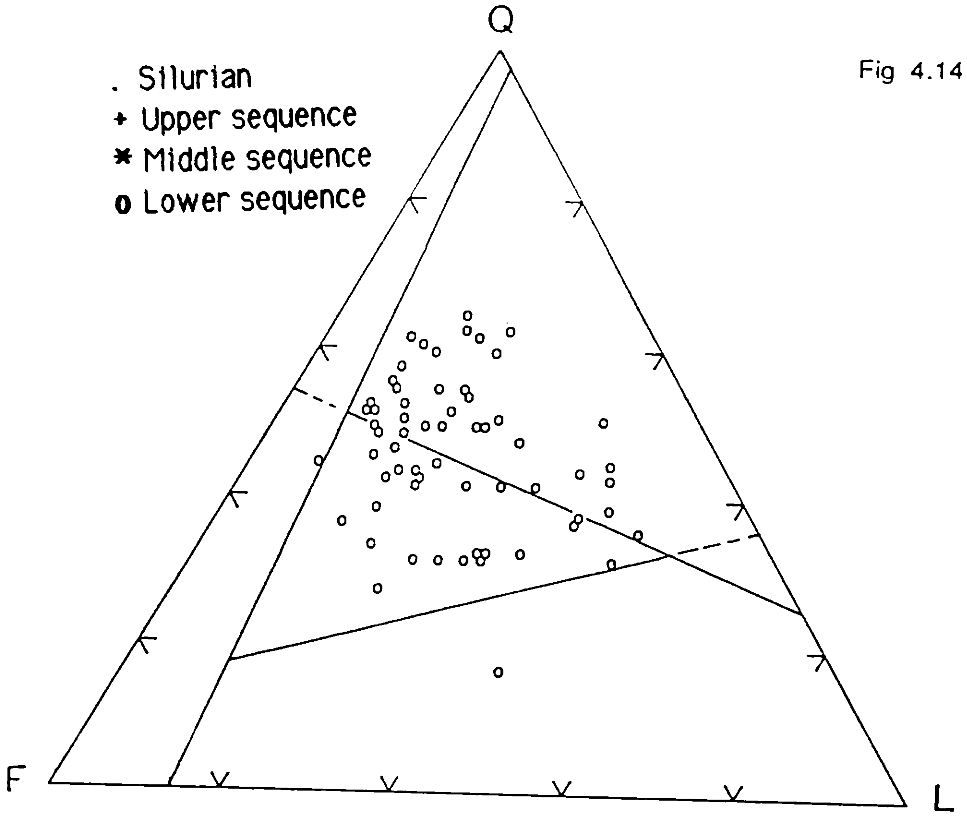


Fig 4.14

Fig 4.15

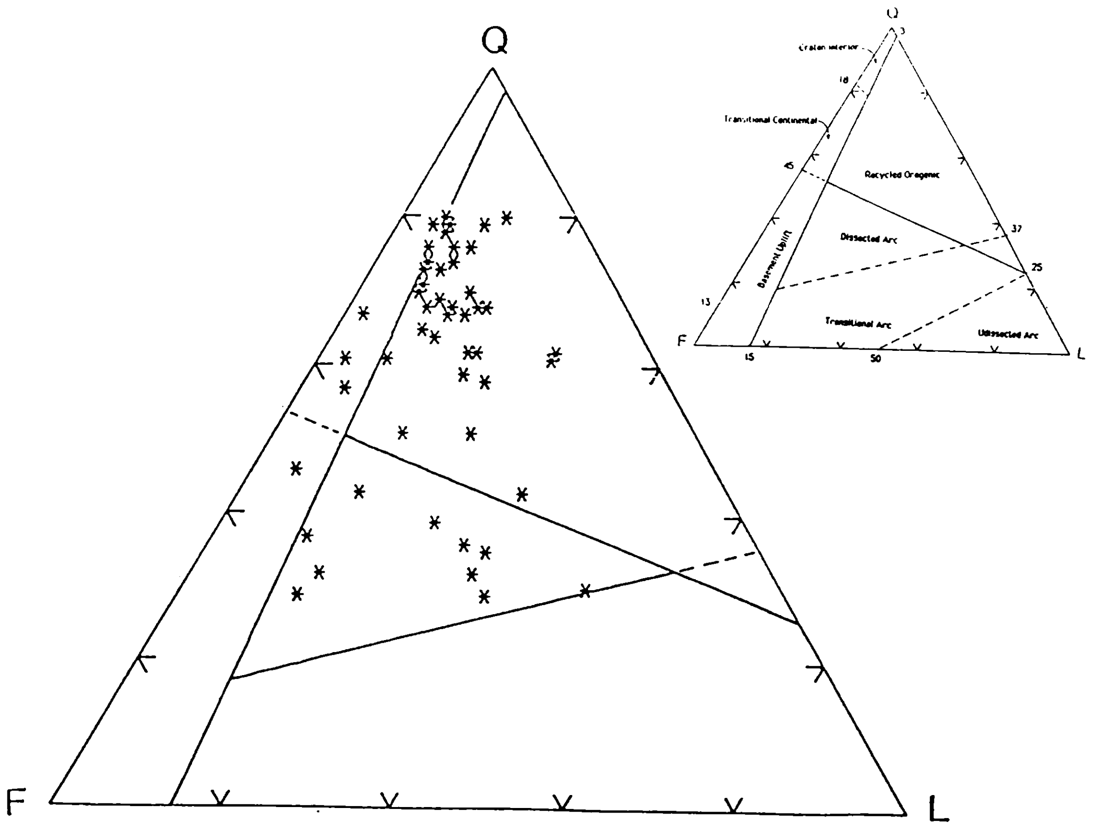


Fig 4.16

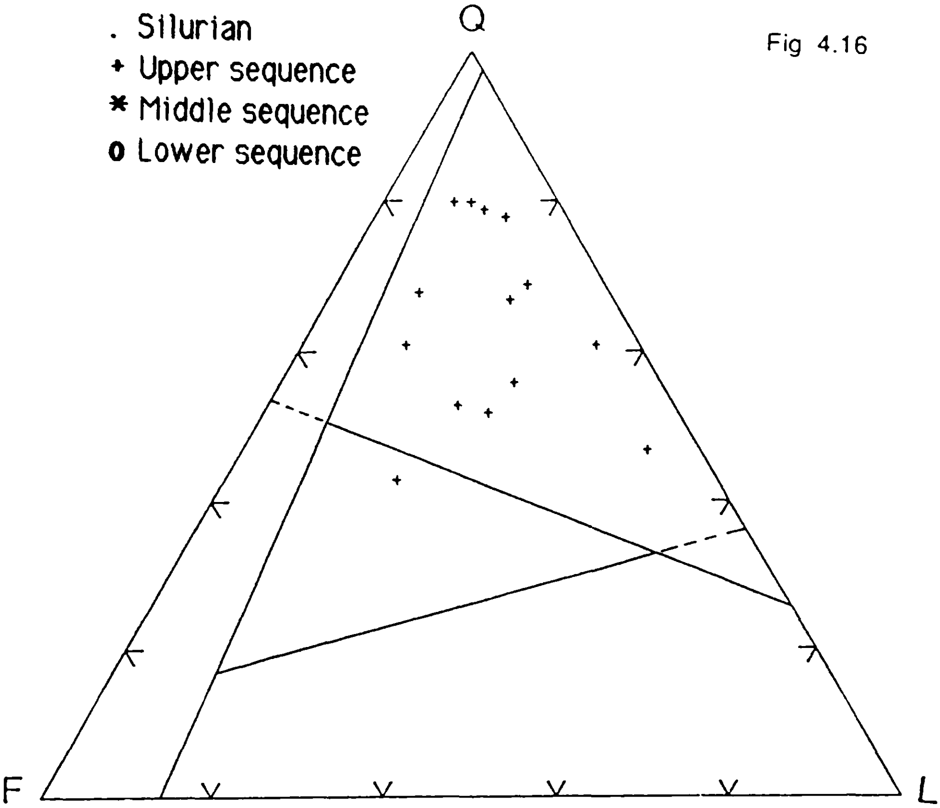
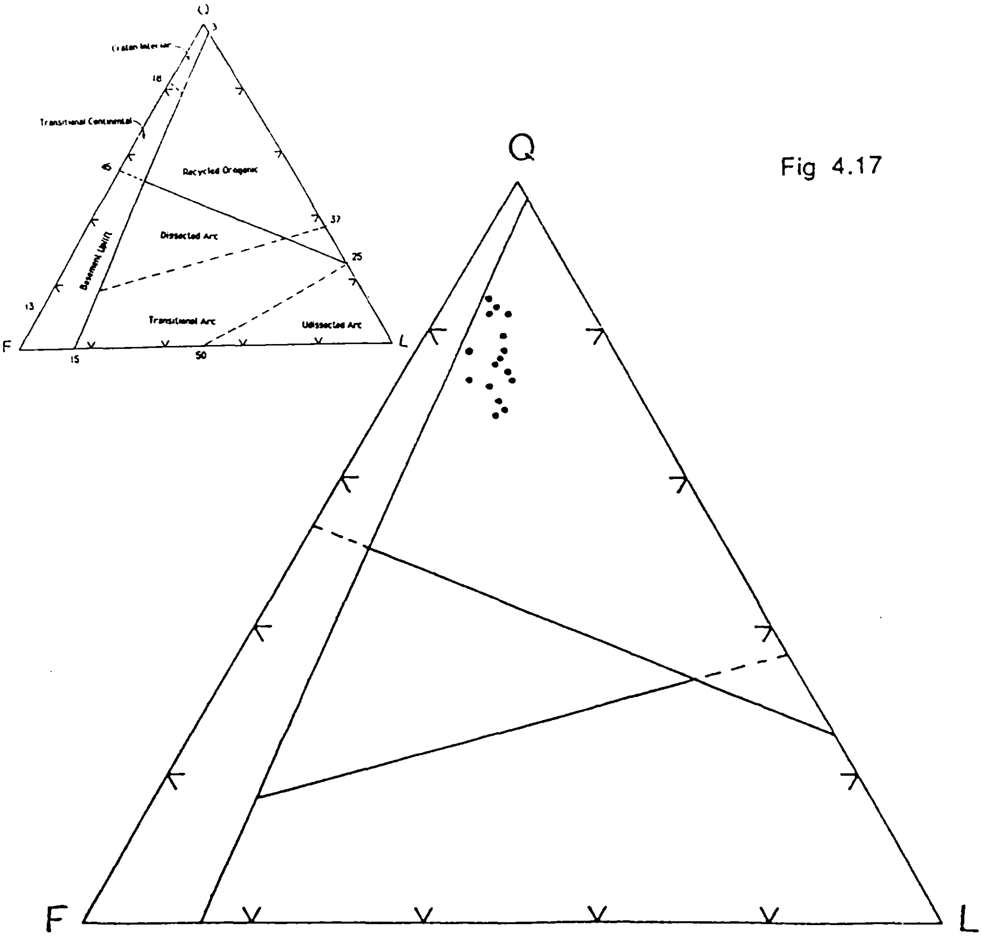


Fig 4.17



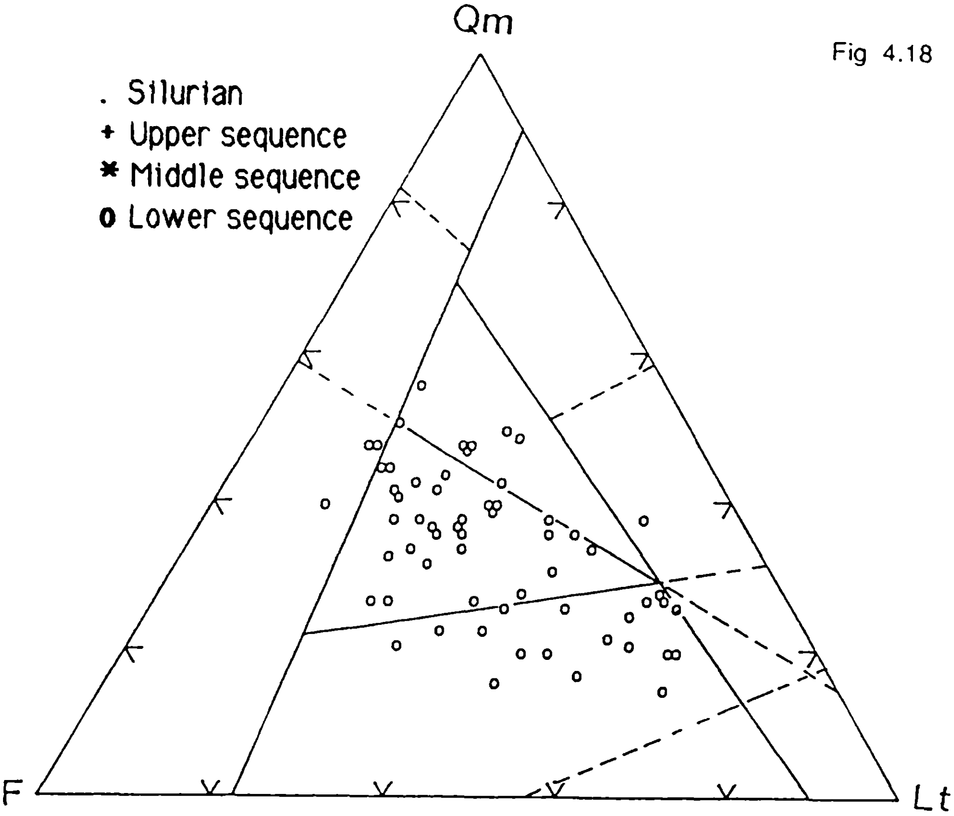


Fig 4.18

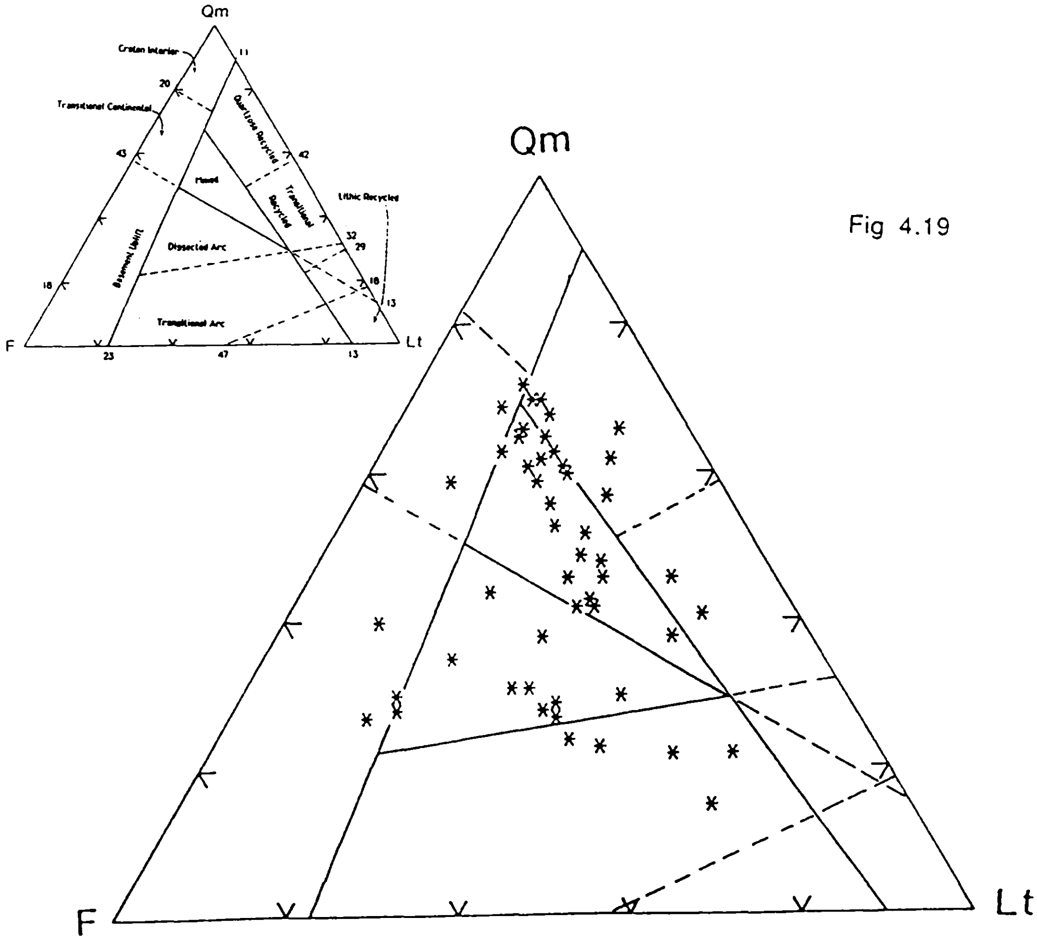


Fig 4.19

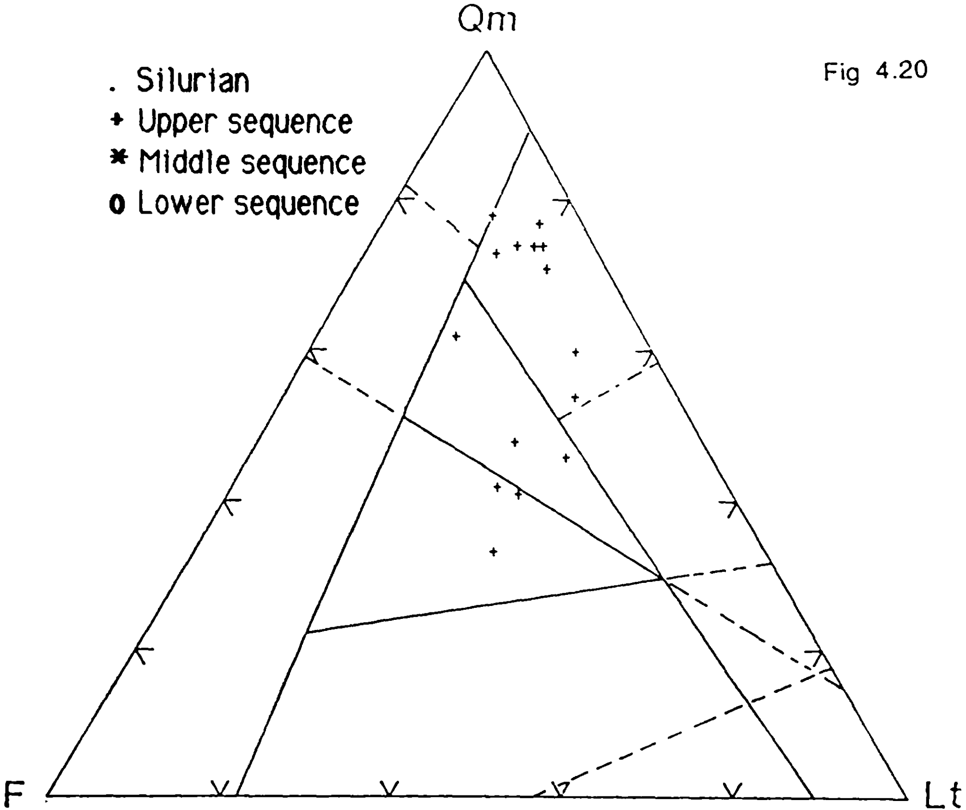


Fig 4.20

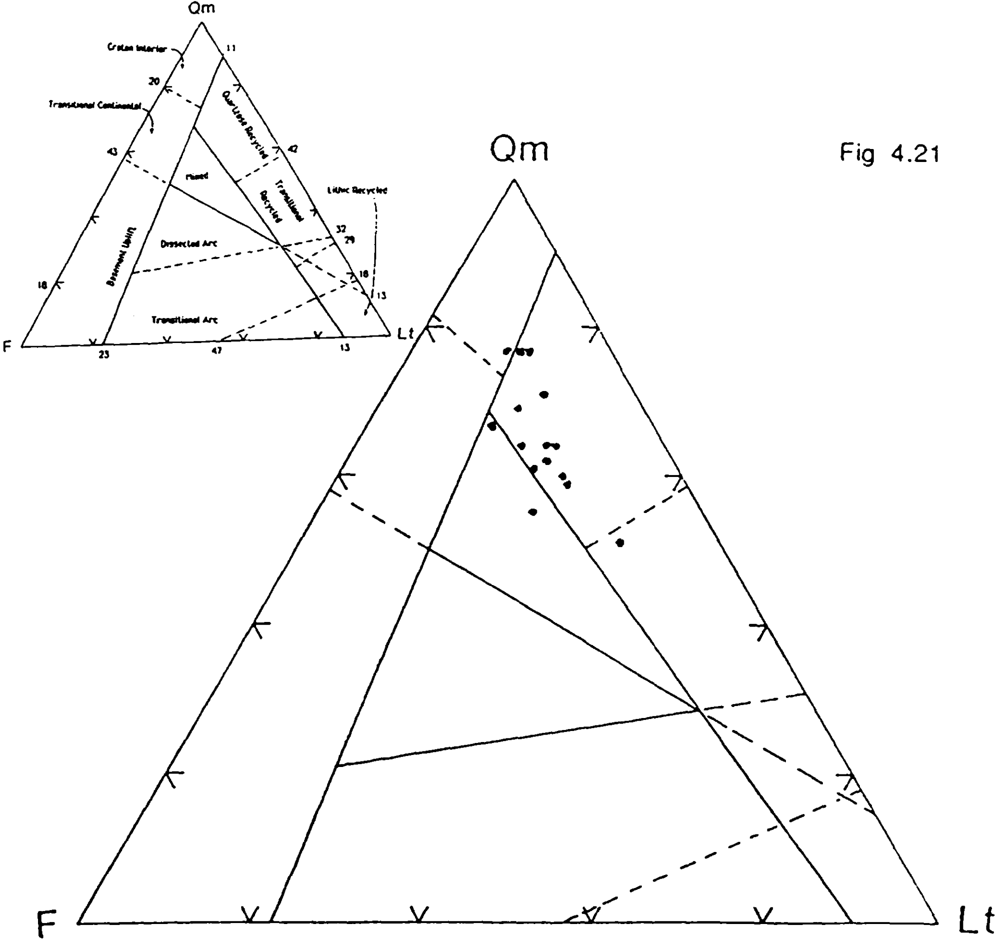


Fig 4.21

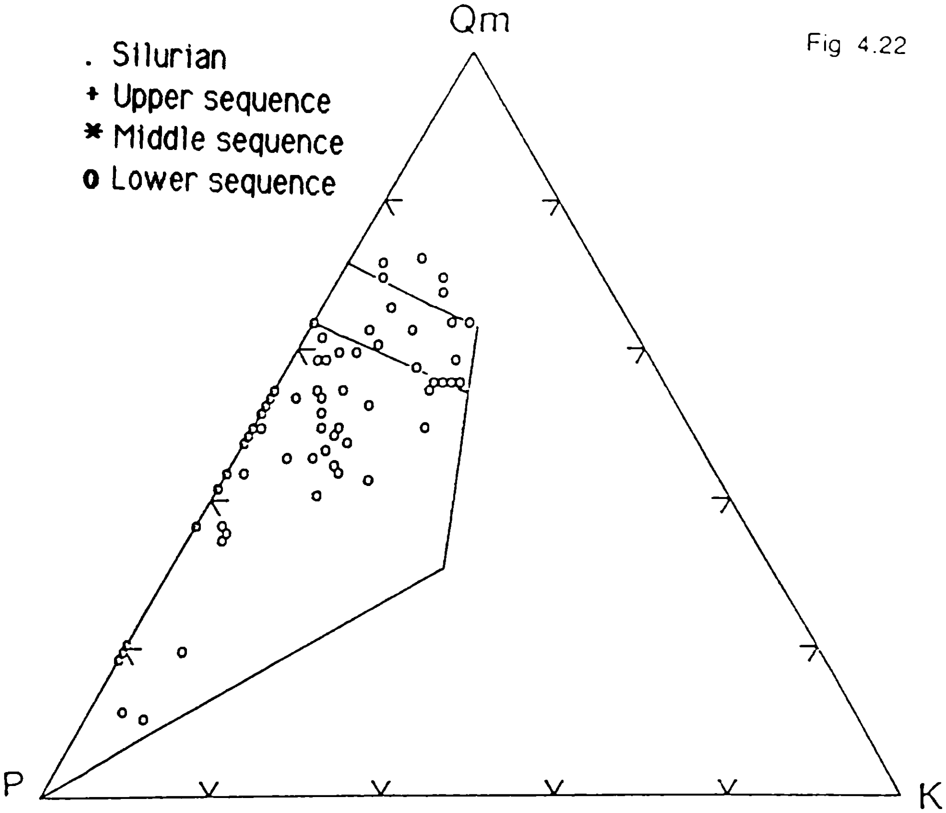


Fig 4.22

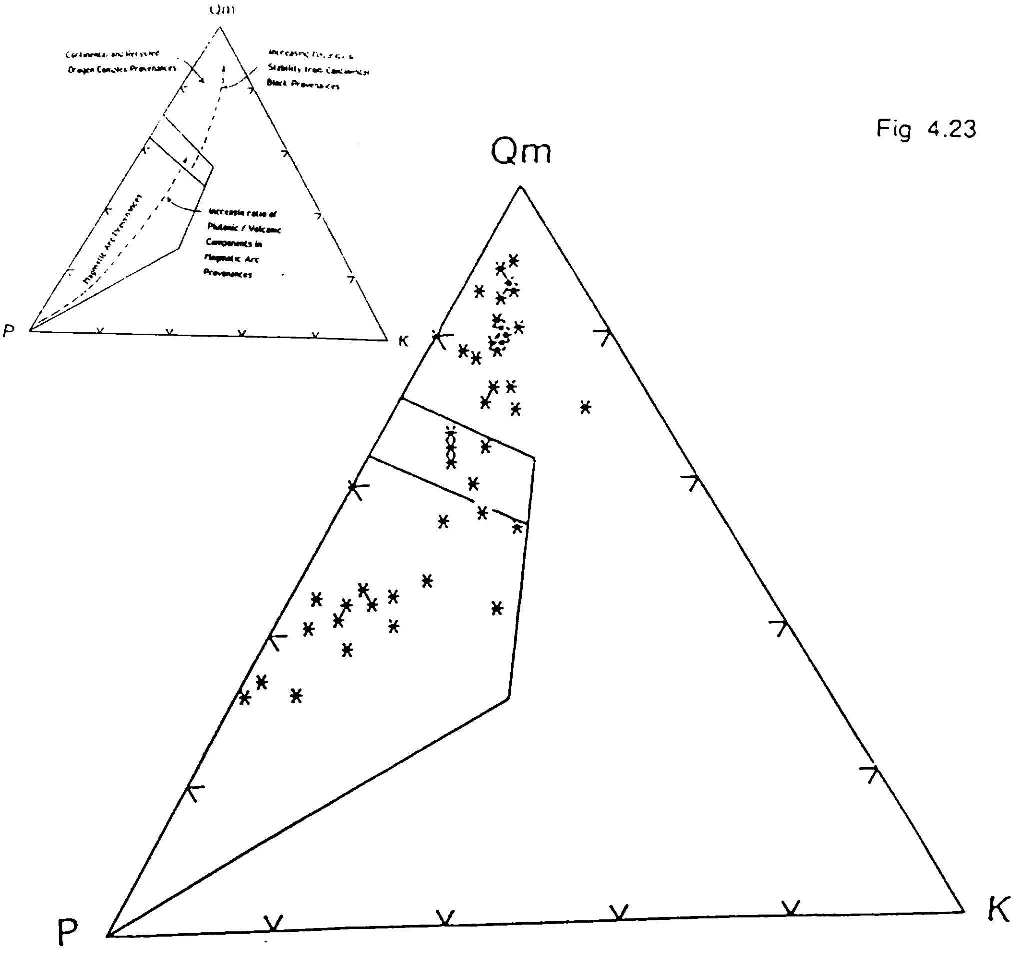


Fig 4.23

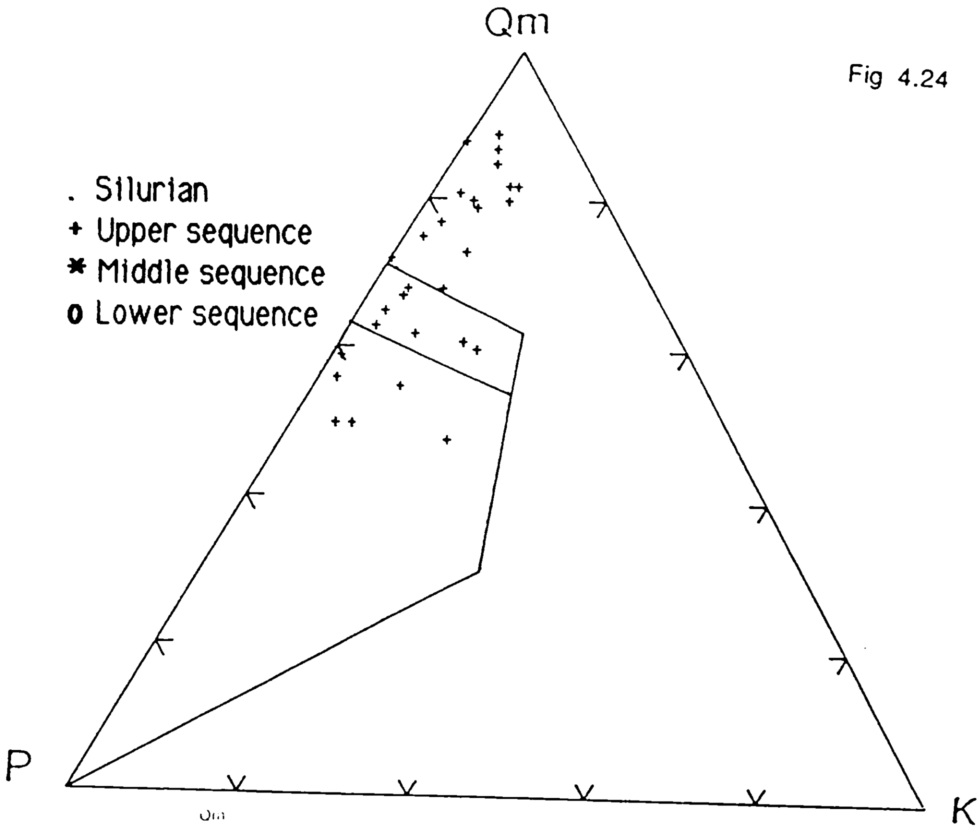


Fig 4.24

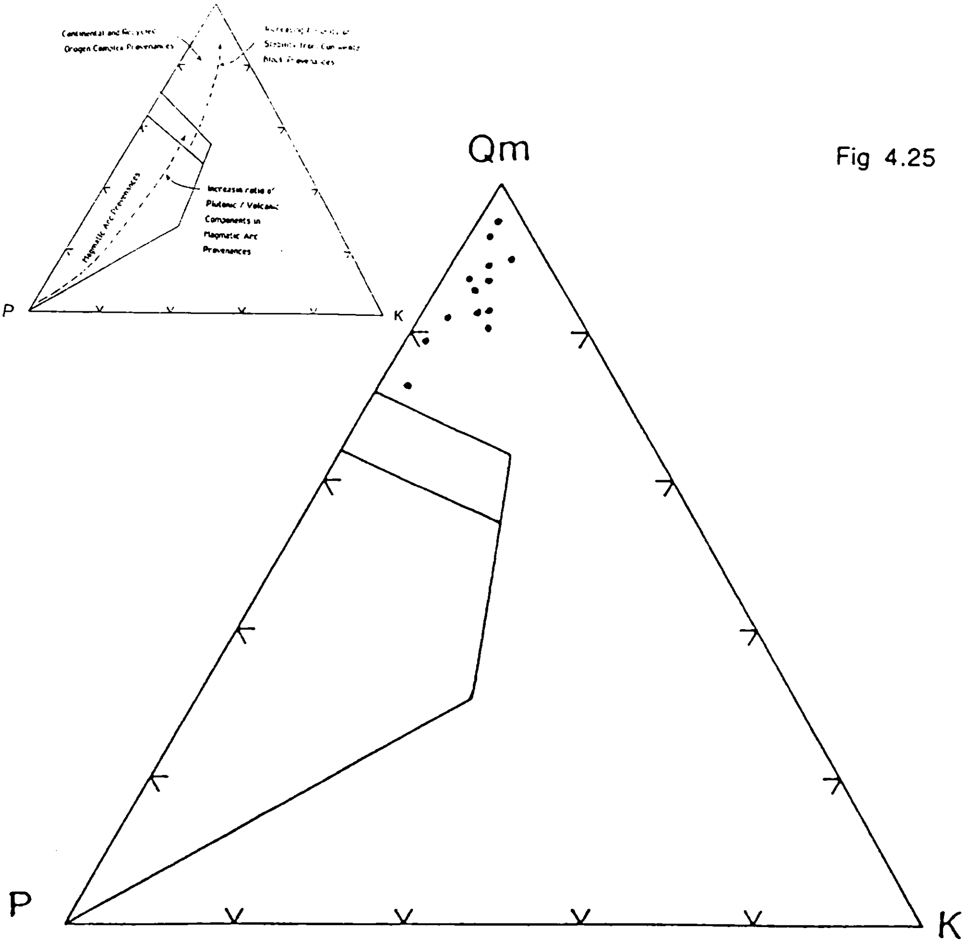


Fig 4.25

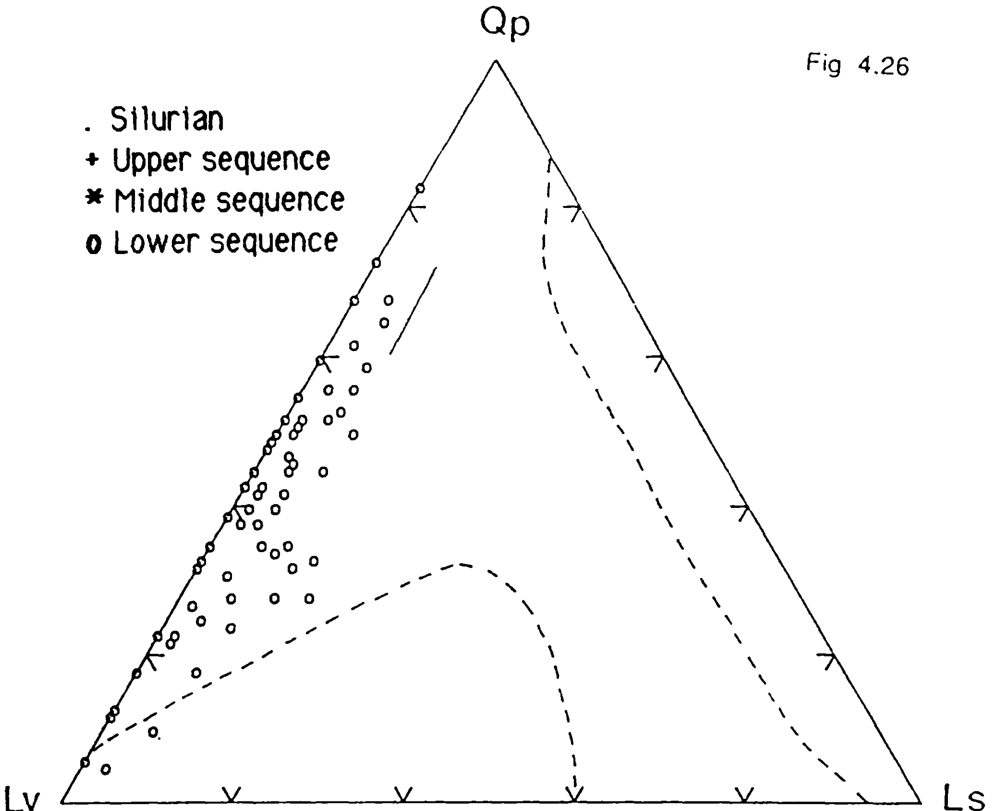


Fig 4.26

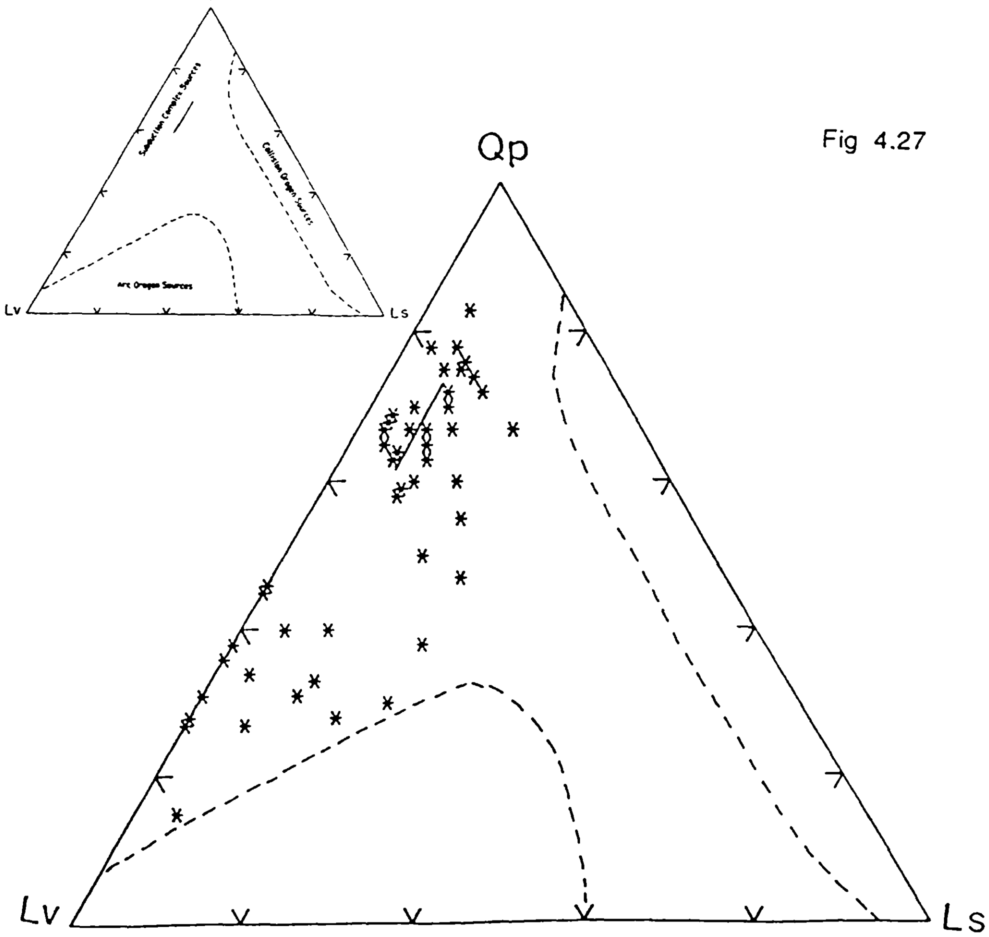


Fig 4.27

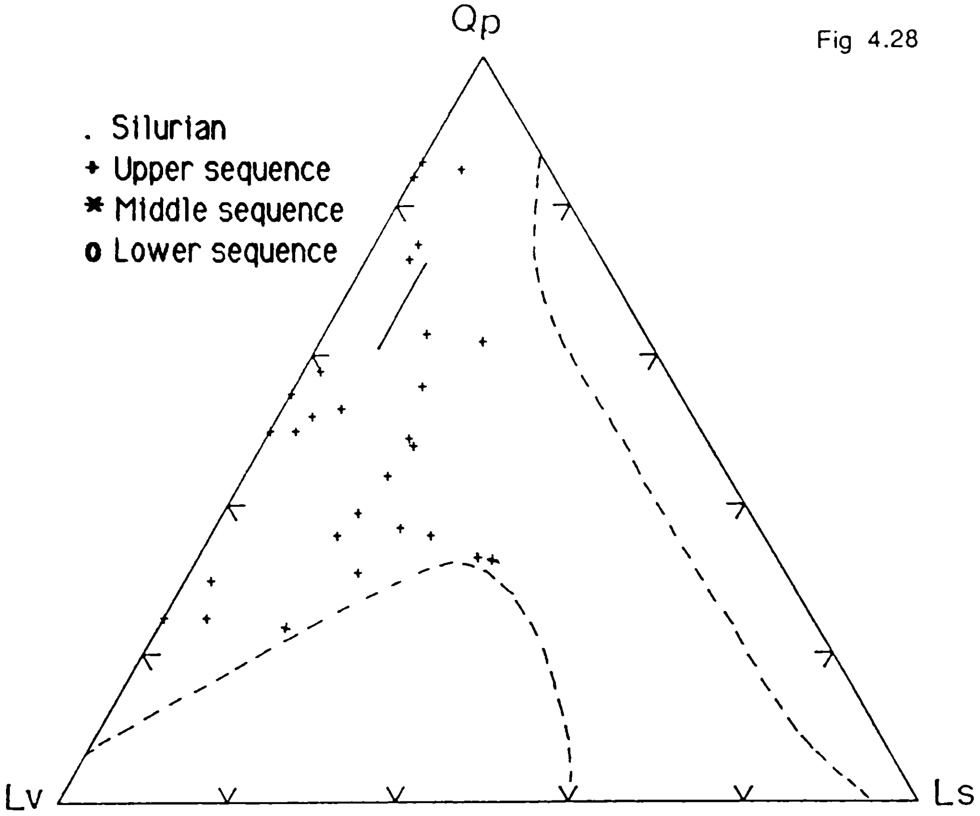


Fig 4.28

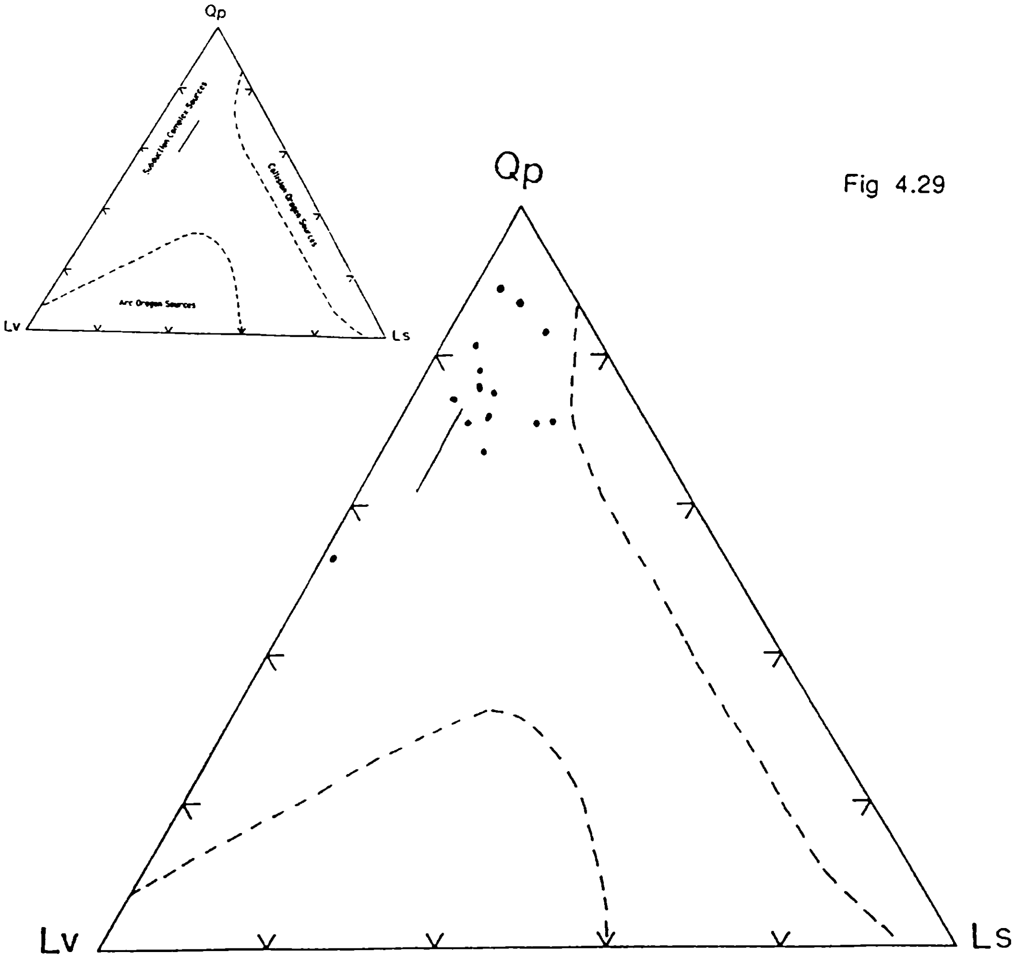
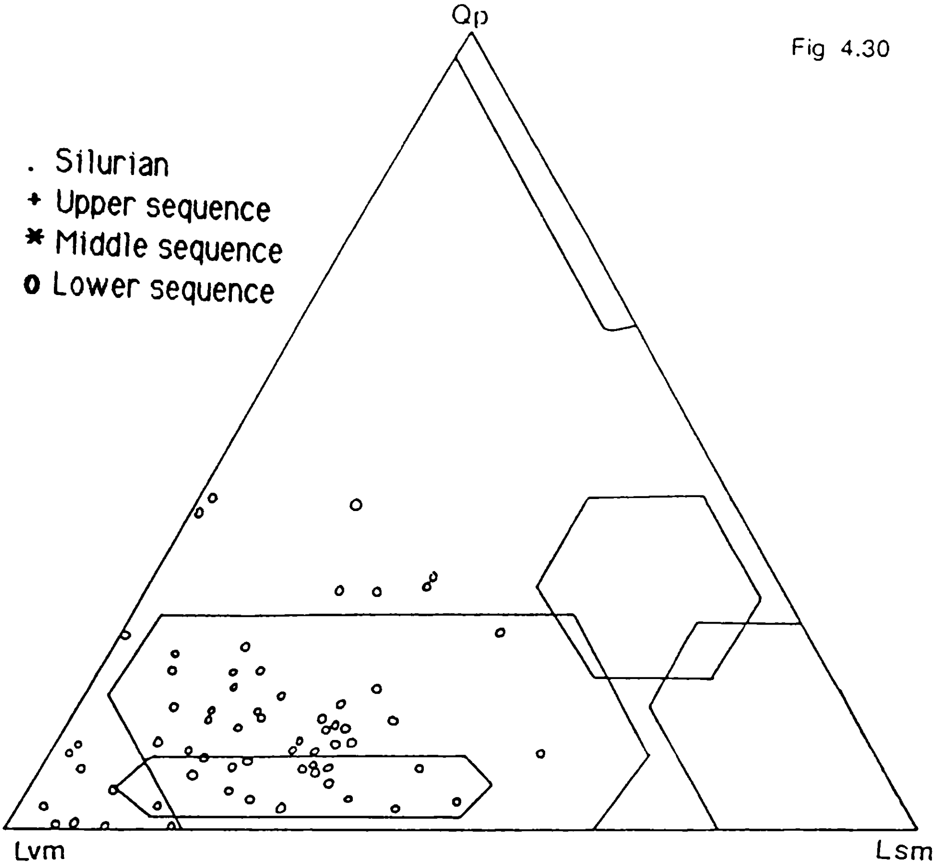


Fig 4.29

Fig 4.30



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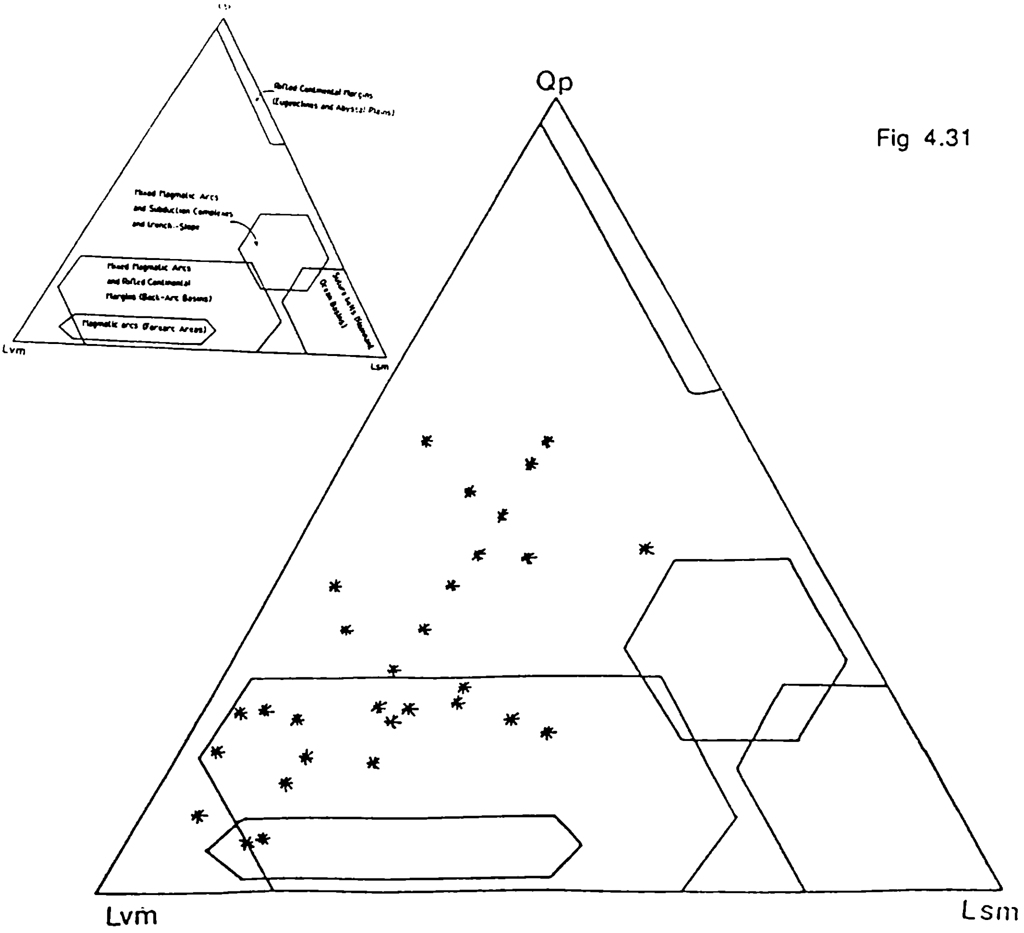


Fig 4.32

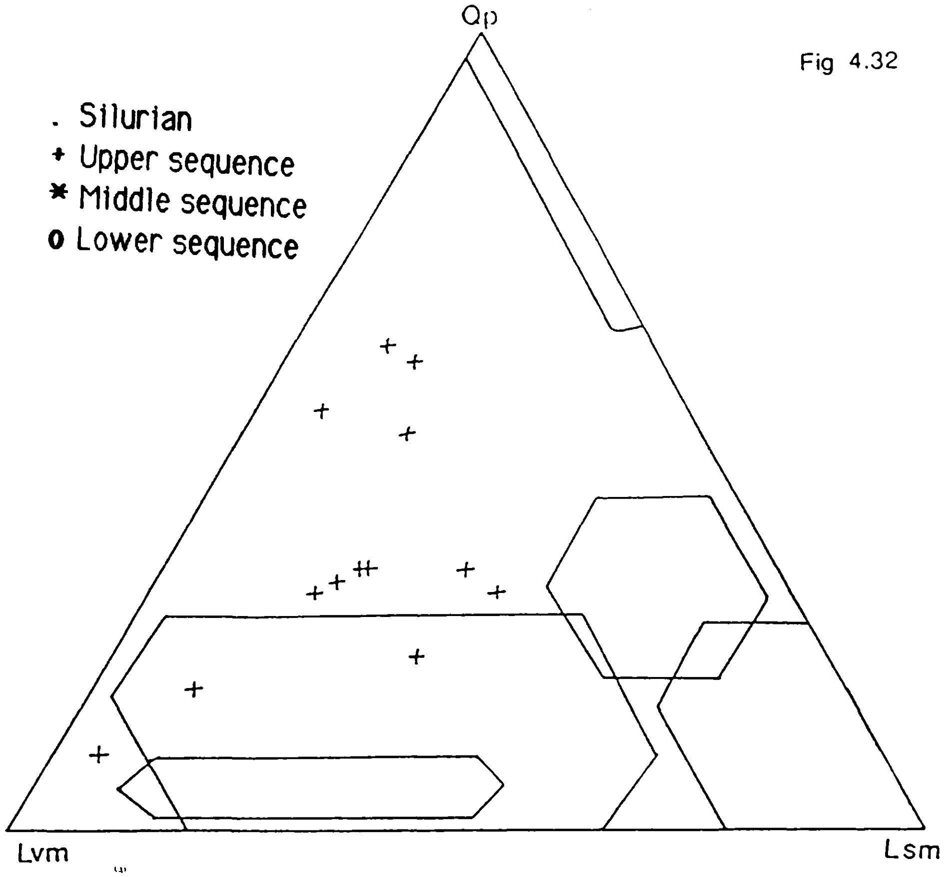


Fig 4.33

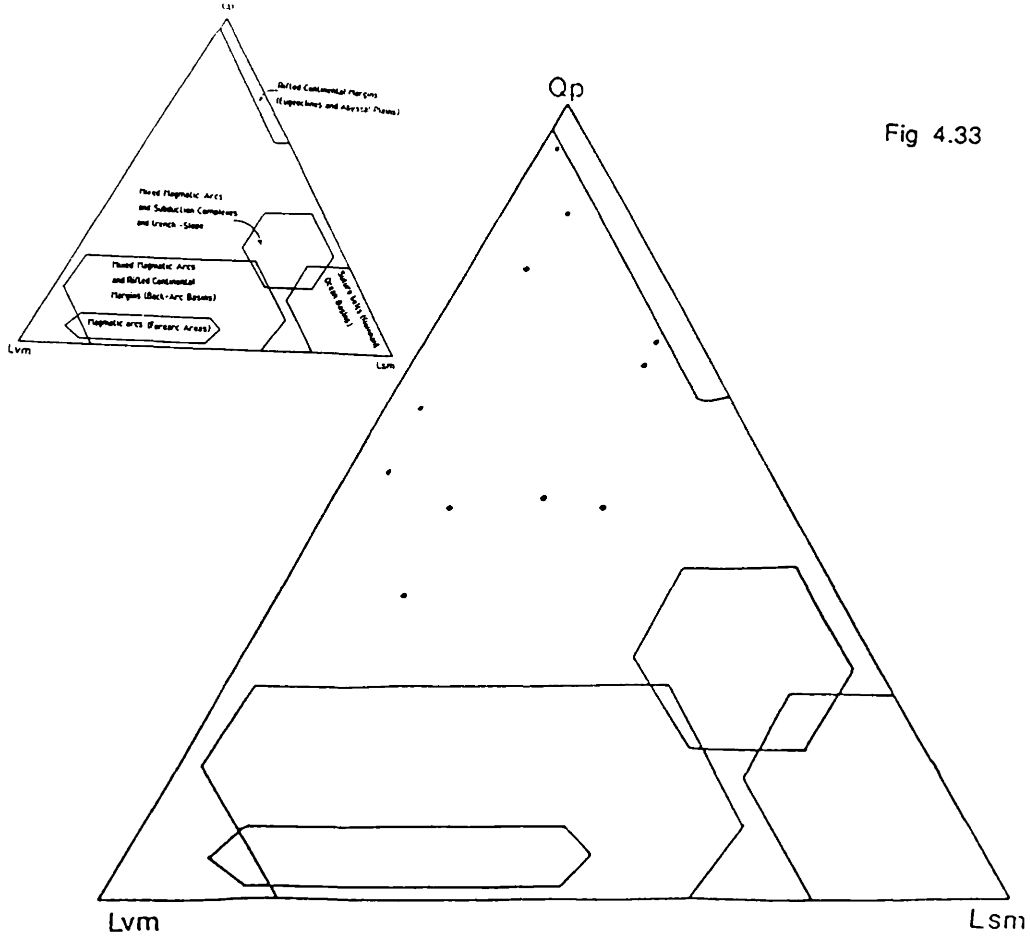


Fig 4.34

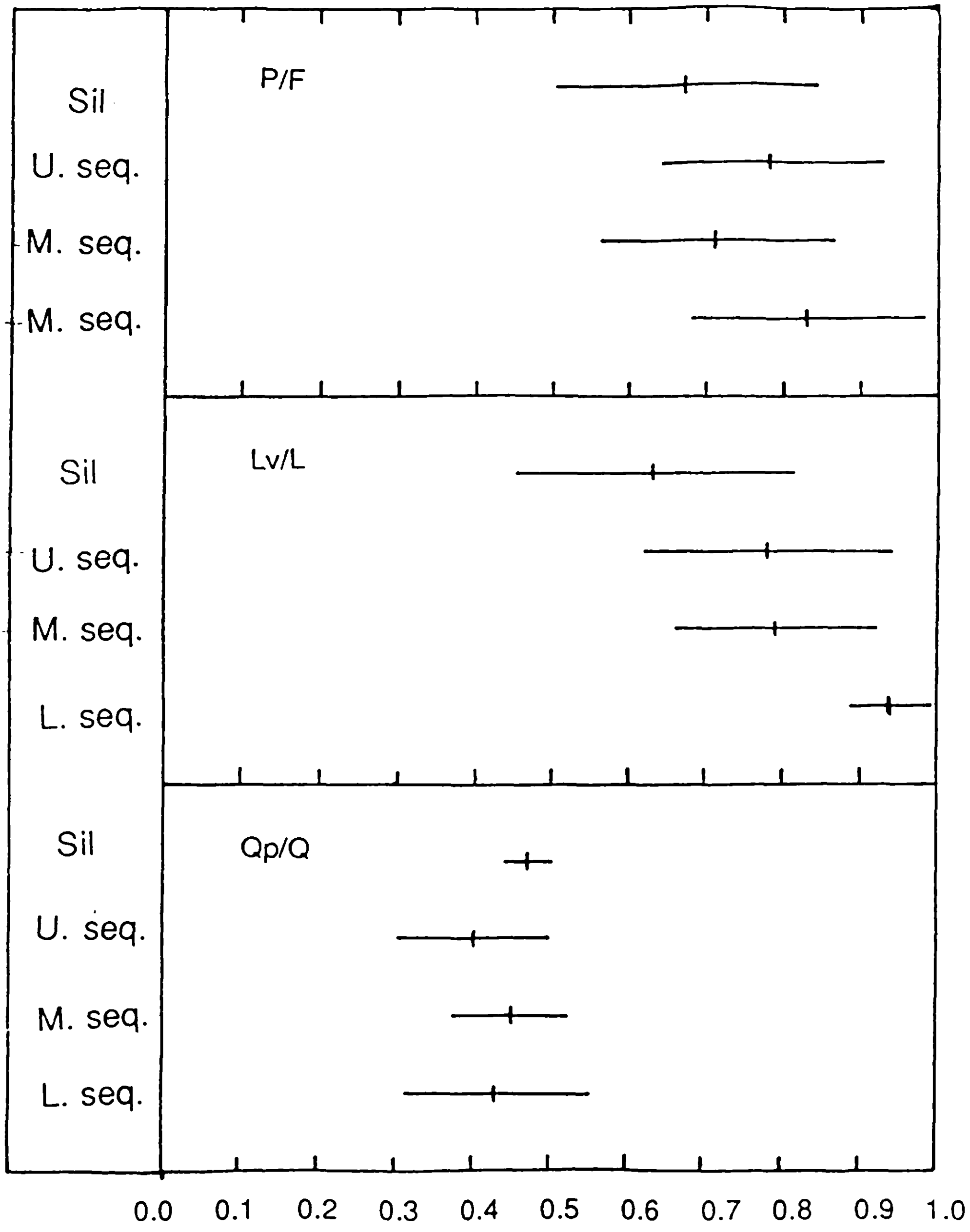

Sil
U. seq.
M. seq.
M. seq.
P/F
Sil
U. seq.
M. seq.
L. seq.
Lv/L
Sil
U. seq.
M. seq.
L. seq.
Qp/Q
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Fig 4.35

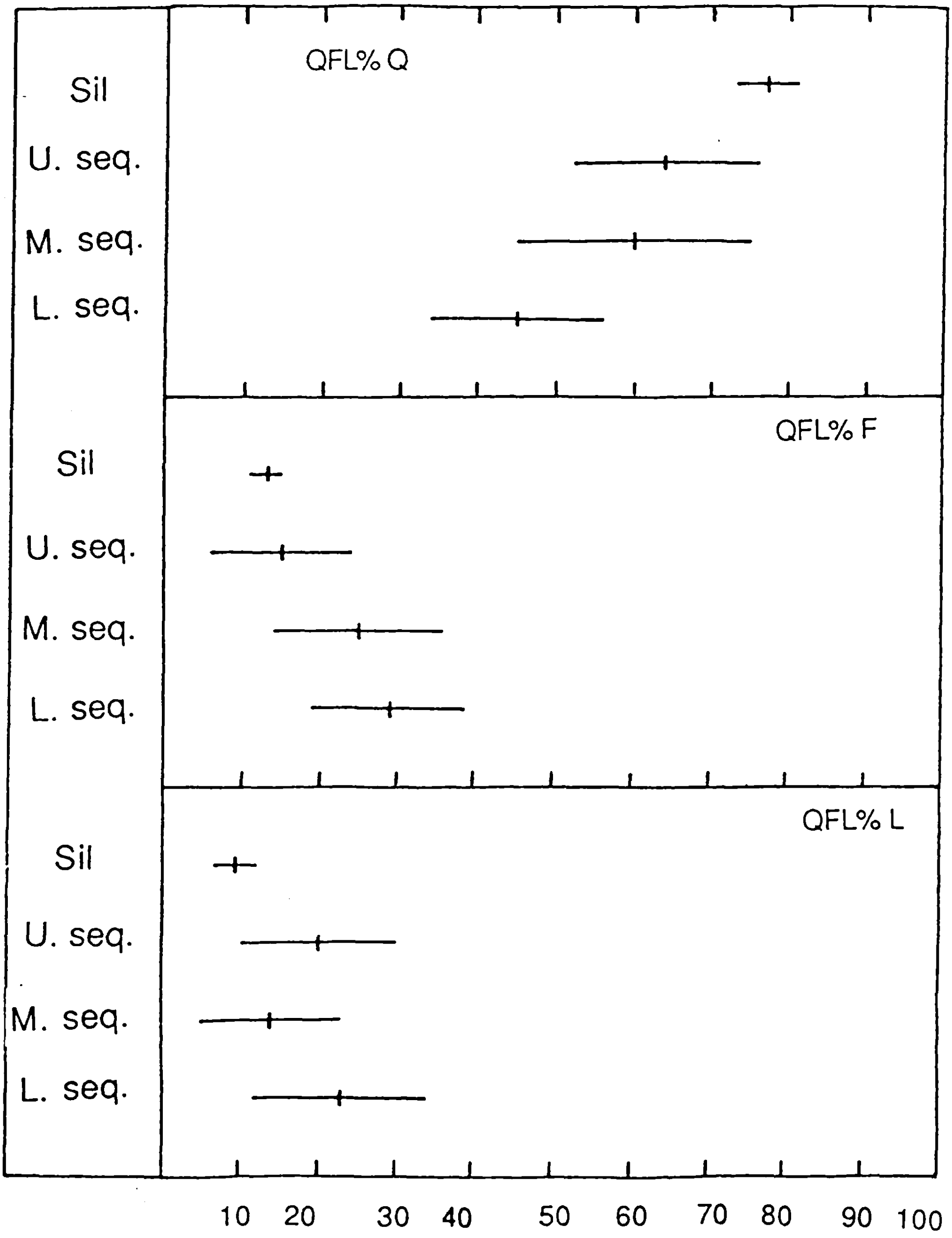

QFL% Q
QFL% F
QFL% L
Sil
U. seq.
M. seq.
L. seq.
Sil
U. seq.
M. seq.
L. seq.
Sil
U. seq.
M. seq.
L. seq.
10
20
30
40
50
60
70
80
90
100

Fig 4.36

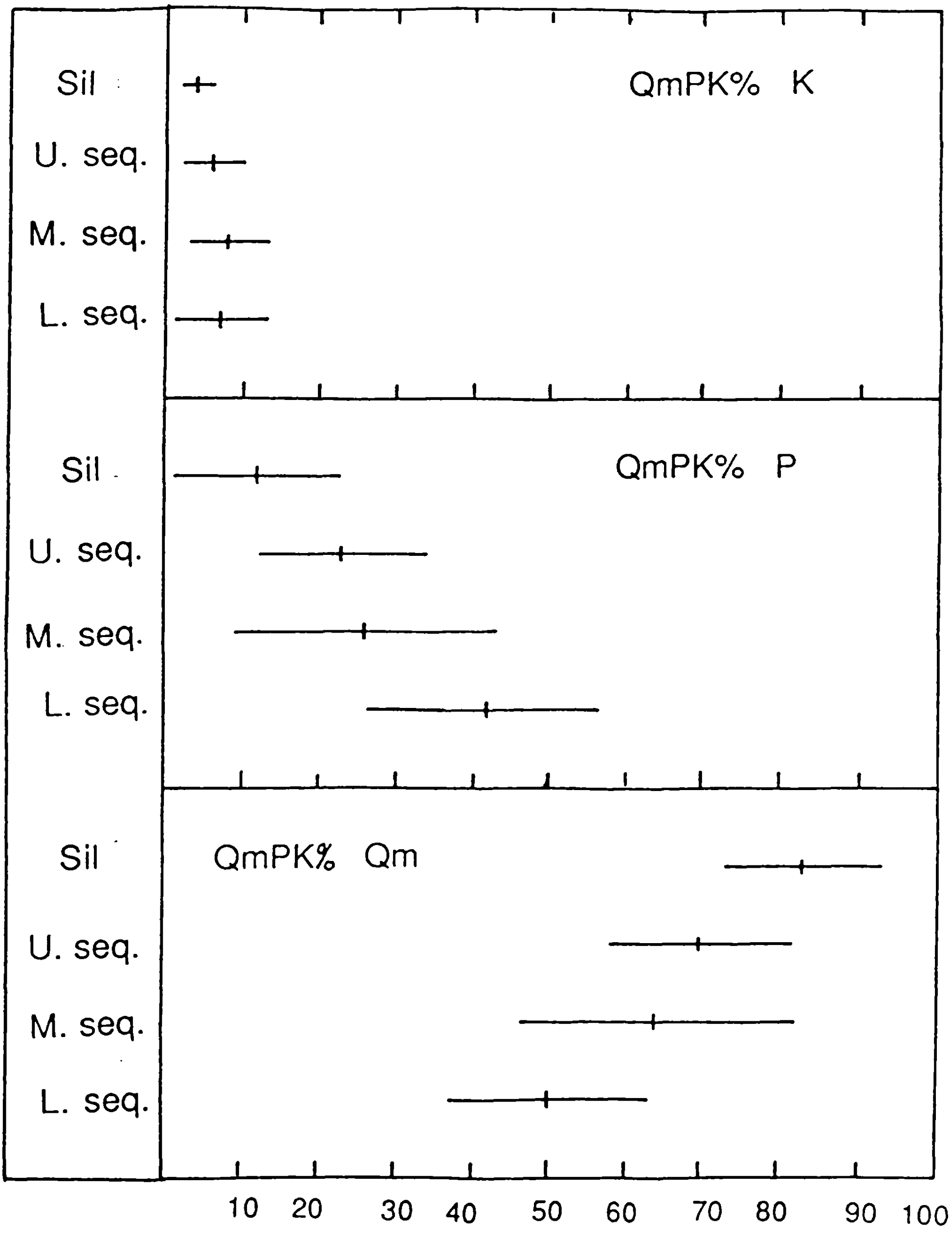

Sil
U. seq.
M. seq.
L. seq.
QmPK% K
QmPK% P
QmPK% Qm
10
20
30
40
50
60
70
80
90
100

Fig 4.37

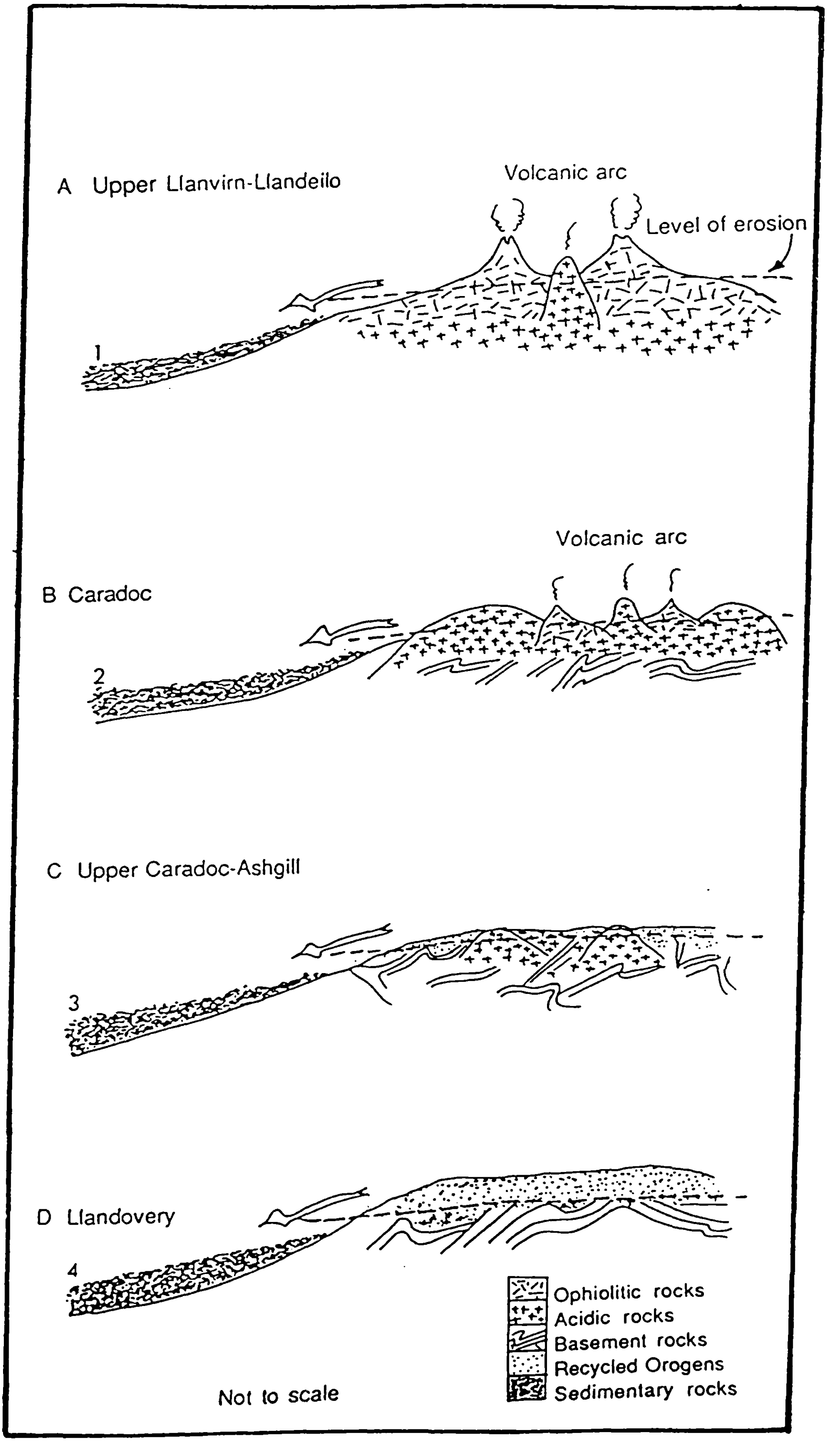
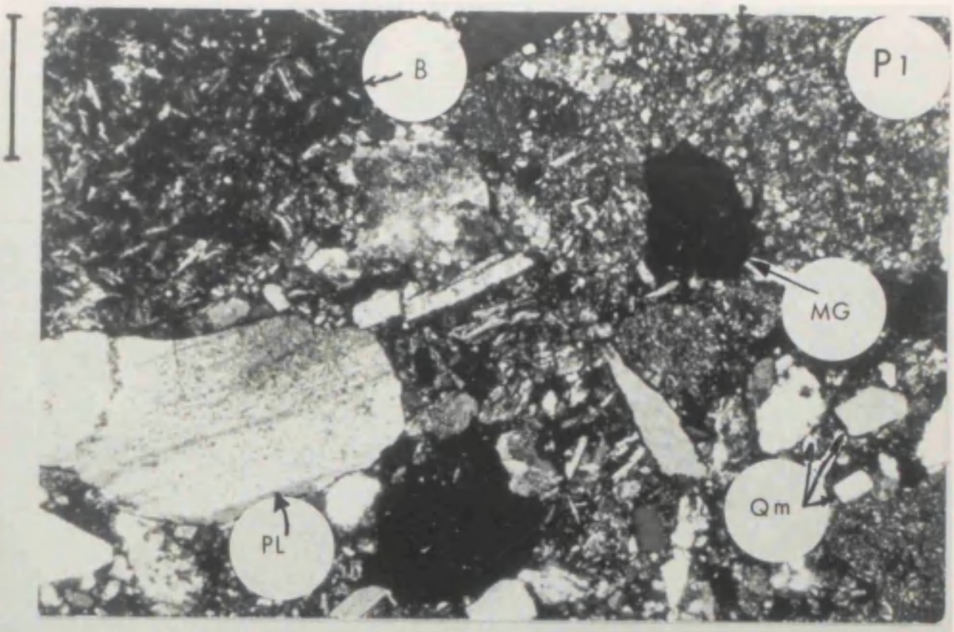
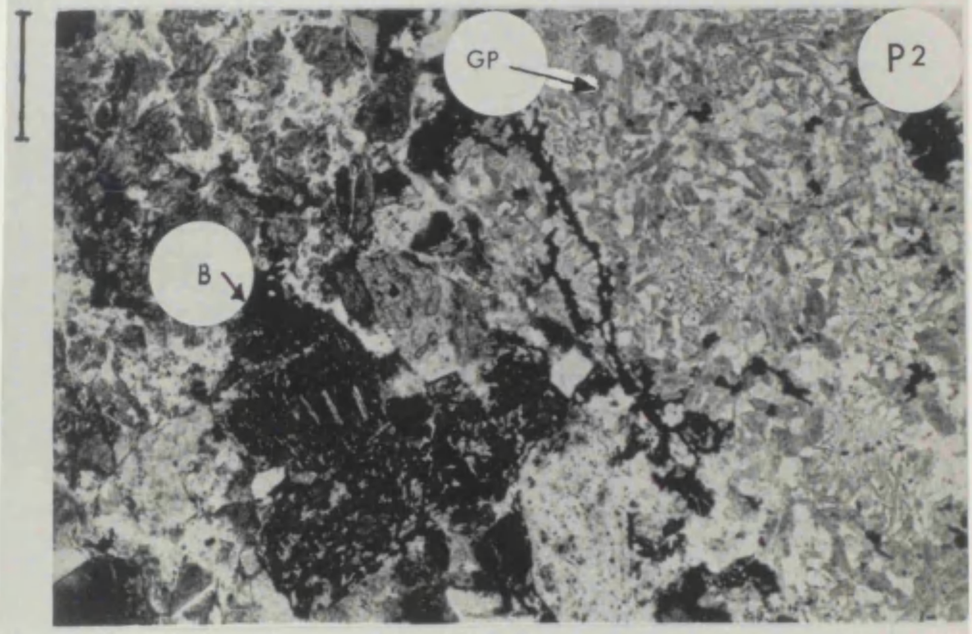

A Upper Llanvirn-Llandeilo
Volcanic arc
Level of erosion
1
B Caradoc
Volcanic arc
2
C Upper Caradoc-Ashgill
3
D Llandovery
4
Ophiolitic rocks
Acidic rocks
Basement rocks
Recycled Orogens
Sedimentary rocks
Not to scale

Plate 1: Photomicrograph from the lower sequence greywackes (Changue Formation) showing some rock fragments and minerals. PL=plagioclase, Qm=monocrystalline quartz, MG=magnetite, B=basic rock fragment [crossed Nicols]. Bar=0.5 mm

Plate 2: Photomicrograph from the lower sequence greywackes(Craigmalloch Formation) GP=granophyre, B=basic rock fragment [natural light]. Bar=0.5mm

Plate 3: Photomicrograph from the lower sequence greywackes (Craigmalloch Formation) showing a granitic rock fragment [crossed Nicols). Bar=0.25 mm


B
P1
MG
Qm
PL

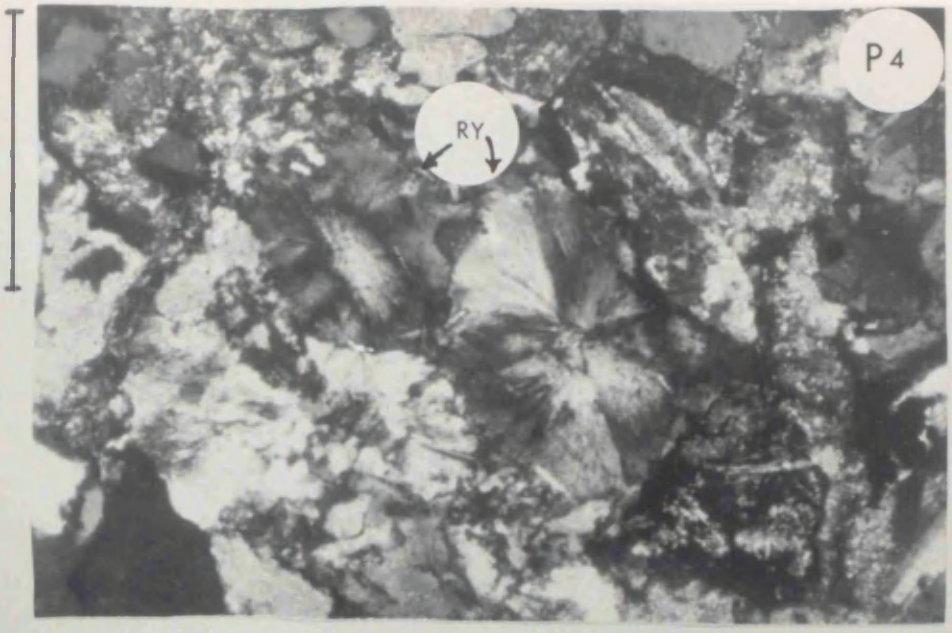

GP
P2
B


P3

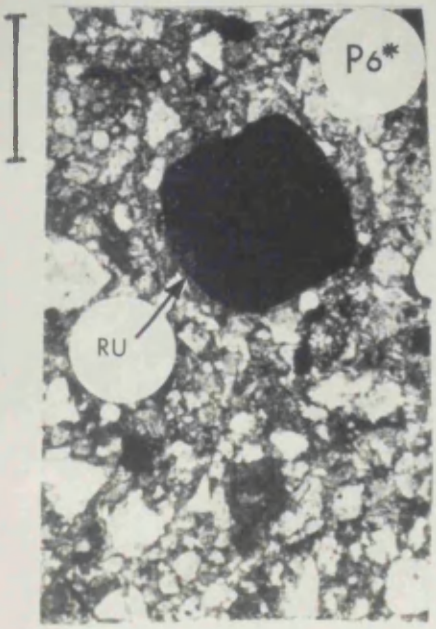
Plate 4: Photomicrograph from the lower sequence greywackes (Darley Formation) showing spherulitic rhyolite (RY) [crossed Nicols]. Bar=0.25 mm

Plate 5: Photomicrograph from the lower sequence greywackes (Kirkland Formation) showing large roch fragments of serpentinite (SP) [crossed Nicols]. Bar=0.25 mm

Plates 6&6*: Photomicrograh from the lower sequence greywackes (changue Formation) showing an euhedral crystal of rutile (RU, in P6*) and garnet (GT in P6)] P6=natural light and P6* crossed Nicols]. Bar=0.6 mm for P6* and 0.25 mm for P6


P4
RY


P5
SP


P6*
RU

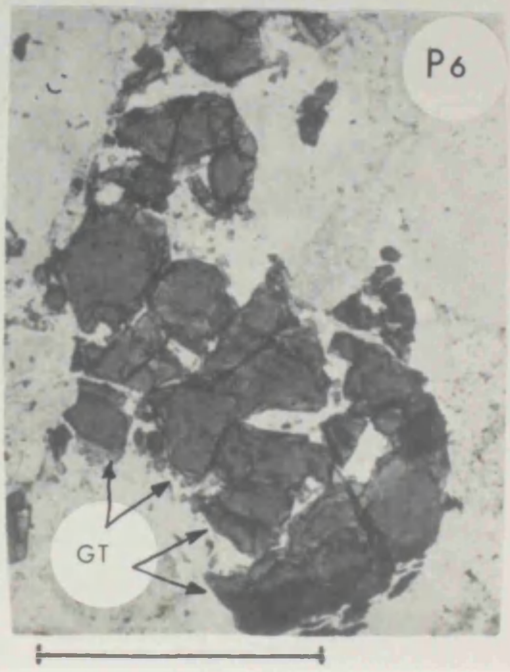
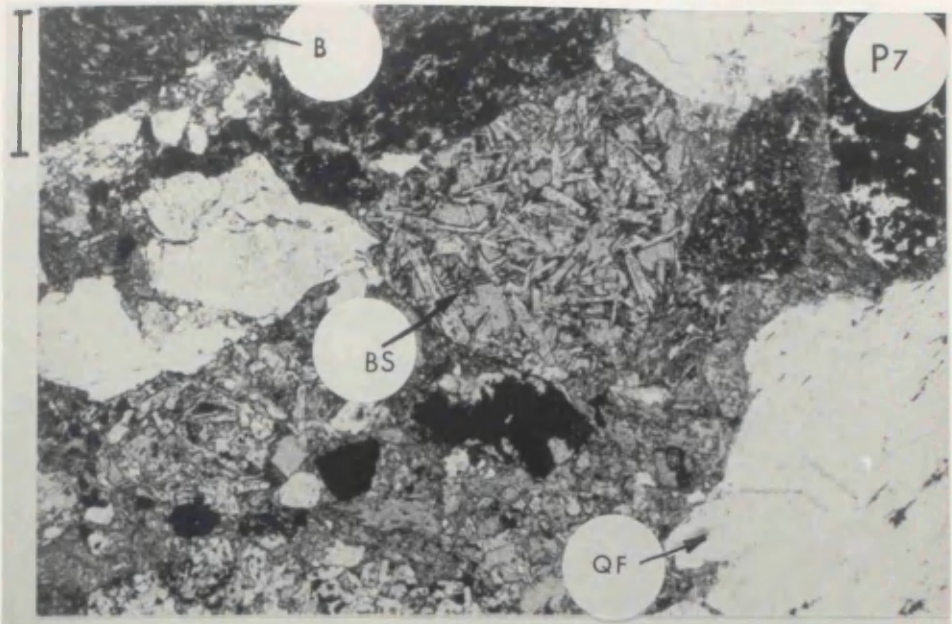
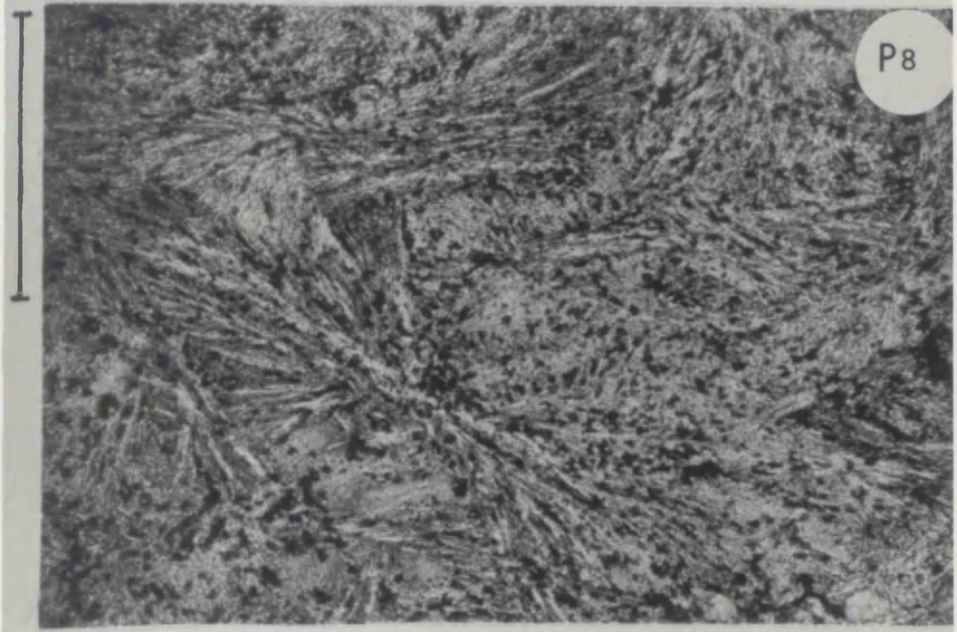

P6
GT

Plate 7: Photomicrograph from the lower sequence greywackes (InfraKilrany Formation) showing some rock fragments and minerals. B=basic rock fragments, BS=basalt, QF=K-feldspar [natural light]. Bar=0.5 mm

Plate 8: Photomicrograph from the lower sequence greywackes (Infrakilrany Formation) showing a dolerite rock fragment [natural light]. Bar=0.25 mm

Plate 9: Photomicrograph from the middle sequence greywackes (Cascade Grits) showing some minerals. PL=albitic plagioclase, KF=K-feldspar, Qm=monocrystalline quartz. Not the abundance of quartz [crossed Nicols]. Bar=0.5 mm


P7
B
BS
QF


P8

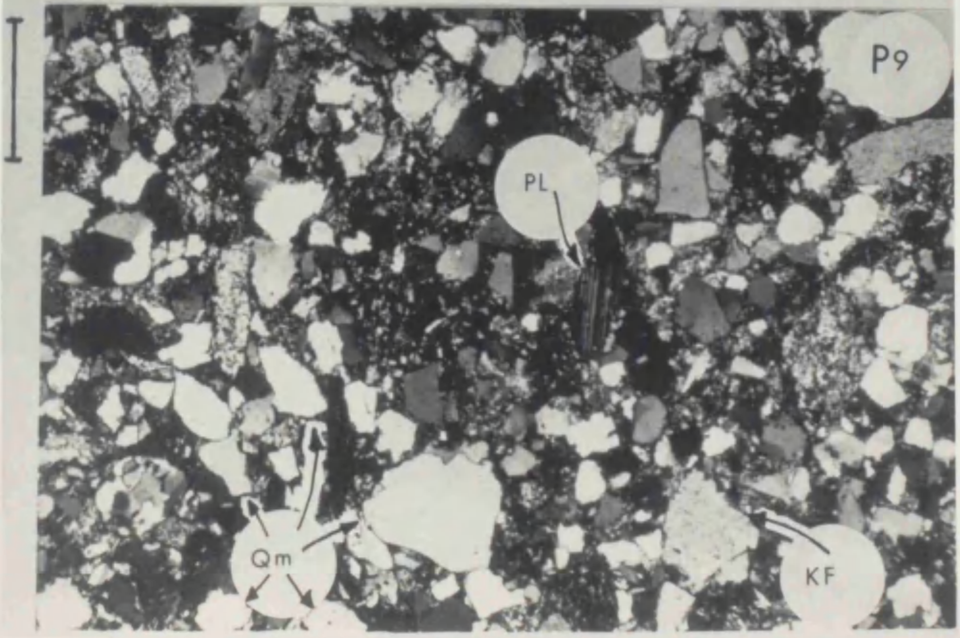
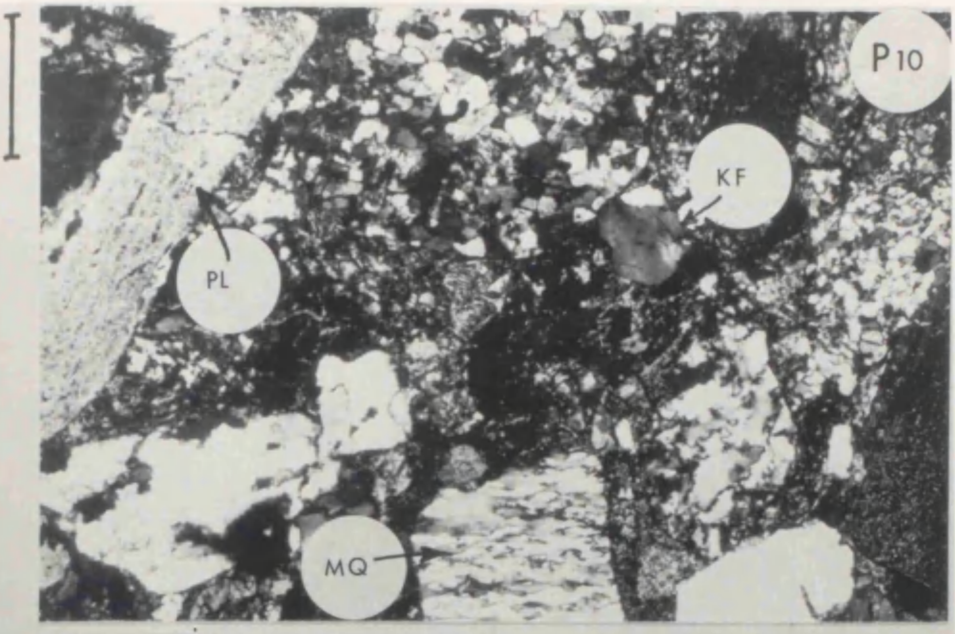
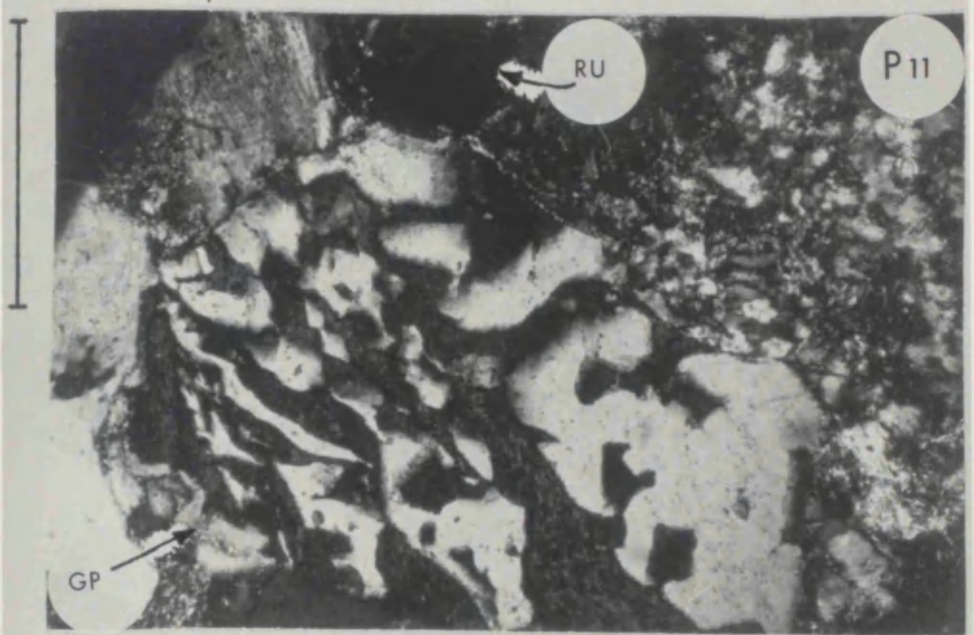

P9
PL
Qm
KF

Plate 10: Photomicrographfrom the middle sequence greywackes (Whitehouse Group) showing some rock fragments and minerals. PL=plagioclase, KF=K-feldspar, MQ=metaquartzite [crossed Nicols]. Bar=0.5 mm

Plate 11: Photomicrograph from the lower sequence greywackes (InfraKilrany Formation) showing euhedral crystal of rutile (RU) and a granophyre rock fragment (GP) [crossed Nicols]. Bar=0.25 mm

Plate 12: Photomicrograph for the lower sequence greywackes (Kilrany Formation) showing cherts [crossed Nicols]. Bar=0.25 mm


P10


P11

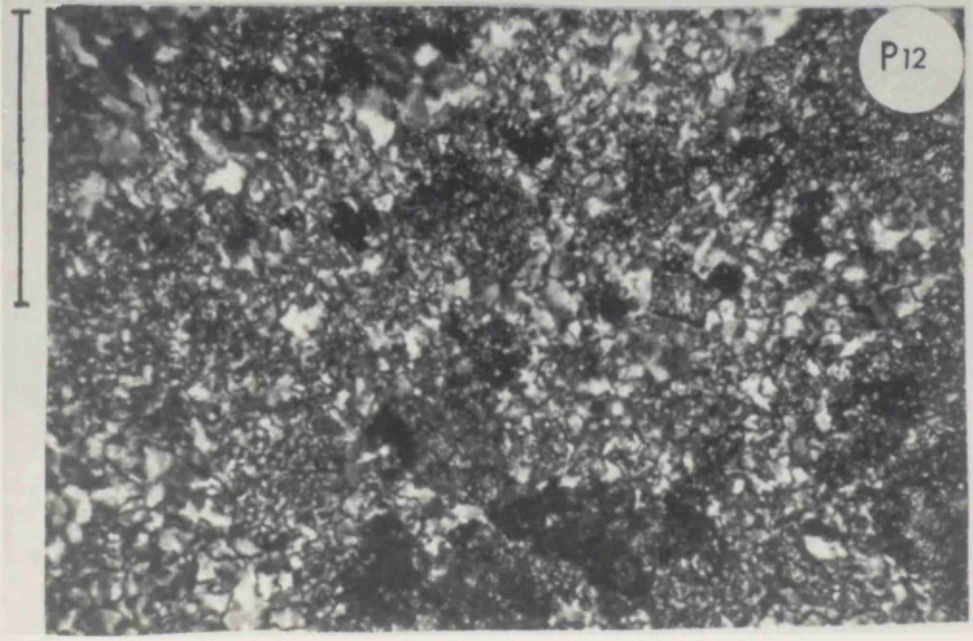
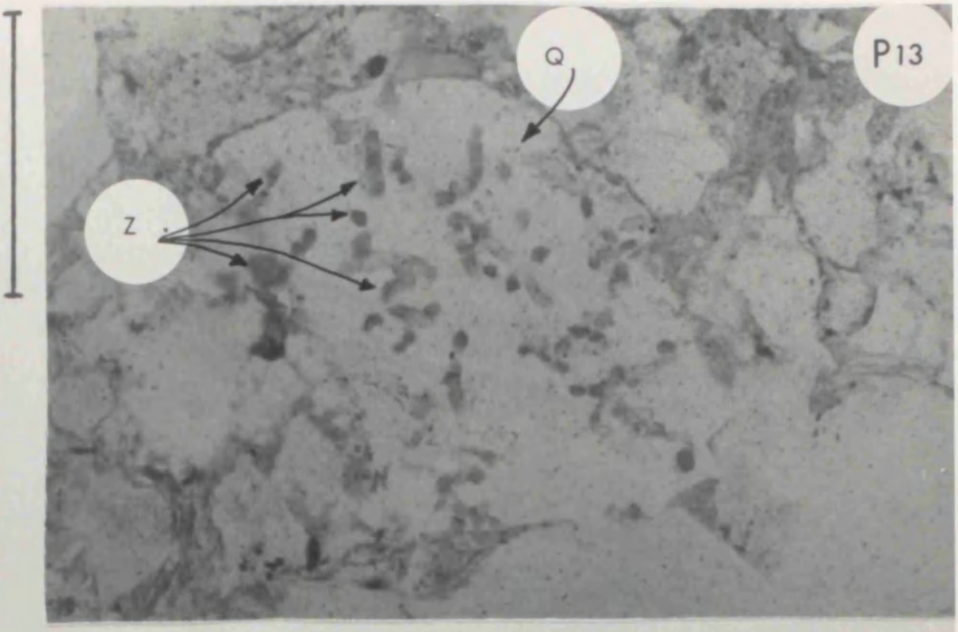
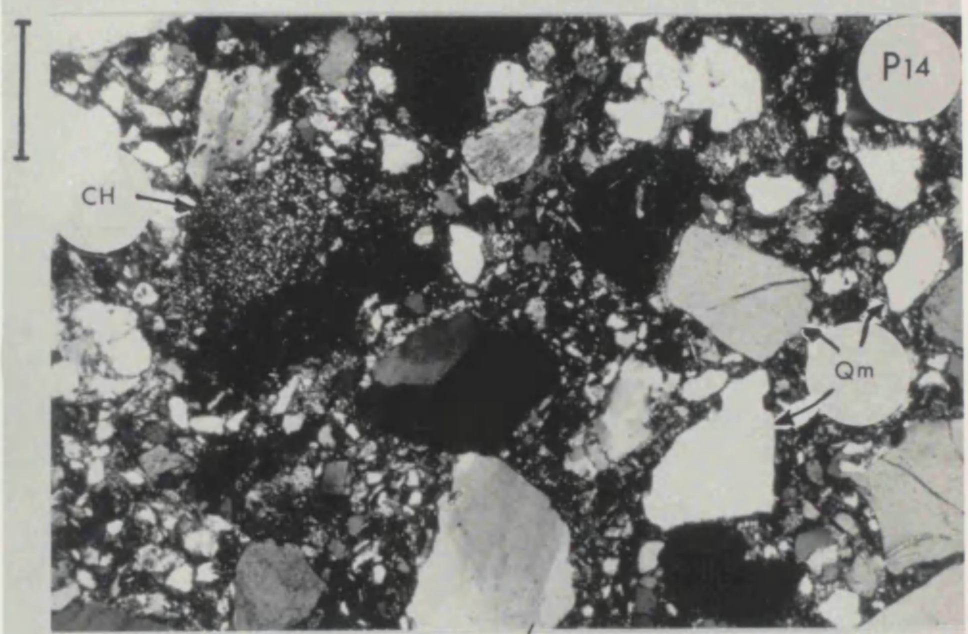

P12

Plate 13: Photomicrograph from the lower sequence greywackes (Cascade Grits) showing zoisite inclusions (Z) in quartz (Q) [crossed Nicols]. Bar=0.25 mm

Plate 14: Photomicrograph from the upper sequence greywackes (Shalloch Formation) showing some rock fragments and minerals. Qm= monocrystalline quartz, CH=chert fragment [crossed Nicols]. Bar= 0.5 mm

Plate 15: Photomicrograph from the upper sequence greywackes (Shalloch Formation) showing a granophyre rock fragment (GP) [crossed Nicols]. Bar=0.25 mm


P13
Q
Z


P14
CH
Qm

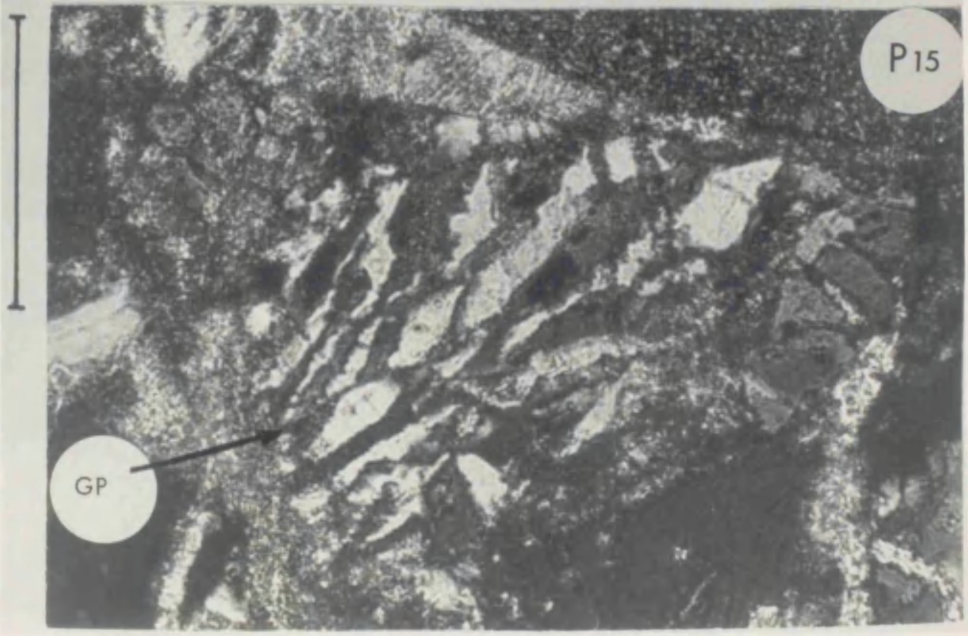
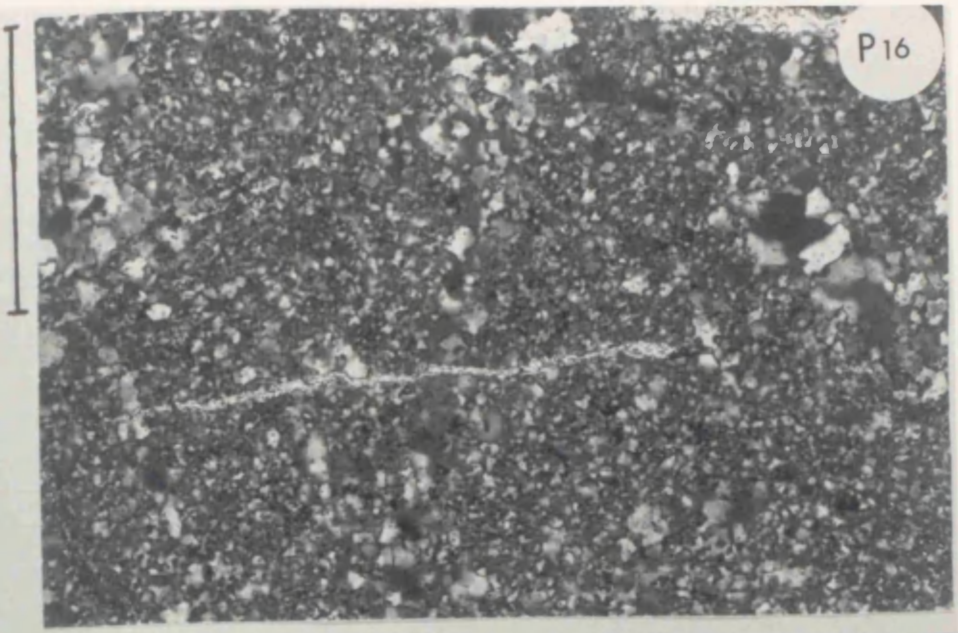

P15
GP

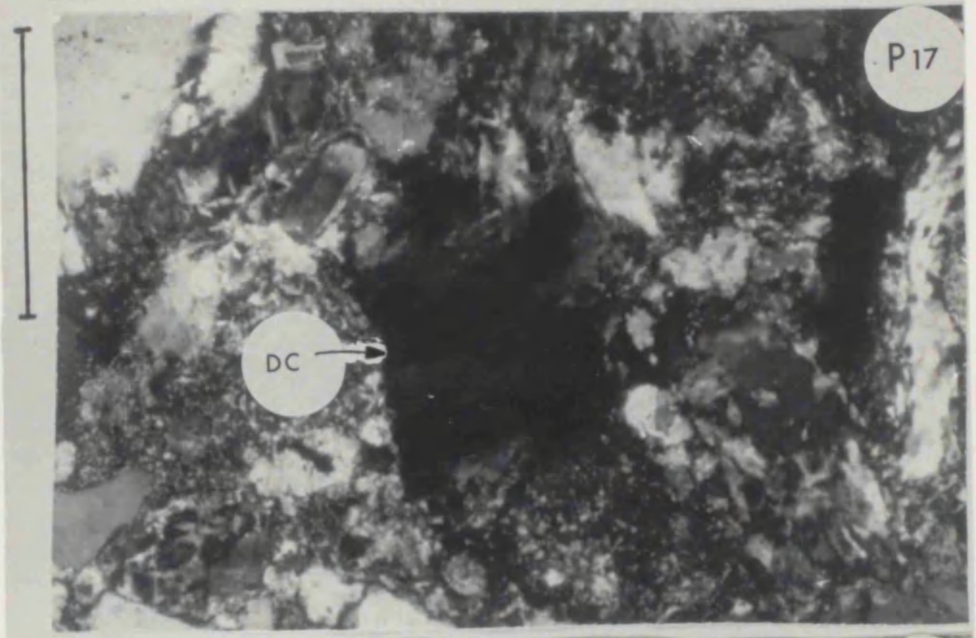
Plate 16: Photomicrograph from the upper sequence greywackes (Shalloch Formation) showing cherts [crossed Nicols]. Bar=0.25 mm

Plate 17: Photomicrograph from the upper sequence greywackes (Shalloch Formation) showing a detrital grain of chlorite (DC) [crossed Nicols]. Bar=0.25 mm

Plate 18: Photomicrograph from the upper sequence greywackes (Whitehouse Group) showing bended mica (M) [natural light]. Bar=0.25mm



P16



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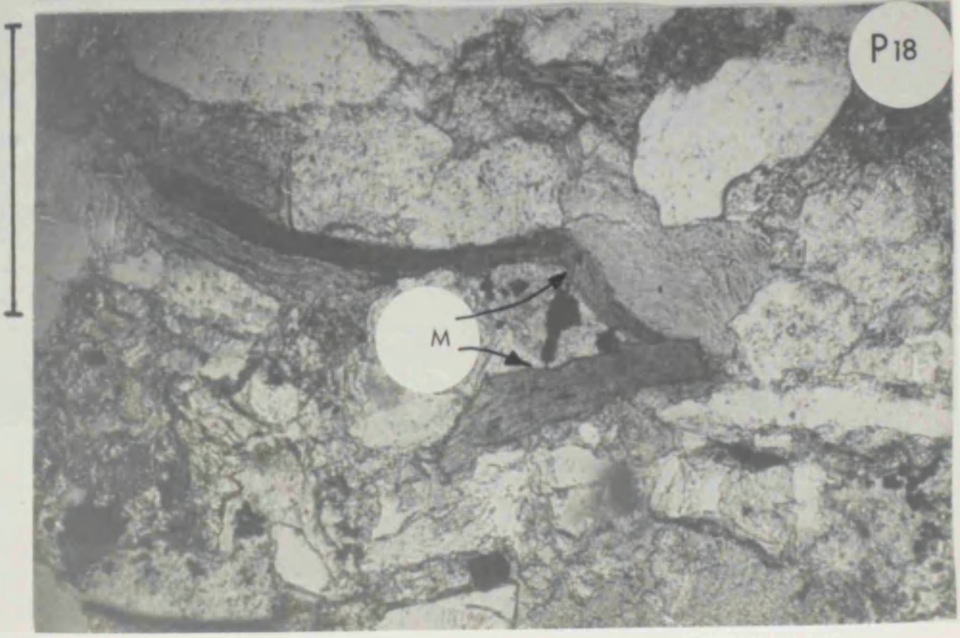
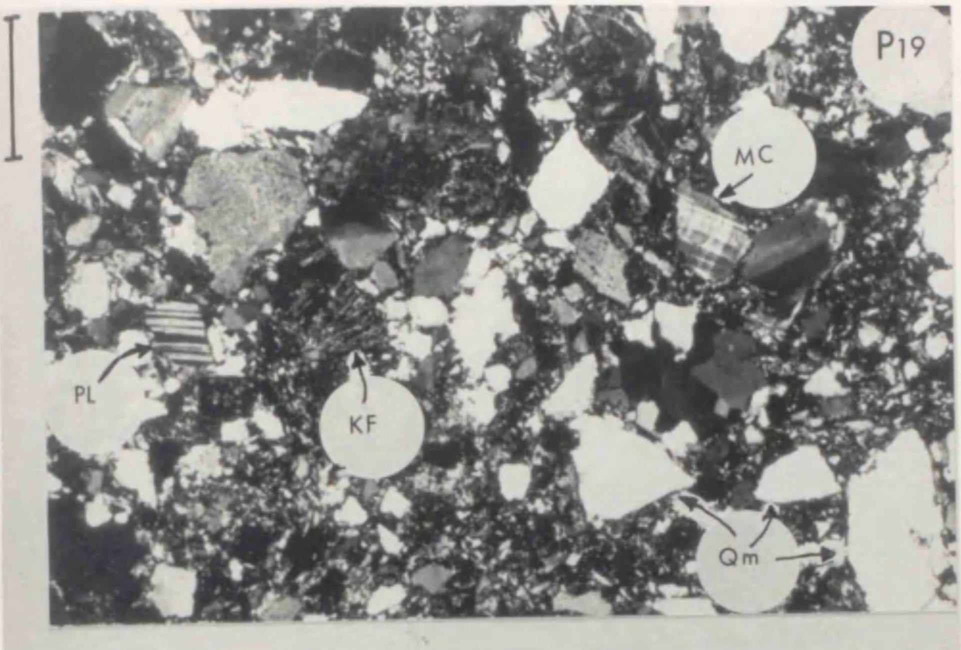


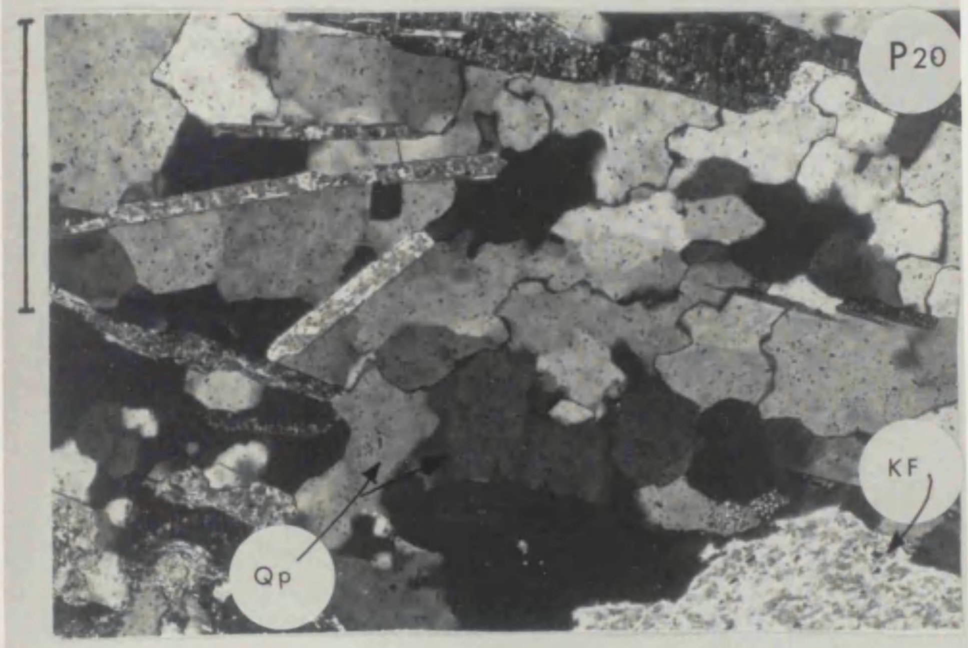
P18

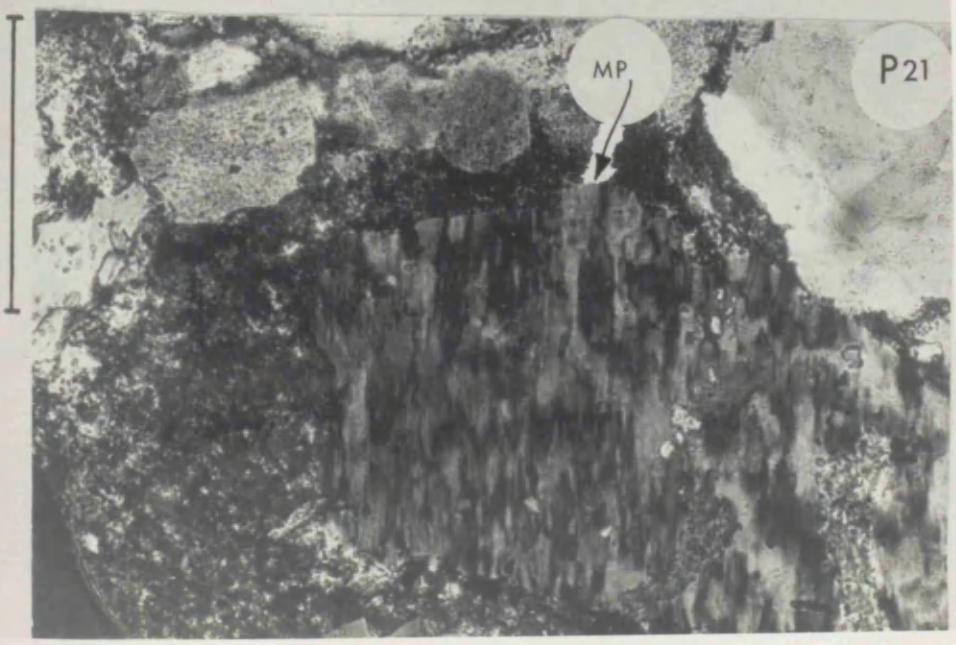
Plate 19: Photomicrograph from the Silurian rocks (Craigskelly Formation) showing some minerals. MC=microcline, Qm=monocrystalline quartz, PL=plagiolcase, KF=K-feldspar. Note the absence of basic rock fragments and minerals [crossed Nicols]. Bar=0.5 mm

Plate 20: Photomicrograph from the Silurian rocks at Woodlands Point showing polycrystalline quartz (Qp) and K-feldspar (KF) [crossed Nicols]. Bar=0.25 mm

Plate 21: Photomicrograph from the Silurian rocks at Woodland Point showing a crystal of microperthite (MP) [crossed Nicols]. Bar=0.25mm


P19


P20


P21

CHAPTER FIVE GEOCHEMISTRY

5.1 INTRODUCTION

There has been a good deal of interest during the last 18 years in interpreting the origin of sandstones and greywackes from their petrographic characters, and in particular using the nature and abundance of the detrital grains to establish petrofacies of the sediments. The identification of plutonic and volcanic, metamorphic or sedimentary source terranes is clearly a most significant constraint in plate tectonic reconstructions. However, during the last decade much effort has been expended in interpreting the relationships between whole rock chemistry of sediments, their provenance areas and hence the plate tectonic environment of formation. This interest partly stems from the earlier ideas of Dickinson (1970) and his coworkers (e.g Dickinson and Seely, 1979, Dickinson and Suczek, 1979, Ingersol and Suczek, 1979, Dickinson et al. 1982) who presented evidence to show that petrography is related to source areas which in their turn are controlled by tectonic settings (see chapter four).

However, the application of these early proposals to older sedimentary suites are most significant but can be hindered by many disadvantages particularly if the sediments were affected by diagenetic alterations, medium- to high-grade metamorphism and/or secondary alteration. Whilst these influnces can make some changes to the original chemistry (e.g Bhatia, 1983; Roser and Korsch, 1986, van de Kamp and Leake, 1985; Argast and Donnelly, 1987) they are not thought to be so radical that all the original signatures are providing suitably resistant elements are studied.

While the chemical composition of a rock suite could be indicative of its provenance, there is only very little published work (e.g Schwab, 1974; Bhatia, 1983; van de Kamp and Leake, 1985, Roser and Korsch, 1986) on the chemical compositions of sedimentary suites from known provenance areas and well defined tectonic settings .

An important group of studies (e.g Bhatia, 1983; Roser and Korsch, 1986) used some variant of discriminant analyses to group characteristic sediment compositions into broadly defined tectonic or sediementary environments. Isotopes, rare earths and major and trace elements are also often of great importance as discriminating criteria. For instance, it has long been suggested that various sandstone types can be distinguished on the basis of the SiO_2 content and K_2O/Na_2O ratio (Middleton ,1960; Crook, 1974; Schwab, 1975). Pettijohn (1963) showed that the K contents of sandstones increase with decreasing grain size and that greywackes have lower SiO_2, higher Al_2O_3, magnesium and excess Na_2O over K_2O than do most sandstones. Maynard et al. (1982) carried out major and trace elements determinations on modern deep sea turbidite sands and suggested that sands from forearc basins and the passive margins are distinct but that sands from other settings cannot be separated on the basis of bulk composition. Bhatia (1983) noted that the oceanic island arc sandstones dominantly derived from calc-alkaline andesites have higher abundance of TiO2, Al2O3, Na2O,and Fe2O3 and lower abundance of SiO2 and K2O compared to all sandstones. The continental island arc sandstones, dominantly derived from felsic volcanic rocks, have higher SiO2, K2O, and the K2O/Na2O ratio (≈0.60) and lower Fetot + MgO than the oceanic island arc sandstones. The active continental margin sandstones are dominantly derived from the uplifted basement and reflect the composition of the upper continental crust in their higher SiO2 and K2O contents and K2O/Na2O ≈ 1. The passive margin type sandstones could not be charaterized due to their large chemical variations but sometimes overlap with those of the continental margins. They are significantly enriched in SiO2 and depleted in Al2O3, TiO2, Na2O, and CaO and have a K2O/Na2O ratio>1. Although Roser and Korsch (1985) have criticized these criteria, Van De Kamp and Leake (1985) found that their results on the northern Pacific margin to be generally but not invariably compatible with those of Bhatia (1983).

5.2 Objectives of the study

From the Girvan district 222 samples of greywackes and sandstones from 19 localities 196 samples from Ordovician and 16 from Silurian rocks, have been analyzed for the all major and 12 trace elements using x-ray fluorescence technique as decribed by Harvey *et al*. (1973) and Leake *et al*. (1969) respectively. The main aims were to determine if there are any vertical changes in the chemistry of the rocks and relate them where possible to the evolution in the magmatic arc as deduced from the petrography, establish the general chemistry of the Girvan sequence relate the rock geochemistry to petrography and look for elements which show co-variance so that a better idea of arc evolution is possible. In the section below, the vertical variability of certain elements is first established, followed by the general geochemistry of the Girvan sequence. Next the chemisrty is used as a guide to the evolution of the source areas and the tectonic settings of the source area are investigated and finally some conclusions are attempted.

5.3 Vertical variability

The major and trace elements contents of the rocks from the Girvan sequence are given in appendix two, statistically summarized below in Table 5.1 and diagramatically shown in Figures 5.1-12.

Table 5.1 Summary statistics of the major and trace elements in the Girvan sequence

	1.		2.		3.		4.	
	x	σ	x	σ	x	σ	x	σ
Major elements (wt%)								
SiO2	71.04	6.93	61.51	8.89	60.29	8.12	60.79	7.43
TiO2	0.79	0.12	0.76	0.17	1.01	0.37	0.93	0.28
Al2O3	9.06	2.50	9.72	1.65	11.49	2.07	11.82	1.14
Fetot	4.91	1.63	5.14	1.47	7.12	1.70	7.46	1.80
MgO	2.24	1.30	2.46	0.93	3.85	1.51	5.49	1.88
MnO	0.08	0.02	0.18	0.15	0.14	0.14	0.20	0.63
CaO	2.60	1.92	8.32	5.97	5.50	4.62	3.63	3.50
Na2O	1.81	1.04	2.25	0.64	2.70	0.72	2.91	0.45
K2O	1.01	0.28	0.86	0.45	0.93	0.35	1.32	0.39
P2O5	0.11	0.02	0.08	0.06	0.11	0.03	0.15	0.19

cntd

Table 5.1: Continued

	1.		2.		3.		4.	
	x	σ	x	σ	x	σ	x	σ
Trace elements (ppm)								
Rb	35	10	21	11	20	11	31	13
Ba	242	82	190	116	183	73	233	104
Sr	145	68	249	144	143	50	107	33
Zr	274	71	151	74	140	76	144	27
Ga	11	3	10	2	14	8	12	2
Co	11	8	11	5	22	17	24	8
Ni	22	12	27	19	64	45	173	94
Cr	87	38	99	44	179	118	439	219
Cu	12	7	9	6	26	9	15	10
Zn	57	32	48	15	58	14	64	11
Pb	6	3	5	4	6	3	5	2
La	21	7	14	5	20	29	16	10
Ce	43	15	28	14	32	32	27	25
Y	26	10	26	7	30	25	26	3
Th	5	2	2	1	5	25	2	2

key to Table 5.1

1= (Llandovery) = average of 16 samples

2= (Upper Caradoc-Lower Ashgill) = average of 22 samples

3= (Caradoc) = average of 72 samples

4= (Upper Llanvirn-Llandeilo) = average of 102 samples.

x = average and σ = standard deviations.

As Table 5.1 and Figures 5.1-12 show, There are progressive and continuous chemical changes in passing from the Upper Llanvirn through to Llandovery. The Llandovery samples tend to be poorer in MgO, Fetot, Cr, Ni and to a lesser extent Na2O and CaO but are somewhat richer in SiO2 and Zr compared to the Upper Llanvirn rocks. K2O, Ba, Sr and Rb are rather inconclusive due to their large standard deviations. Rocks from the middle and upper sequences frequently span the range between the lower sequence and Silurian rocks. This is consistent with the petrography where the basic lithic fragments decrease systematically in passing from the Upper Llanvirn to Llandovery but the quartz contents generally increase with time especially in the Silurian.

5.4 General geochemistry of the Girvan sequence

Fetot (as Fe2O3) exhibits a good positive correlation with MgO throughout the whole sequence (Fig 5.13) which indicates that these elements are probably held in the mafic and utramafic components (i.e in the ferromagnesian minerals such as chlorite, amphibole, pyroxene), although some Fe is certainly coming in pyrite, magnetite and ilmenite, minerals that are sometimes present in the Girvan sequence.

Both Cr and Ni show excellent positive correlation between each other(Fig 5.14) and both elements correlate well with Fetot + MgO (Figs 5.15-16) which suggests that these elements and probably also Co are held in amphibole, pyroxene and chlorite.

There is no obvious correlation between Na_2O and CaO (Fig 5.17) as if plagioclase is not the only control over Ca and probably also Sr (Fig 5.18). Although this is partly due the fact that plagioclase is of albite-rich nature, it is probably because much of Ca and Sr are probably coming in carbonate minerals, epidote and K-feldspar;

minerals that are frequently present in the sequence.

Al_2O_3 exhibits the usual positive correlation with Ga (Fig 5.19) as is favoured by their similar ionic radii and charges. Sample AK1 is so abnormally high in Ga that an analytical error is very likely.

Both Rb and Ba exhibit very good positive correlations with K2O (Figs 5.20-21) which indicates that both elements are coming essentially in K-feldspars and micas (where present). La and probably also Ce and Th (only the diagram of Ba versus La is shown in Figure 5.22) are therefore also held in K-feldspar, biotite and muscovite. Sample Af 26 is exceptionally high in La and sample TB21 in Ba that an analytical error is probable.

Senior and Leake (1978) noted that the parameter Niggli al-alk provides a measure of Al in the original sediments contained in the clay minerals and micas rather than Al added in feldspar because al-alk in albite and K-feldspar is zero while detrital anorthite-rich plagioclase is absent from the Girvan sequence (see Fig.4.7). Therefore, Figures 5.23-28 suggest that at least some K, Rb, Ba, La and Th and to lesser extent Sr were dominantly added in clay minerals, where as,the lack of either a positive or negative correlation of sr and al-alk show that sr was neither. It is very likely that some Ba and Sr were added in detrital feldspar, probably K-feldspar, because Figures 5.17-18 exclude Sr to have been added in plagioclase feldspar. The good positive correlation of Niggli al-alk and Niggli ti (Fig 5.29) indicates that Ti was predominantly originally added in clay minerals and micas but with some caused by minor detrital ilmenite, rutile and magnetite dominantly added in clay minerals nor totally exluded from them.

Zr also seems to have been partly added in clay fractions (Fig 5.30), although it was probably also added in detrital zircons,especially for the high zr values.

None of the strongly compatible elements Mg, Cr, Ni and probably also Co were added in the clay fractions (Figs 5.31-33) but were substantially held in the mafic and ultramafic rock fragments and this suggestion is supported by the good positive correlation of Niggli mg with Co, Cr, and Ni (Figs 5.34-36).

5.5 Major and trace elements as a guide to magmatic evolution

The results of the major and trace elements are summarized in Table 5.1 and portrayed in terms of Harker type diagrams in Figures 5.37-49. In these digrams, the wt% of the principale oxides of each analysed rock sample are plotted against the wt% SiO2; the assumption being that silica percentage represents the stage of magmatic evolution that has been reached. However, the "constant sum effects" should be taken into considerations before reading any petrogenetic significance into these diagrams (Chayes, 1964). The constant sum effects result from the fact that the major oxides taken together make up almost 100% of the rock analysis and since the wt% SiO2 is by far the most abundant constituent of most rock types, at least some negative correlations with SiO2 are therefore expected among the other oxides irrespective of petrogenetic considerations. These effects are not clearly noticeable in Figures 5.37-43 because of the great chemical variations of the rocks although the steep slope of Fetot + MgO may be due partly to these effects. Definite proof is lacking, however.

There are great chemical variations among the three sequences (i.e lower, middle and upper), although it is very interesting to note that the variations are continuous, progressive and show very similar trends. SiO2 increases with decreasing Al2O3, CaO, MgO, Fetot, Fetot + MgO but increases with increasing K2O and to a lesser extent Na2O Figs 5.37-43). These trends coupled with the large range in SiO2 contents among the Ordovician rocks (SiO2 ranges from as low as 38 wt% up to 75 wt%) indicate that the Ordovician rocks must have been derived from a dominantly magmatic source that ranged from pure basic and ultrabasic rocks (i.e less differentiated) through to pure acidic rocks (i.e most differentiated). The chemical data are equally consistent with one fractionating magma series or a number of totally unrelated magmatic rocks varing from basic or ultrabasic to acidic. The available geochronology of the clasts supports the second alternative. However, the rocks from the lower sequence, although they span the range stated above, they tend to cluster between 60 and 70 wt % SiO2 and are particularly rich in K2O and poor in CaO indicating that they included both basic and acidic components.

Both the middle and upper sequences vary within large limits in terms of their major elements and generally no significant differences could be found between the two set of rocks.

The evidence presented above therefore indicates that the Ordovician rocks were probably dominantly derived from the same magmatic source and the continuous and progressive chemical and mineralogical changes described above and in chapter four respectively are related to the evolution in the composition of the magma, although, as deduced from the mineralogy, some recycled sedimentary and metasedimentary material might have been incorporated especially during Lower Ashgill.

Table 5.2: Comparison of some diagnostic parameters after Bhatia (1983) with those from the study area.

elements (wt%)	oceanic island arc	continental island arc	active cotinental margin	1	2	3	4
Fetot+MgO	8-14	5-8	2-5	12.95±3.30	10.97±3.15	7.60±2.32	7.16±2.8
Al2O3/SiO2	0.24-0.33	0.15-0.20	0.1-0.2	0.20±0.03	0.19±0.04	0.16±0.04	0.13±0.04
K2O/Na2O	0.2-0.4	0.4-0.8	>0.8	0.46±0.14	0.36±0.14	0.40±0.20	2.30±4.02
Al2O3/(CaO+ Na2O)	1-2	0.5-2.5	-	2.22±0.82	1.71±0.69	1.26±0.76	2.3±0.85
TiO2	0.8-1.4	0.5-0.7	0.25-0.45	0.93±0.28	1.01±0.37	0.76±0.17	0.79±0.12

1 = average of 102 Lower sequence samples
2 = average of 72 Middle sequence samples
3 = average of 22 Upper sequence samples
4 = average of 16 Llandovery samples
\- not numerically estimated

Among the Silurian rocks studied, many of the conclusions remain equivocal because of the small sample size analysed in this study (16 samples). However, the available analyses show that MgO, Fetot, Fetot + MgO, Al2O3, CaO and to a much lesser extent Na2O decrease with increasing silica. The case of K2O is much more complex and rather equivocal. The majority of the samples reveal a weak but positive correlation with SiO2 while few other are particularly SiO2-rich but K2O- and also Na2O-poor that they plot separately from the remaining samples (Fig 5.38, 5.42). If all the Silurian rocks have originated from acidic igneous rocks only, then SiO2 should exhibits a good positive correlation with both K2O and to some extent Na2O but this is not the case in the studied area. The only tenable explanation therefore is that the Silurian rocks must have incorporated some quartz-rich sedimentary and metasedimentary material. This is in excellent agreement with petrographic evidence where the rocks contain in addition to granitic fragments, abundant quartz and quartzite fragments. Previous findings by Bluck (1983) that pre-existing sedimentary conglomerates have contributed to the Silurian conglomerates is clearly a further support to the present conclusion.

The trace elements generally mirror their major equivalents in that Rb, Ba, and to some extent Zr increase with increasing SiO2 (Figs 5.44-46) whereas Cr, Ni, and to some exetent Sr increase with decreasing silica in passing from Upper Llanvirn through to Llandovery (Figs 5.47-49) thus confirming the conclusions reached from the major elements.

5.6 Comparison of the chemistry of the Girvan sequence

with published tectonic settings deduced from the chemistry

5.6.1 Major element geochemistry

Literature analyses of sandstones and argillites/shales from ancient sedimentary sequences of inferred tectonic setting have been used by Roser and Korsch (1986) to establish a tectonic classification based on the SiO2 contents and K2O/Na2O ratios of rock samples. these authors, who suggested that individual data should be used rather than averages so that trends can be highlighted, defined three main tectonic fields namely: Oceanic Island Arc, Active Continental Margin and Passive continental Margins. These three parameters will hereafter be referred to as ARC, ACM and PM respectively following Bhatia (1983). These three tectonic fields are precisely reported in Figure 5.50 in which the data from the Girvan sequence are also plotted to descipher their provenance areas and tectonic setting.

As Figure 5.50 shows, most of the Girvan rock samples fall within the ARC field with relatively fewer samples falling within the ACM field. This therefore indicates that the substantial contribution from the magmatic arc material was possibly accompanied by little contributions from the continental block. However, only 2/16th of the Silurian rocks fall within the ARC field which strongly support previous conclusions that these rocks were derived from magmatic origins but with substantial contributions from sedimentary sources. Petrographic results also excellently agree with this conclusion. Four of the Silurian samples fall well within the PM field which might suggests that the recycled quartz-rich materials were derived from passive margins, although this suggestion does not seem to be shared by the petrography (see chapter four) and Figures 5.53-57 (see below).

Roser and Korsch (1986) showed that the forearc basin sediments of Baldwin Formation sediments of the Baldwin Formation Austaralia (Chappell, 1968), and the Vyak and Cape current greywackes fall within the arc field, Alaska (Connelley, 1978) which were deposited in a trench adjacent to an active volcanic arc. Within the ACM field, fall the Franciscan Complex, California (Bailey et al. 1964; Taliaferro 1943) and Kodiak Formation, Alaska (Connelley, 1978) which were incorporated into an accretionary wedge, and the Santa Ynez Mountains, California (Van De Kamp et al. 1976) which were deposited in a complicated continental margin where both subduction and strike-slip processes were active. Hence, this category includes complex active margins which were deposited in a variety of basin settings including trench, forearc, interarc and backarc. Therefore, in terms of ARC field, it can be inferred that most of the Girvan sequence was deposited in a forearc basin. The depositional environment of the rocks plotting inside the ACM field are very difficult to delimit because various sources could lead to the same plotting. For instance, data of Valloni and Maynard (1981) for modern marine sediments which plot within the ACM field have been discussed by Roser and Korsch (1986) who found that these rocks could have been deposited in backarc basin or leading edge settings. This therefore indicates that the diagrams proposed by Roser and Korsch (1986) are indeed useful but only broadly in distinguishing the source areas and tectonic settings but cannot be used as guides to more detailed interpretations.

The Girvan data are also represented on a CaO-Na2O-K2O ternary diagram in Figure 5.51 to further deduce the contributing constituents from chemical analyses. Also plotted are the average of andesite (A), dacite (D), granodiorite (G*) and granite (G) after le Maitre (1976) and the two fields representing rocks derived mainly from oceanic island arc and continental island arc after Bhatia (1983). As illustarted in Figure 5.51, the Girvan samples fall almost equally within the two fields outlined with many samples falling outside the two fields. However, this diagram is clearly much less reliable than that proposed by Roser and Korsch (1986) on account that the defined fields were based on a relatively few samples, the effect of carbonate present in the matrix has not been taken into account and albitization of plagioclase could have also been enhanced. However, it is very interesting to note that most of the samples plot near the andesite, dacite and granodiorite composition of Le Maitre (1976), in agreement with the mineralogy where the Ordovician rocks are composed mainly of basic and intermediate rock fragments but also with some acidic material. Some of the middle and upper sequence and Silurian rocks plot in the CaO apex due the abundance of carbonate in the matrix mainly as calcite and dolomite.

The substantial contribution of andesitic and basaltic material to the Ordovician rocks of the Girvan sequence is also highlighted by the K2O-Na2O scatter diagram (Fig 5.52) in which the fields of basalts, andesites, granites and subalkaline tholeiites after Condie and Snansieng (1971) are also reported. However, as shown in chapter four, granitic rock fragments are present especially in the upper sequence, but the data when plotted on the K_2O-Na_2O diagram do not show this. This trend is probably caused by the fact that some K may have migrated due to its highly mobile nature or more probably is caused by the mixing of various amounts of volcanic, basic and ultrabasic, granitic and sedimentary components.

Bhatia (1983) showed that there is a progressive decrease in Fetot + MgO, TiO_2, and Al_2O_3/SiO_2 and increase in K_2O/Na_2O and $Al_2O_3/(CaO + Na_2O)$ in sandstones from oceanic island arc to continental island arc to active continental to passive margins. Fe and Ti are most useful because of their low mobility and low residence times in sea-water (Holland, 1978). Although Mg has a high residence time in sea-water, it will remain unchanged in the continental-margin type sandstones deposited by turbidites during burial because of the low permeability of these rocks (Blatt et al.1980). The ratio Al_2O_3/SiO_2 gives an indication of the quartz enrichment in sandstones. The ratio K_2O/Na_2O is a measure of the K-feldspar and mica versus plagioclase content in the rock, and the $Al_2O_3/(CaO+Na_2O)$ parameter in the ratio of the least mobile to the most mobile elements

The average of the above mentioned five parameters are compared with those for the Girvan sequence in Table 5.2 and compared in Figures 5.53-57. In these diagrams, the TiO_2, Al_2O_3/SiO_2, K_2O/Na_2O and $Al_2O_3/(CaO+Na_2O)$ are plotted versus Fetot + MgO and the tectonic settings of Bhatia (1983) are also shown for comparison.

As is clear from Table 5.2, the Ordovician rocks show a wide range of TiO_2, Fetot+MgO, Al_2O_3/SiO_2, K_2O/Na_2O and $Al_2O_3/(CaO+Na_2O)$

values but they suggest contributions from both the continental and possibly oceanic arcs. However, the Al2O3/SiO2 ratios tend to be lower in the Girvan sequence so that they coincide with the upper limits of those from the continental arcs. This is expected because as shown in chapter four many of the Ordovician rocks include in addition to the dominantly continental and oceanic arc-derived rock fragments some recycled quartz-rich material which was probably derived from active continental margins. These trends are not highlighted by the somewhat different major element contents of the Girvan sequence with those of Bhatia (1983)(see Tables 5.3-4) probably because of the few samples given by Bhatia and the large standard deviations exhibited by the analysed samples due to the large geochemical heterogeneity of the rocks.

Inspection of Figures 5.53-57 show that only very few samples, if any, fall within the fields of passive margins and continental margin suggesting only very little or no contribution from these two sources to the Girvan sequence at all times; in agreement with the conclusions reached from the petrography discussed in chapter four. However as is clear from the Figures, the tectonic fields of Bhatia (1983) are rather small due to the selective nature of the rocks he used and the small sample size and there fore these fields cannot be used reliably to decipher the source areas and tectonic settings of particularly heterogeneous rocks such as those of Girvan. However, as suggested by Van De Kamp and Leake (1985), the general trends should be used rather that the absolute values or fields. Despite the possible complicating factors such as contributions from some quartz-rich recycled material to almost all the Girvan sequence, (i.e not all the material was derived from only one source) at any age as deduced from chapter four and supported by the relatively low Al_2O_3/SiO_2 ratio, many samples do fall within two fields of Bhatia (1983); the oceanic and continental island arcs confirming these two possible sources. It should be noted, however, that the Silurian samples are not shown in Figure 5.55 because some samples have abnormally high K_2O/Na_2O ratios, obscuring the real trends of the Ordovician rocks (see Figure 5.56).

Table 5.3 Average chemical composition of sandstone from various tectonic setting(after Bhatia, 1983) given on the basis of volatile free basis.

	oceanic island arc		continental island arc		active continental margin		passive margin	
	x	σ	x	σ	x	σ	x	σ
SiO_2	58.83	1.6	70.69	2.6	73.86	4.0	81.95	6.2
TiO_2	1.06	0.2	0.64	0.1	0.46	0.1	0.49	0.2
Al_2O_3	17.11	1.7	14.04	1.1	12.89	2.1	8.41	2.2
Fe_2O_3	1.95	0.5	1.43	0.5	1.30	0.5	1.32	1.6
FeO	5.52	2.1	3.05	0.4	1.58	0.9	1.76	1.2
MnO	0.15	-	0.1	-	0.1	-	0.05	-
MgO	3.65	0.7	1.97	0.5	1.23	0.5	1.39	0.8
CaO	5.83	1.3	2.68	0.9	2.48	1.0	1.89	2.3
Na_2O	4.10	0.8	3.12	0.4	2.77	0.7	1.07	0.6
K_2O	1.60	0.6	1.89	0.5	2.90	0.5	1.71	0.6
P_2O_5	0.26	0.1	0.16	0.1	0.09	-	0.12	-
Total	100.00		100.00		100.00		100.00	
Fe_2O_3+MgO	11.73		6.79		4.63		2.89	
Al_2O_3/SiO_2	0.29		0.20		0.18		0.10	
K_2O/Na_2O	0.39		0.61		0.99		1.60	
Al_2O_3/(CaO+Na_2O)	1.72		2.42		2.56		4.15	

Table 5.4 Average chemical composition of sandstones from the studied area recalculated to 100% on a volatile-free basis.

	1.		2.		3.		4.	
	x	σ	x	σ	x	σ	x	σ
SiO2	75.85	6.93	67.43	8.89	64.73	8.12	64.37	7.43
TiO2	0.84		0.76		1.08		0.98	
Al2O3	9.67	2.50	10.65	1.65	12.34	2.07	12.50	1.14
Fetot	5.24	1.63	5.63	1.47	7.12	1.7	7.9	1.80
MnO	0.08	0.02	0.20	0.15	0.15	0.14	0.2	0.63
MgO	2.40	1.30	2.70	0.93	4.14	1.51	5.80	1.88
CaO	2.78	1.92	9.12	5.97	5.90	4.62	3.63	3.50
Na2O	1.94	1.02	2.46	0.64	2.90	0.72	3.07	0.45
K2O	1.08	0.28	0.94	0.45	1.0	0.35	1.40	0.39
P2O5	0.12	0.02	0.09	0.06	0.12	0.03	0.15	0.19
Total	100.00		100.00		100.00		100.00	

1 = average of 16 Llandovery samples

2 = average of 22 upper sequence samples

3 = average of 72 middle sequence samples

4 = average of 102 lower sequence samples

5.6.2 Trace element geochemistry

The trace elements could be very important indicators of the source areas and tectonic settings of sedimentary suites but have been little used for this purpose Only three papers (Condie and

Snansieng , 1971; Bhatia and Taylor, 1981; Van De Kamp and Leake, 1985) could be found and all deal only briefly with the source areas or tectonic setting.

Early workers (e.g Prinz, 1967) showed that the major proportions of Cr present in basaltic magmas are incorporated in early crystallized ferromagnesian minerals because of its strongly compatible nature. Shiraki (1966) argued that the ratio of mafic to granitic rocks in provenance sources is important in controlling the Cr contents in clastic sediments. Golberg and Arrahenius (1958) noticed a decrease in the contents of Cr in deep sea samples with increasing distance from the Hawain islands and suggested that an excess of Cr over 100 ppm in the pelagic sediments indicate substantial contribution from basaltic pyroclastics. A frequency distribution of Cr in basalts is given below in Table 5.5. the average Cr, Ni and Co of the Girvan sequence are also given for comparison.

Table 5.5: Frequency distribution of published contents in Cr of basalts. The values of Cr, Ni and Co from the studied area are also given for comparison

	Cr(ppm)	Ni(ppm	Co(ppm)
Published results			
Basalts from mid oceanic ridge and ocean floor	300	-	-
Basalts from oceanic islands	250	-	-
Basalts from continents	200	-	-

cntd

Table 5.5: Continued

<u>Girvan area</u>

Llandovery	87	22	11
upper sequence	99	27	11
middle sequence	179	64	22
lower sequence	439	173	24

- unpublished

In general terms, higher means of these three elements are found in the lower sequence and decrease in passing from this through to the Silurian. The average of Cr in the lower sequence rocks is clearly greater that 300 ppm suggesting significant contributions from basaltic rocks equivalent to those derived from oceanic ridge, ocean floor and oceanic islands. The high Cr values in the Girvan sequence is probably related to significant contributions from the Ballantrae complex. The tendency of Cr and Ni and to some extent Co to decrease towards the Silurian suggests incorporation of more intermediate, acidic and possibly sedimentary components with time. This result is in excellent agreement with conclusions reached from Harker-type diagrams (see Figs 5.37-49) and from Figures 5.51-52 of CaO-Na2O-K2O and K2O versus Na2O respectively.

However, as can be deduced from the petrography and geochemistry, most of the rocks from both the lower and middle sequences were derived from basaltic and andesitic rocks, the values of Cr, Ni and Co are suggested as indicators of proximity to arc. These elements are preferred to the more compatible elements as the latters are easily affected by many geological processes such as diagenesis and oxidation.

The dominantly andesitic and basaltic components forming much of the Ordovician rocks are clearly not confirmed by the Sr versus Ba diagram (Fig 5.58). This trend is caused almost certainly by the clear depletion of the sequence in Sr rather than in Ba because the average Ba and Sr in andesites for instance are 270 ppm and 385 ppm respectively compared to 233 ppm Ba and 107 ppm Sr in the lower sequence for instance. These low Sr contents probably reflect the abundance of Sr-poor calcite cement formed during diagenesis and mixing of various rock fragment types

5.7 Discussion and conclusions

The detailed geochemical investigations resulted in a number of interesting deductions as regards both the vertical variability of the elements and tectonic settings of the Girvan sequence.

The vertical variability of the chemical elements is particularly intriguing because of the somewhat systematic and continuous changes that taken place. In passing from the Llanvirn through to the Llandovery rocks, those compatible elements which are commonly enriched in mafic and ultramafic rocks, such as Mg, Fe, Cr and Ni and to some extent Ca and Co have a general tendency to decrease whereas the more incompatible elements, such as Zr generally increase. The elements K, Ba and Rb should also increase but the available data are rather inconclusive due to the large standard deviation. These elements did not increase probably because they are relatively mobile under oxidizing and weathering conditions and diagenetic processes compared to the compatible elements Mg, Fe, Cr and Ni and hence cannot be so informative about the original sedimentary processes.

The systematic decrease of the mafic elements with age agrees excellently with the petrography where the mafic and ultramafic rock fragments progressively decrease in the upper sequence and Silurian rocks. In chapter four it has been argued these systematic changes have probably resulted from the evolution in the composition of the magmatic arc material (i.e from the least differentiated to the most differentiated) with age and this argument can be examined further based on geochemical evidence.

If the decrease in the mafic minerals and hence the elements Mg, Fe, Cr, Ni etc is the result of the normal compositional variations of a crystallizing magma (i.e from basic to acidic) then, these elements should correlate negatively with the differentiation index (SiO2) whereas the incompatible elements (K, Rb, Ba etc) should correlate positively. Indeed Harker-type diagrams as discussed in subsection 5.4 show that it is the case, thus confirming deductions reached from the petrography that much of the vertical chemical variation is due to changes in the composition of the magmatic arc material. However, as Figures 5.37-49 show thereis great chemical variation among samples from the whole sequence which probably suggest that not all the material-forming the rocks was derived from the magmatic arc. This suggestion coupled with the large variation in the SiO2 content in the lower sequence rocks (i.e the most mafic-bearing rocks) suggests contributions from other sources particularly sedimentary or metasedimentary sources as highlighted by the presence of quartzite rock fragments and quartz grains.

The Silurian rocks do indeed plot in the quartz-rich end of Harker-type diagrams but usually overlap with the Ordovician rocks and exhibit similar trends. This suggests that either the magmatic portions of these rocks were derived from the same magmatic source (ie the same magma series) or they were derived from a range of unrelated magmatic with variable basic to acid composition Geochemical evidence alone cannot answer this question but as discussed in chapter four, Longman et al. (1979) showed that granitic clasts from the Silurian conglomerates are different in age from those from the Ordovician thus favouring the second possibility.

As regards the use of geochemistry as a guide to provenance areas and tectonic settings it has been shown that most of the rock-forming constituents were dominantly derived from basic to intermediate igneous rocks with possible contributions from both granitic and sedimentary/metasedimentary sources The TiO_2 and Fetot+MgO contents and K_2O/Na_2O, and $Al_2O_3/(CaO+Na_2O)$ parameters of the Girvan area also agree well with those proposed by Bhatia (1983) as represenative of rocks derived from oceanic and continental arcs. The tectonic fields have also been applied to the Girvan area and found to be generally consistent, though because this early work was based on a relatively small sample size, with relatively homogeneous samples compared to those from Girvan, the proposed fields were found to be small and not completely representative.

Key to Figures 5.1-60

Figures 5.1-12: Vertical variability of MgO, Fetot, Na2O, CaO, K2O, SiO2, Cr, Ni, Sr, Ba, Rb and Zr respectively.

Figures 5.13-22: Scatter diagrams of:

Figure 5.13 Fetot vs MgO
Figure 5.14 Cr vs Ni
Figure 5.15 Fetot+MgO vs Cr
Figure 5.16 Fetot+MgO vs Ni
Figure 5.17 CaO vs Na2O
Figure 5.18 CaO vs Sr
Figure 5.19 Al2O3 vs Ga
Figure 5.20 K2O vs Rb
Figure 5.21 K2O vs Ba
Figure 5.22 Ba vs La

Figures 5.23-33: Scatter diagrams of Niggli al-alk vs Niggli k, Rb, Ba, La, Th, Sr, Niggli ti, Zr, Niggli mg, Cr and Ni respectively.

Figures 5.34-36: Scatter diagrams of Niggli mg vs Co, Cr and Ni respectively.

Figures 5.37-49: Harker-type diagrams of (i.e SiO2 vs) Al2O3, Na2O, CaO, MgO, Fetot, K2O, Fetot+MgO, Rb, Ba, Zr, Cr, Ni and Sr respectively.

fig 5.1

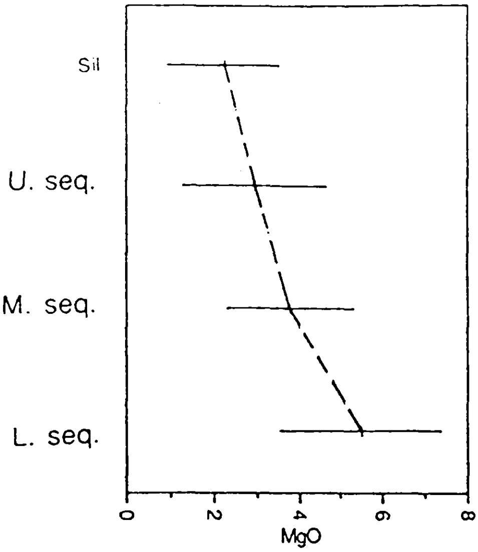


Fig 5.2

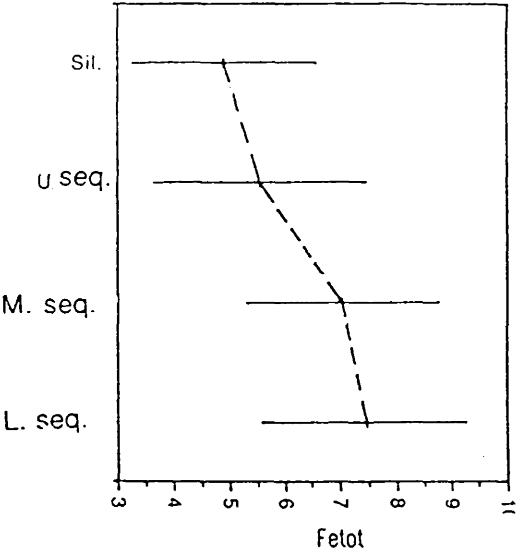


fig 5.3

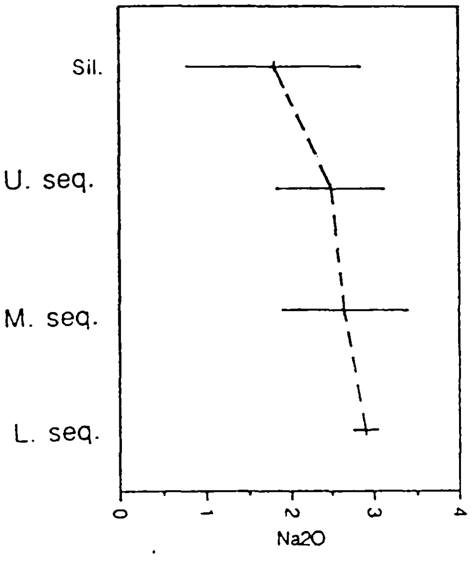


fig 5.4

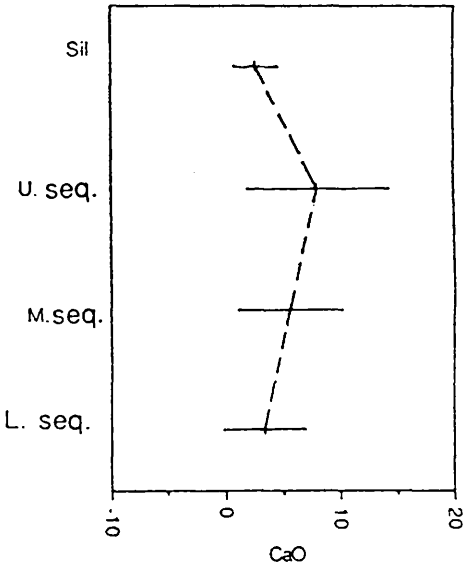


fig 5.5

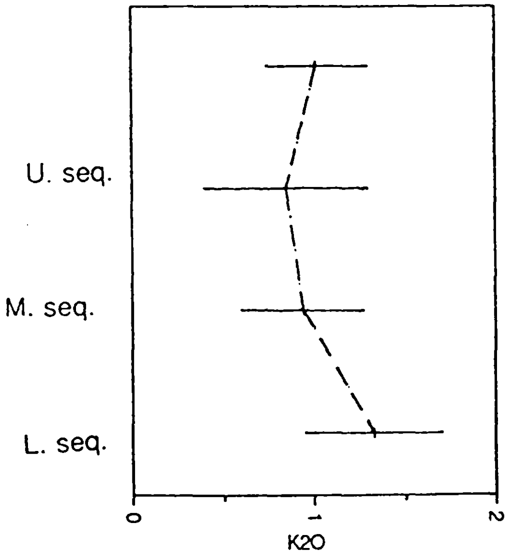


Fig 5.6

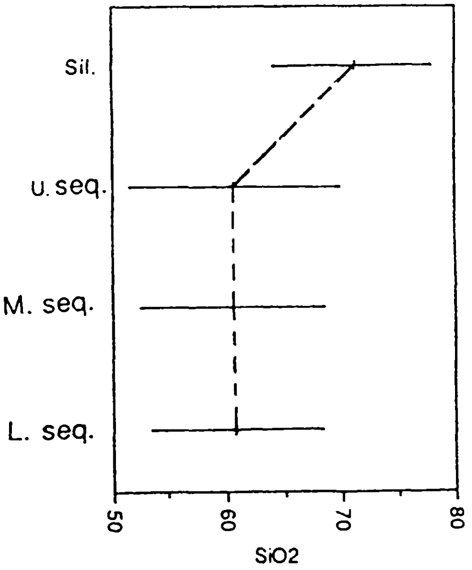


fig 5.7

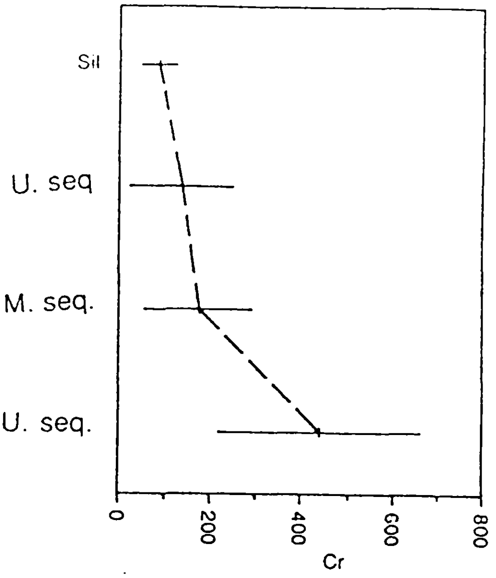


fig 5.8

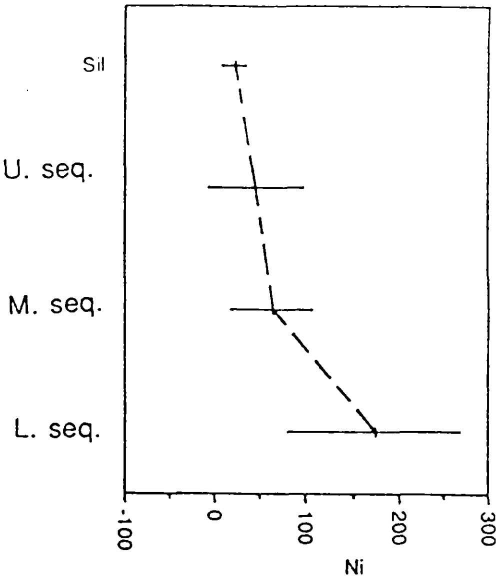


fig 5 .9

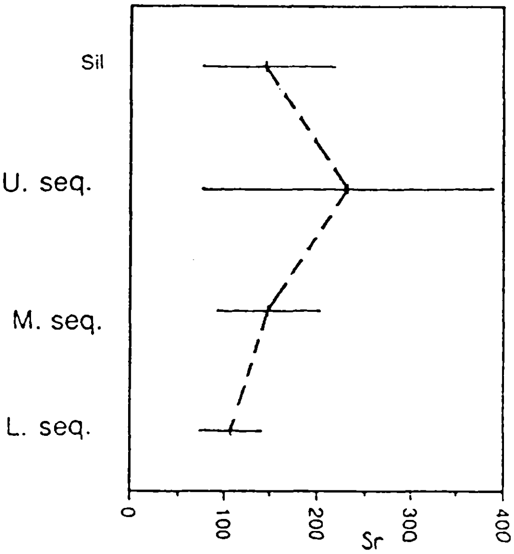


fig 5.10

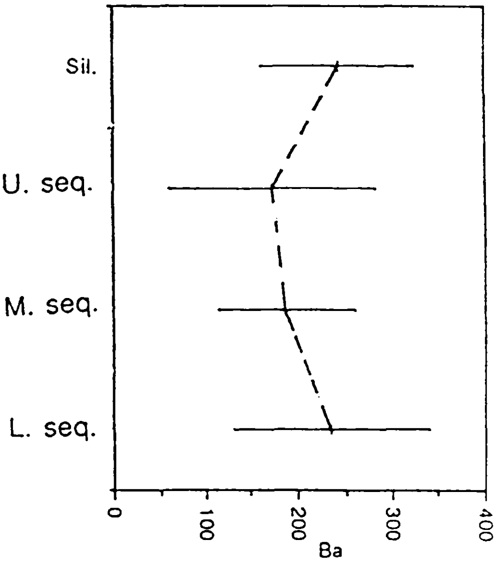


fig 5.11

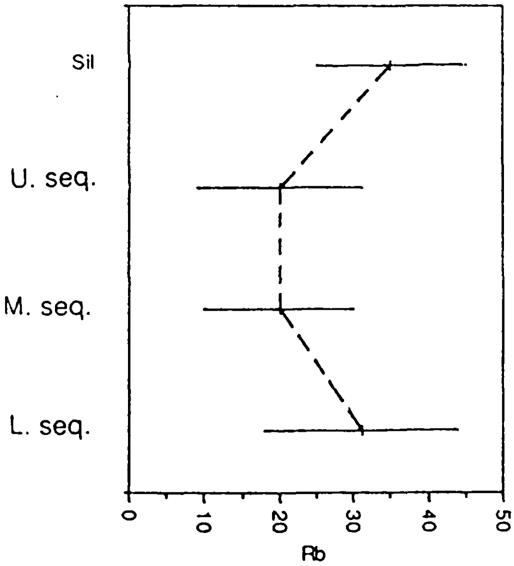


fig 5.12

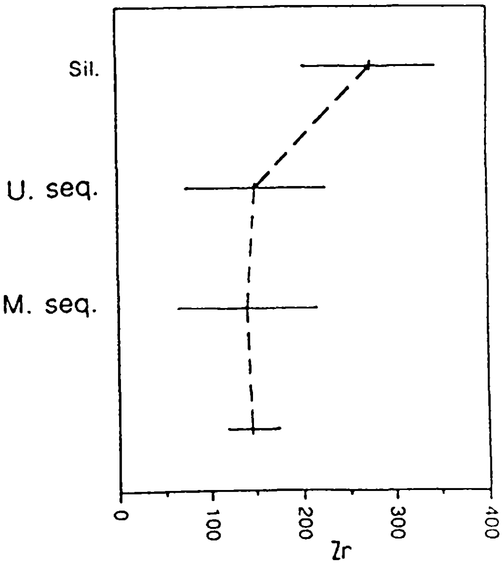
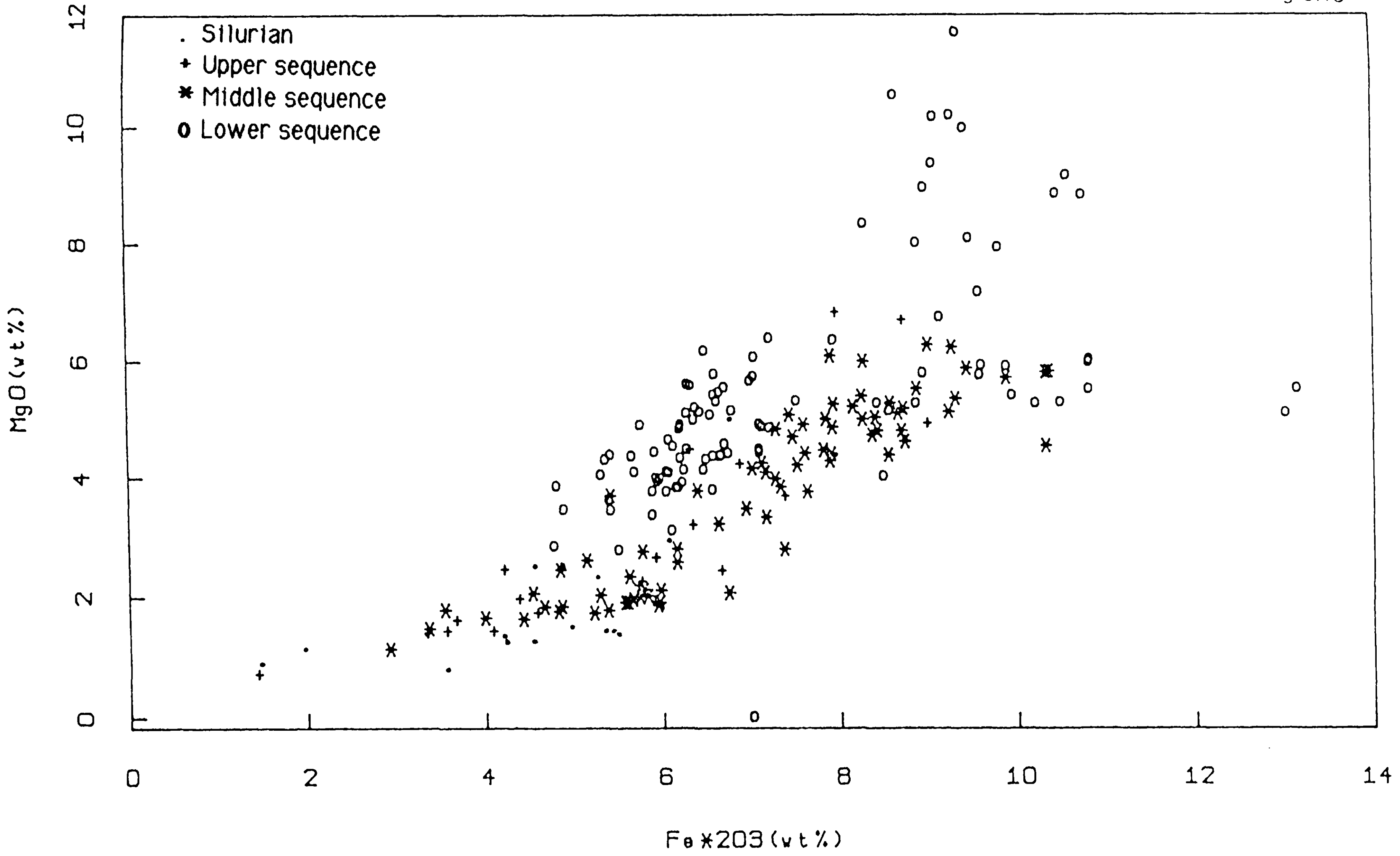


fig 5.13


. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
MgO(wt%)
0
2
4
6
8
10
12
Fe*2O3(wt%)
0
2
4
6
8
10
12
14

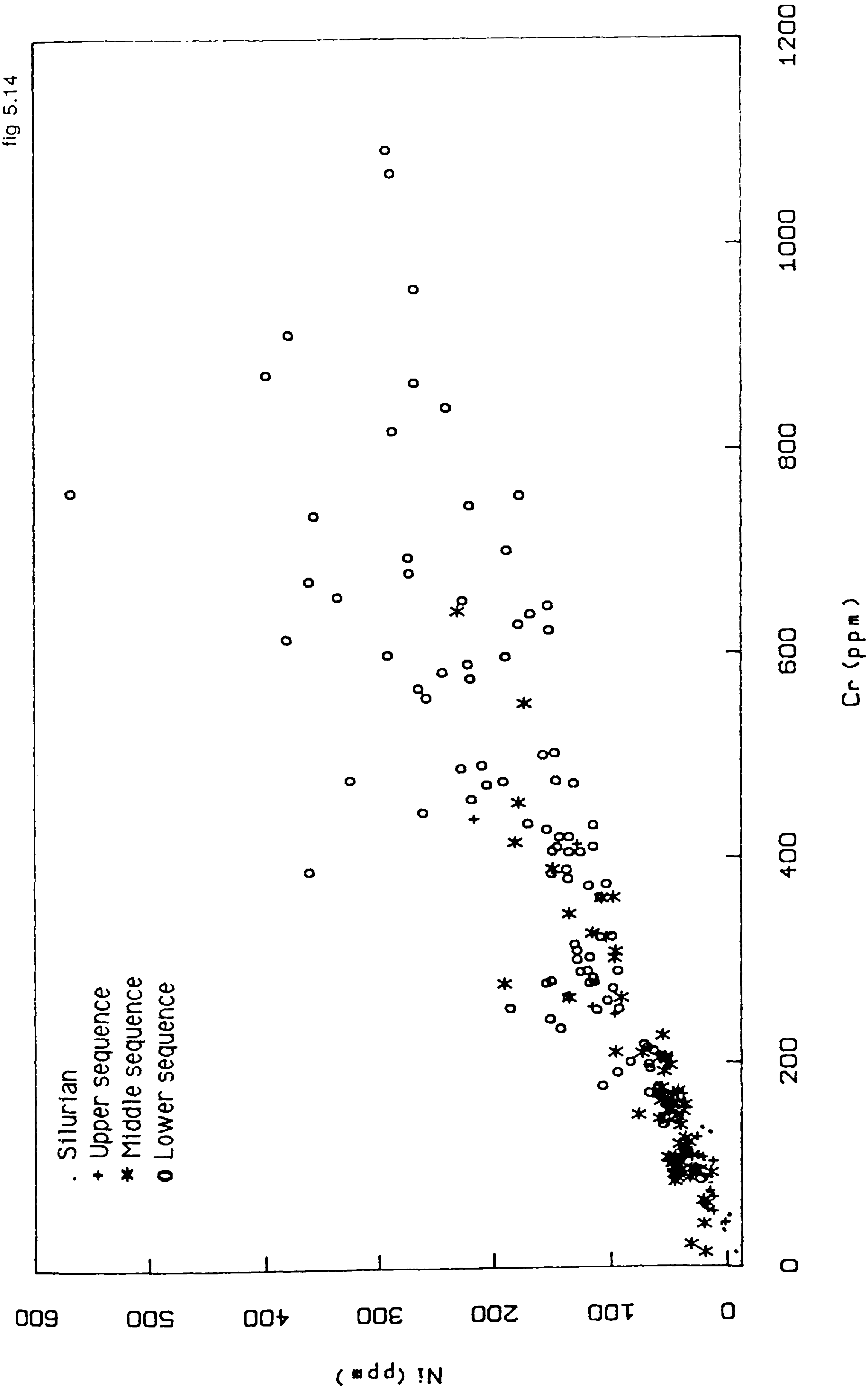
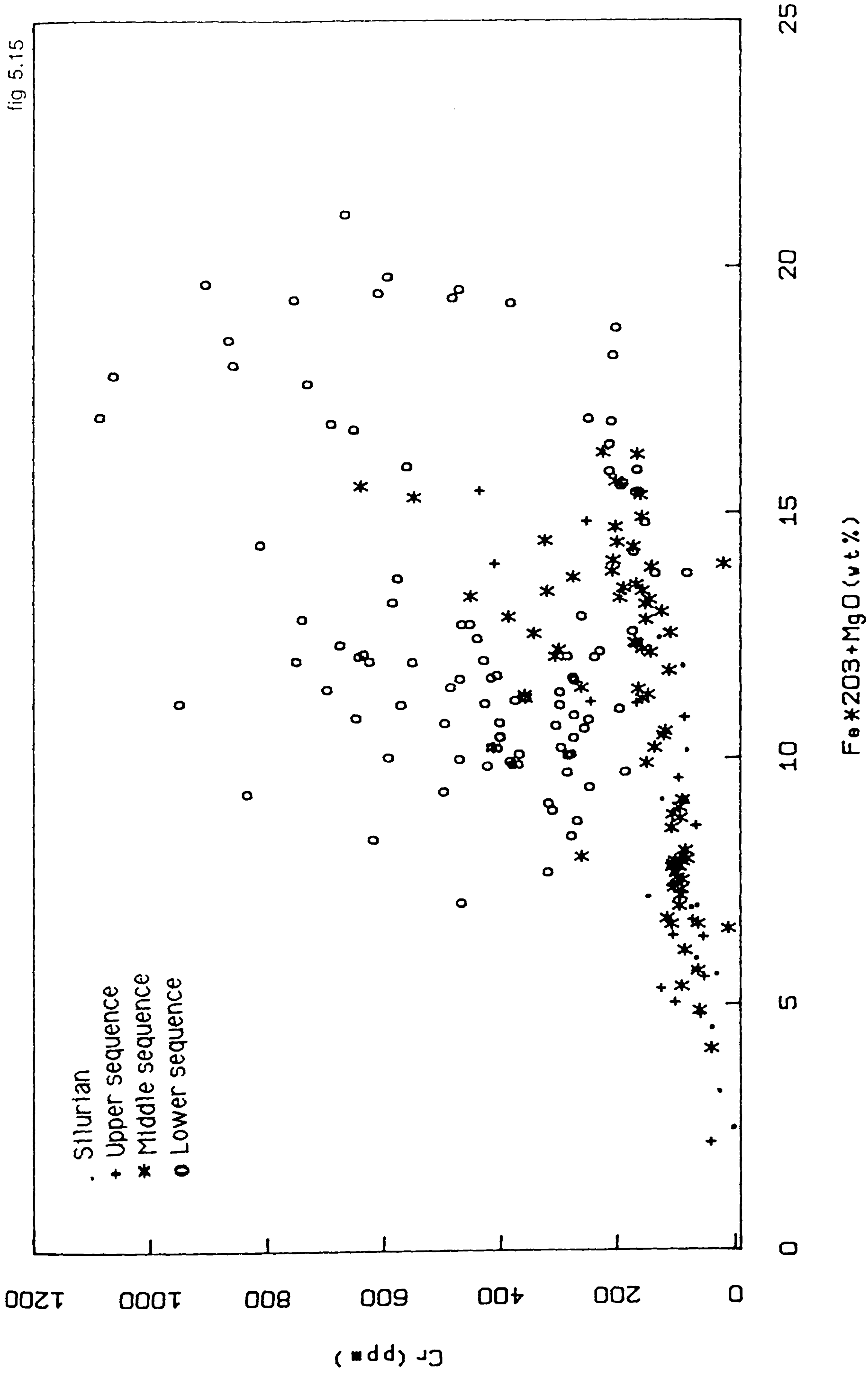

. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
Cr (ppm)
0
200
400
600
800
1000
1200
Ni (ppm)
0
100
200
300
400
500
600

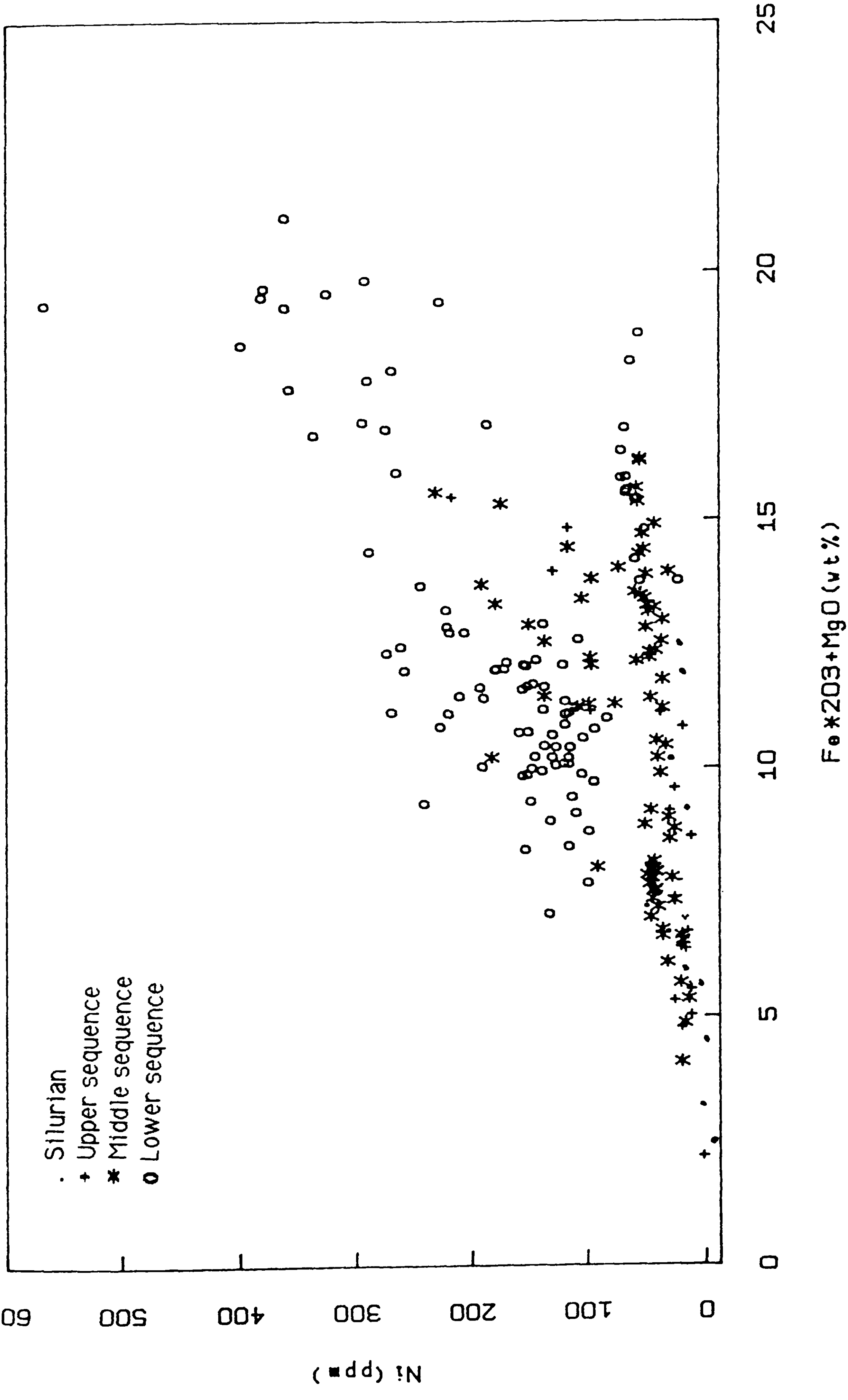
fig 5.14

fig 5.15



Cr (ppm)
0
200
400
600
800
1000
1200
Fe*2O3+MgO(wt%)
0
5
10
15
20
25
. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence

fig 5.16



Silurian
Upper sequence
Middle sequence
Lower sequence
Fe*2O3+MgO(wt%)
0
5
10
15
20
25
Ni (ppm)
0
100
200
300
400
500
600

fig 5.17

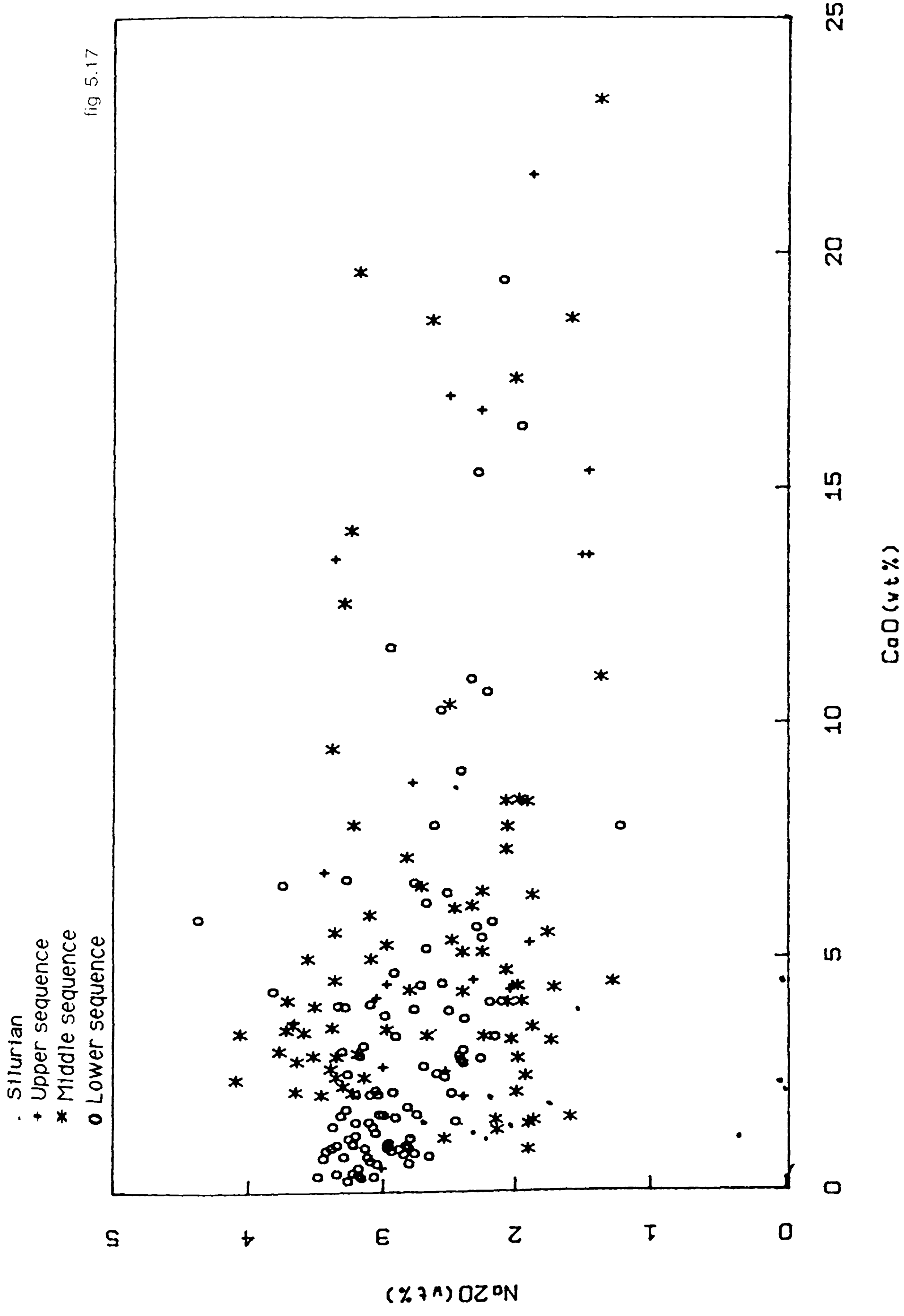

· Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
0
5
10
15
20
25
CaO (wt%)
0
1
2
3
4
5
Na2O (wt%)

fig 5.18

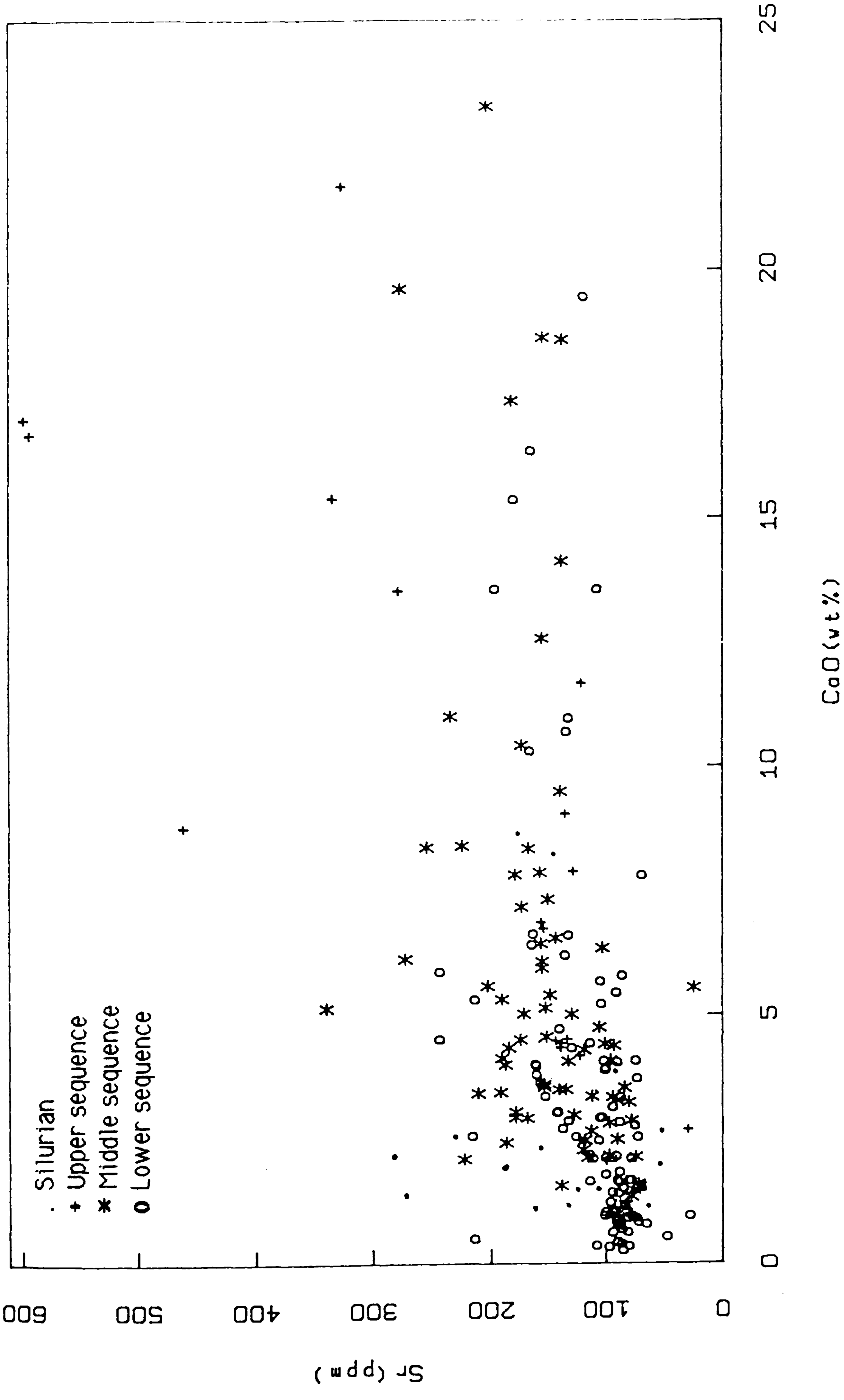
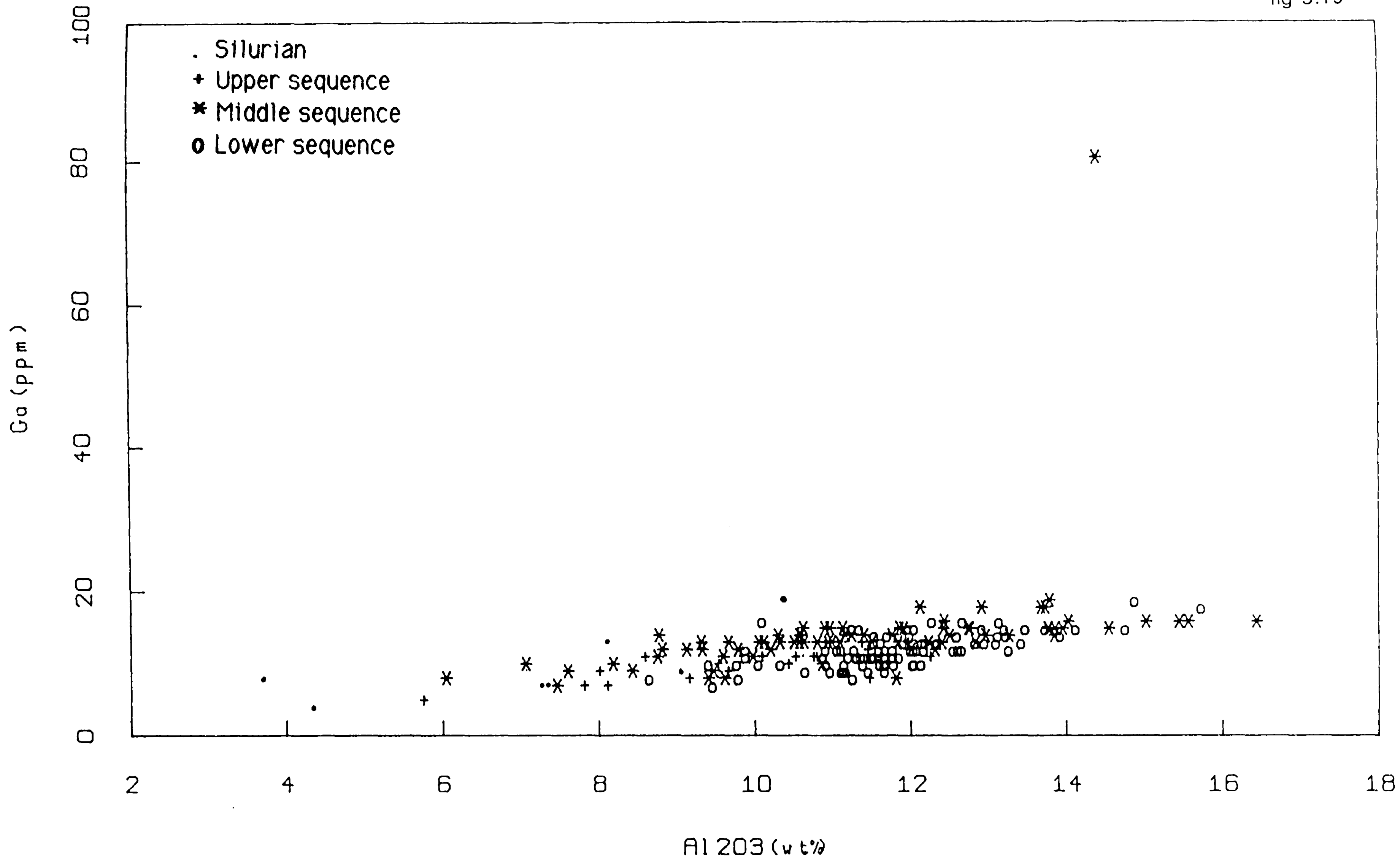

. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
CaO (wt %)
0
5
10
15
20
25
Sr (ppm)
0
100
200
300
400
500
600

fig 5.19



. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
Ga (ppm)
0
20
40
60
80
100
Al 203 (wt%)
2
4
6
8
10
12
14
16
18

fig 5.20

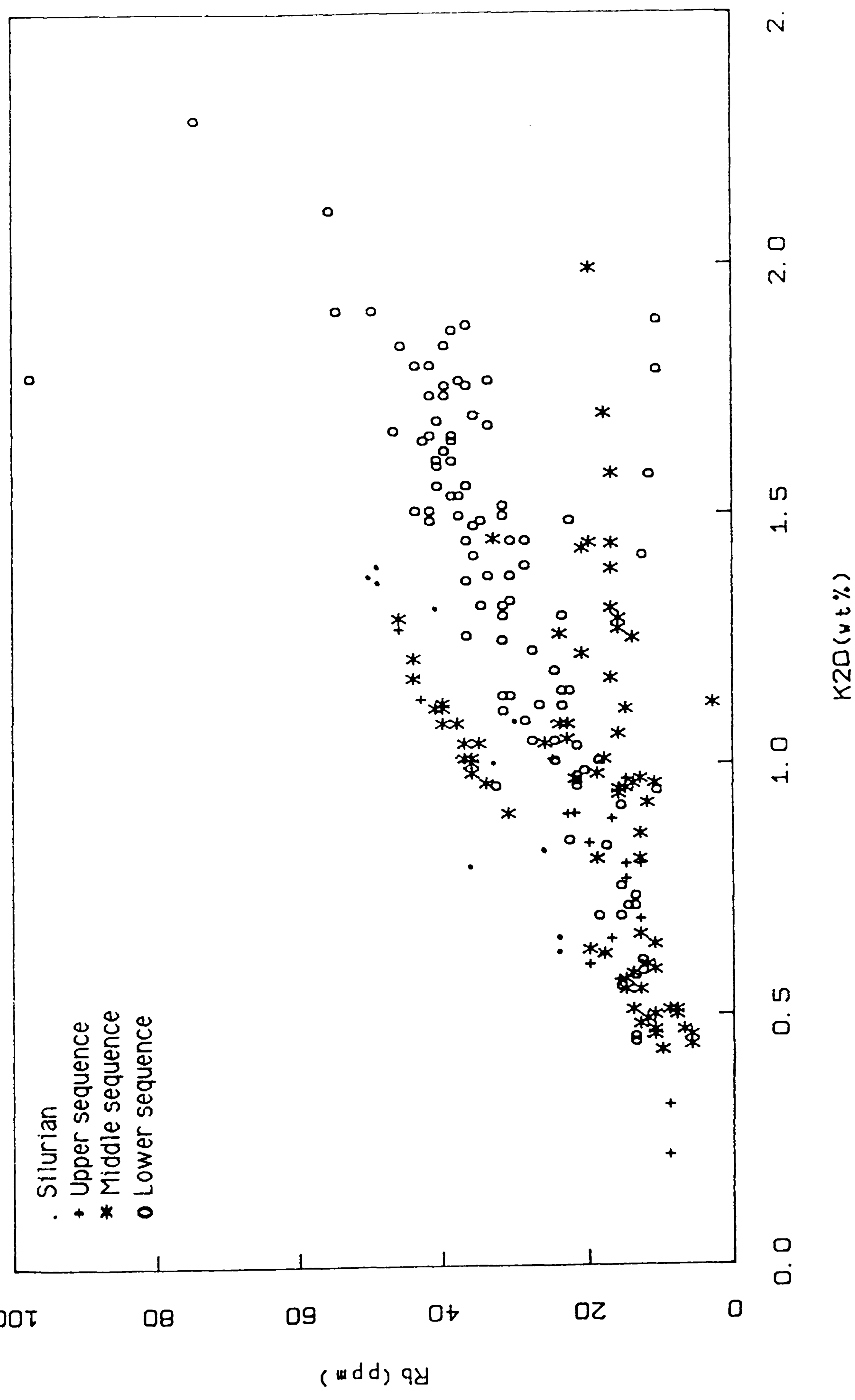
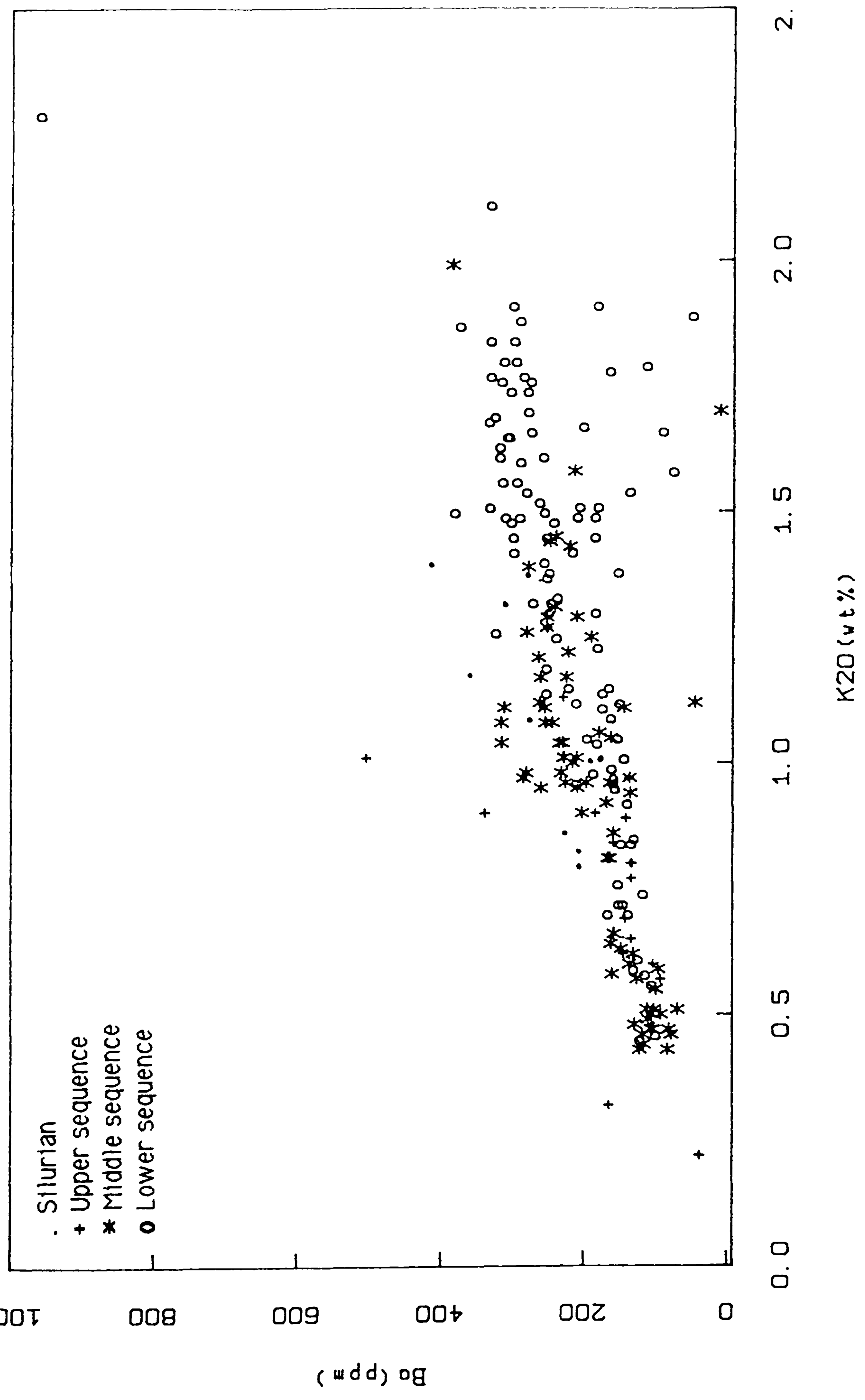

. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
Rb (ppm)
0
20
40
60
80
100
K2O(wt%)
0.0
0.5
1.0
1.5
2.0
2.5

fig 5.21



. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
0.0
0.5
1.0
1.5
2.0
2.5
K2O (wt%)
0
200
400
600
800
1000
Ba (ppm)

fig 5.22

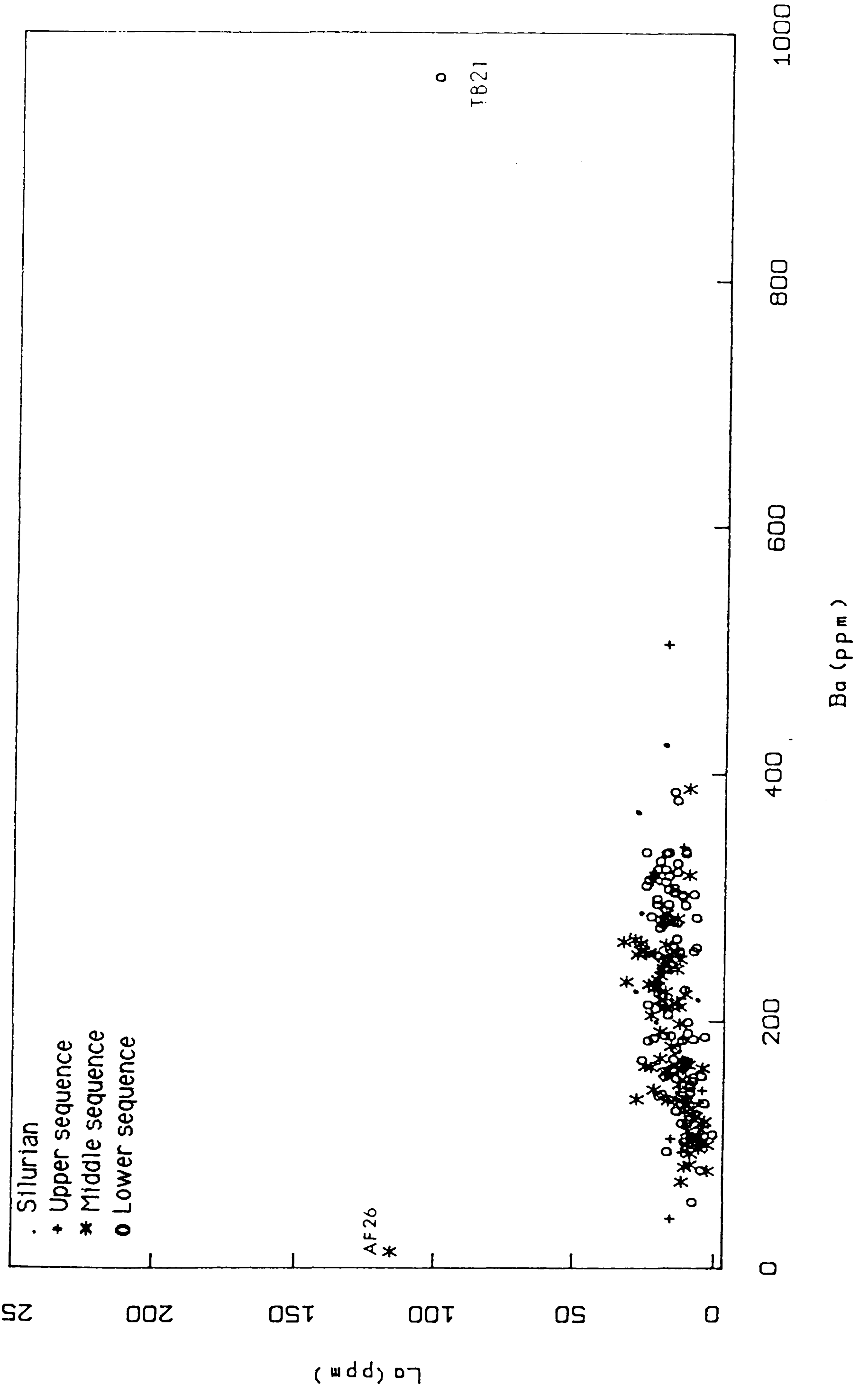

. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
AF26
TB21
Ba (ppm)
La (ppm)
0
200
400
600
800
1000
0
50
100
150
200
250

fig 5.23

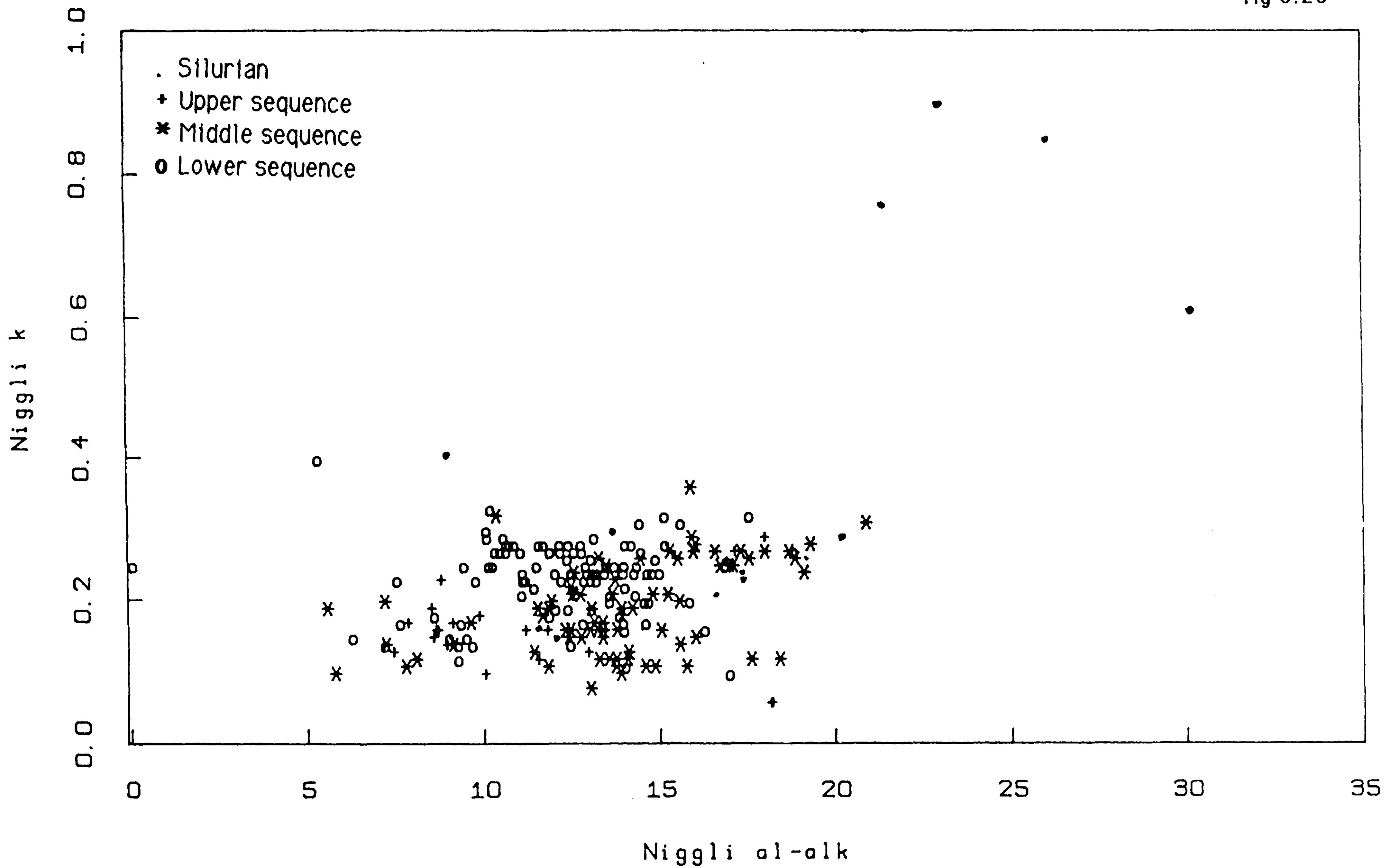

. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
Niggli k
0.0
0.2
0.4
0.6
0.8
1.0
Niggli al-alk
0
5
10
15
20
25
30
35

fig 5.24

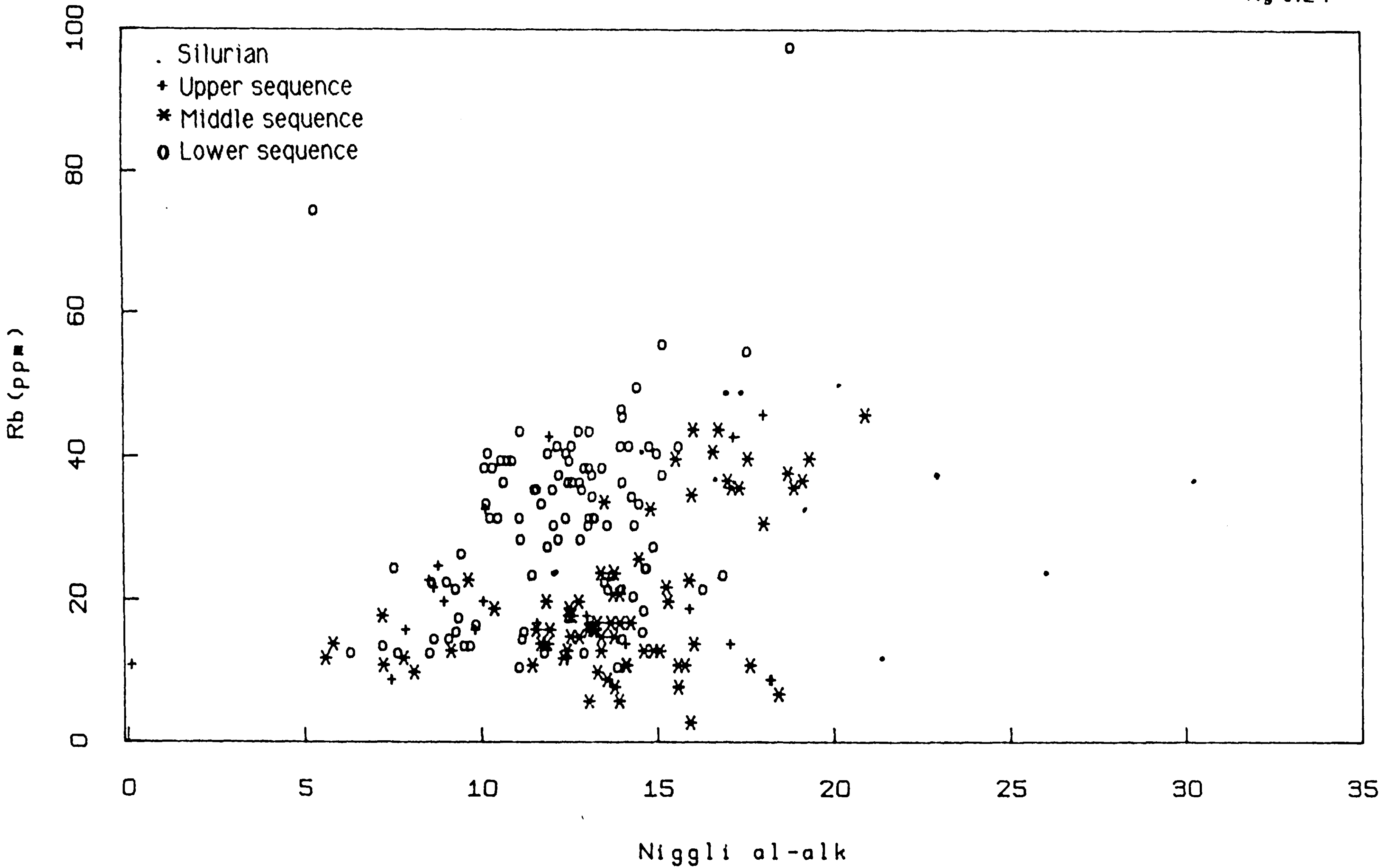

. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
Rb (ppm)
0
20
40
60
80
100
Niggli al-alk
0
5
10
15
20
25
30
35

fig 5.25

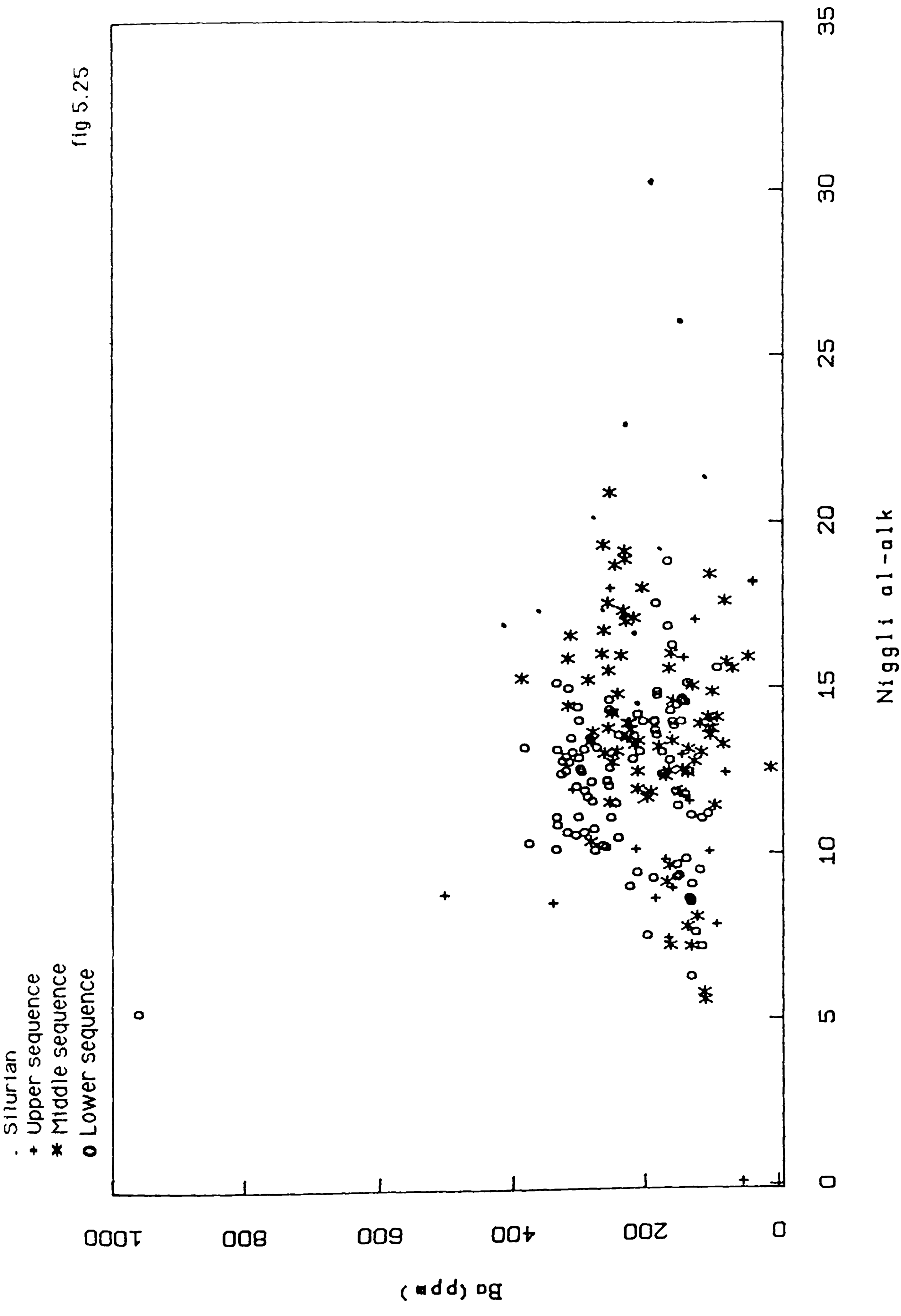

. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
Ba (ppm)
0
200
400
600
800
1000
Niggli al-alk
0
5
10
15
20
25
30
35

fig 5.26

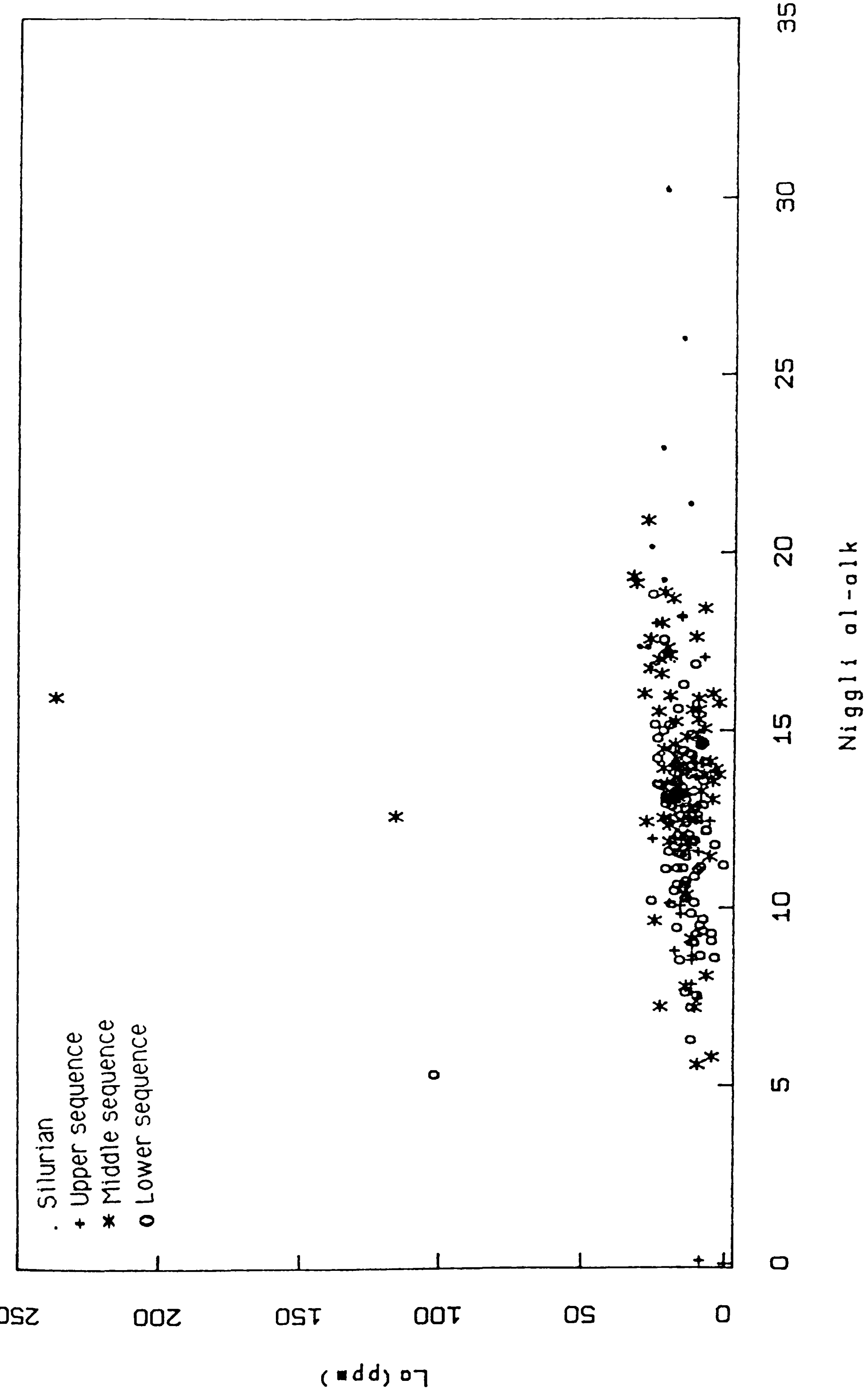

. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
La (ppm)
0
50
100
150
200
250
Niggli al-alk
0
5
10
15
20
25
30
35

fig 5.27

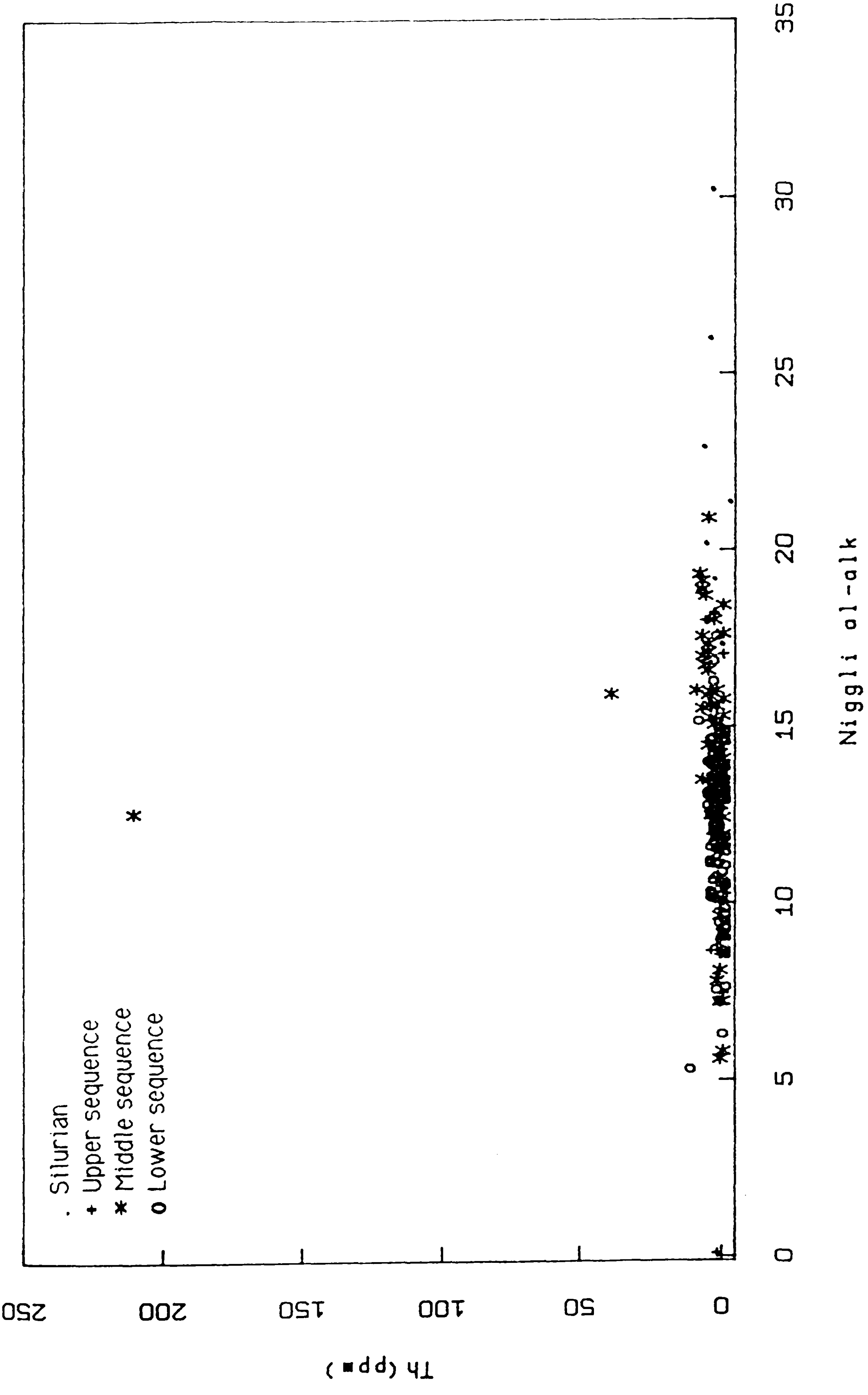
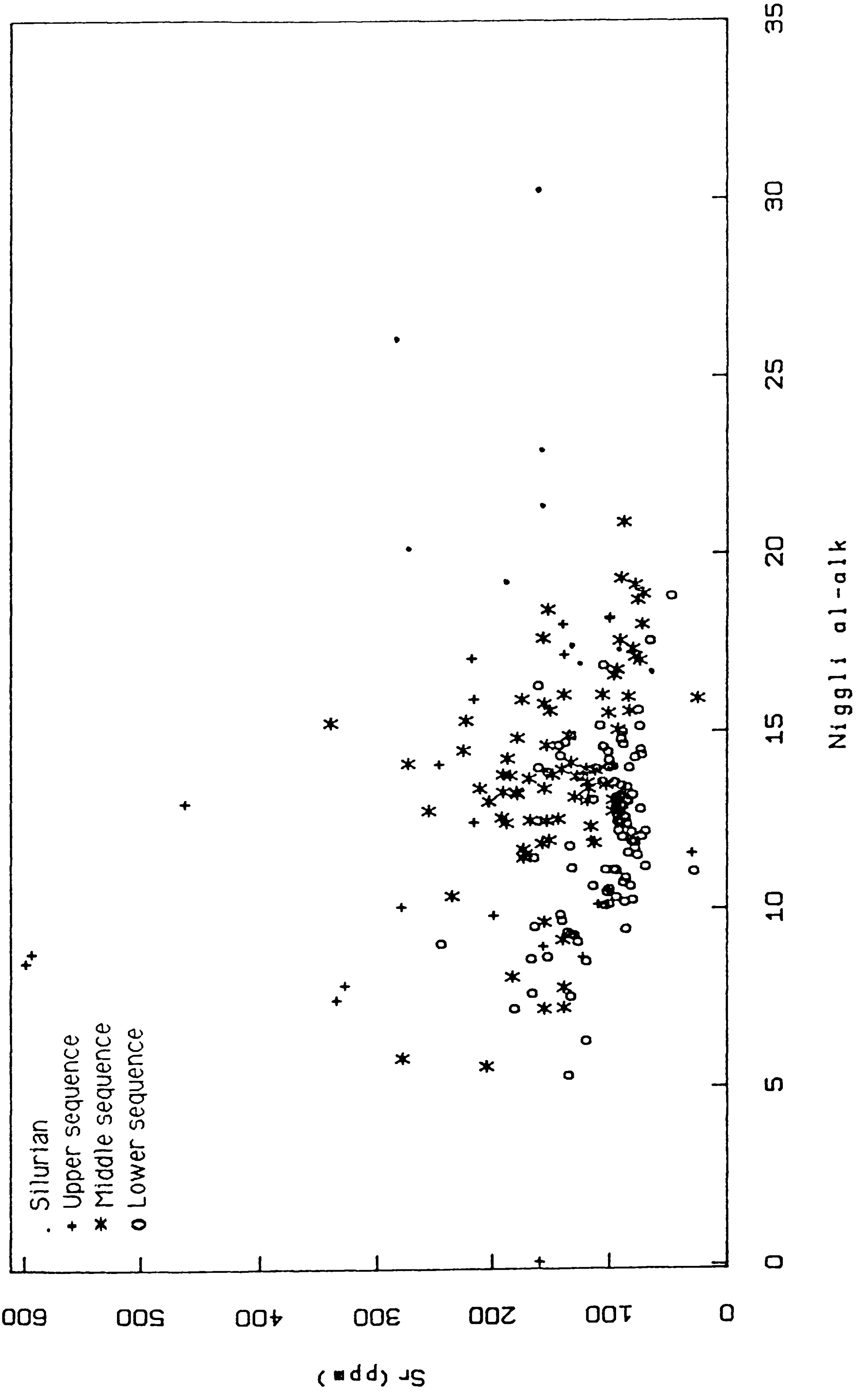

. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
Th (ppm)
0
50
100
150
200
250
Niggli al-alk
0
5
10
15
20
25
30
35

fig 5.28



. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
Niggli al-alk
0
5
10
15
20
25
30
35
Sr (ppm)
0
100
200
300
400
500
600

fig 5.29

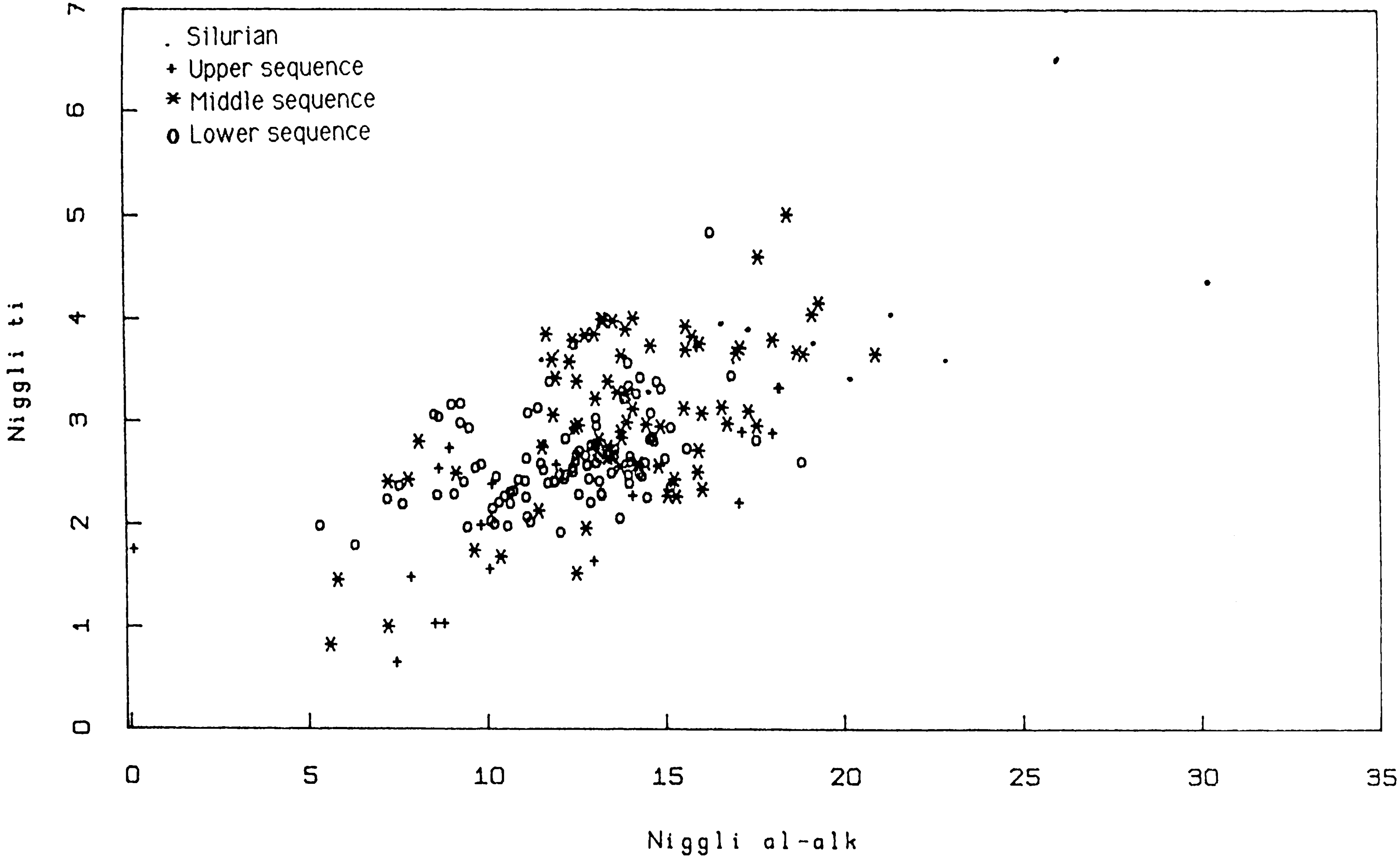

. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
Niggli ti
0
1
2
3
4
5
6
7
0
5
10
15
20
25
30
35
Niggli al-alk

fig 5.30

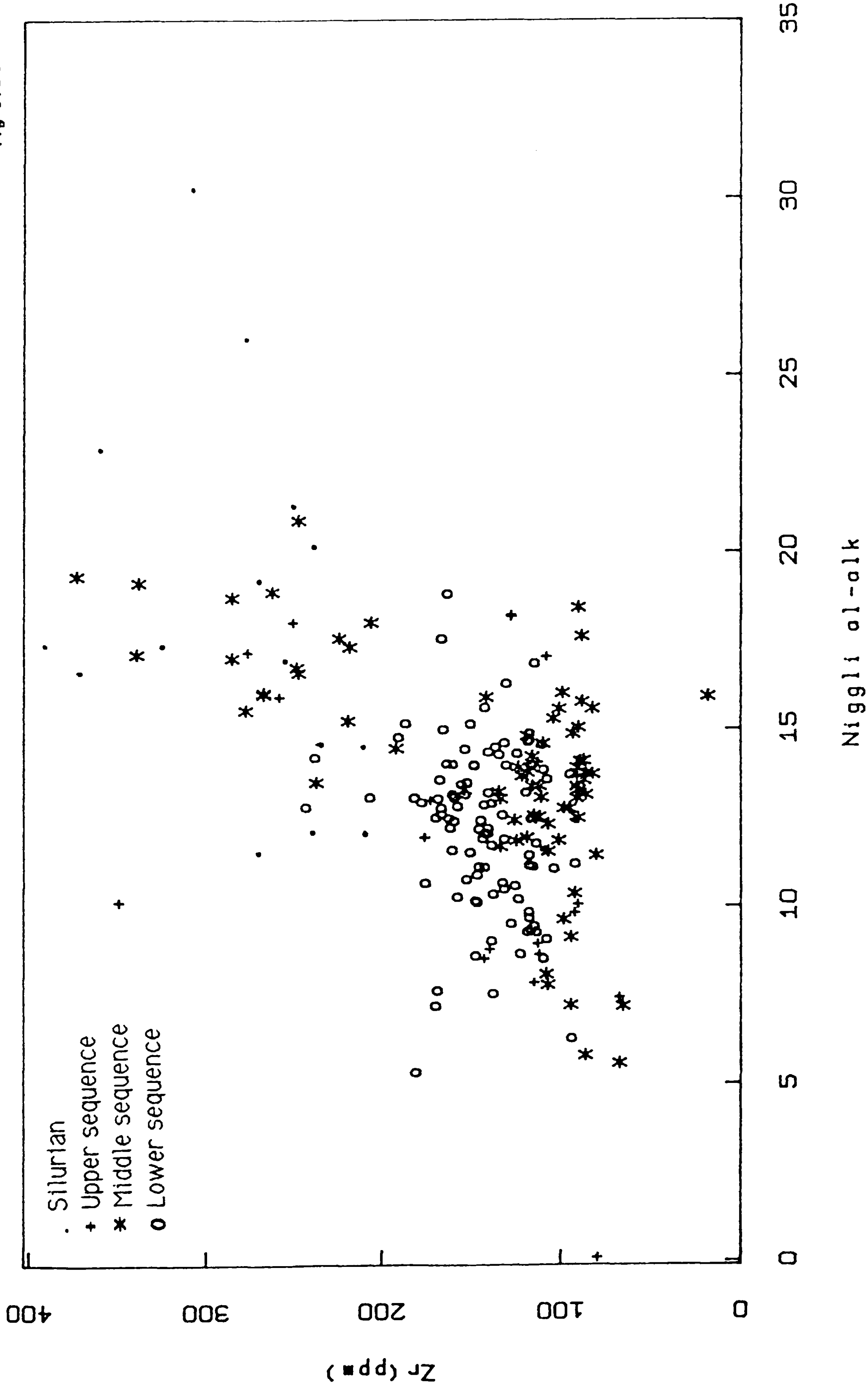
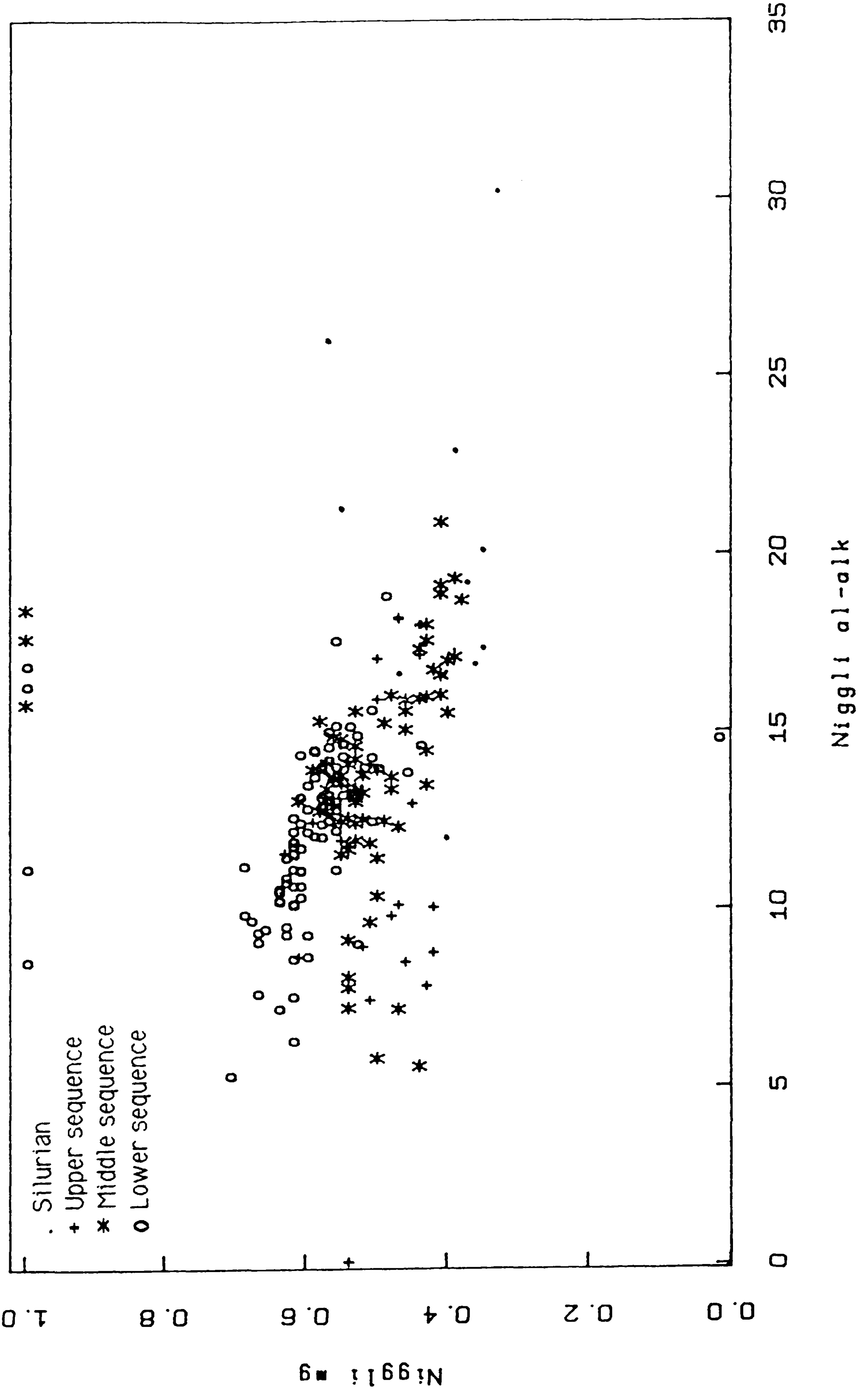

. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
Niggli al-alk
0
5
10
15
20
25
30
35
Zr (ppm)
0
100
200
300
400

fig 5.31


. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
Niggli al-alk
Niggli mg
0
5
10
15
20
25
30
35
0.0
0.2
0.4
0.6
0.8
1.0

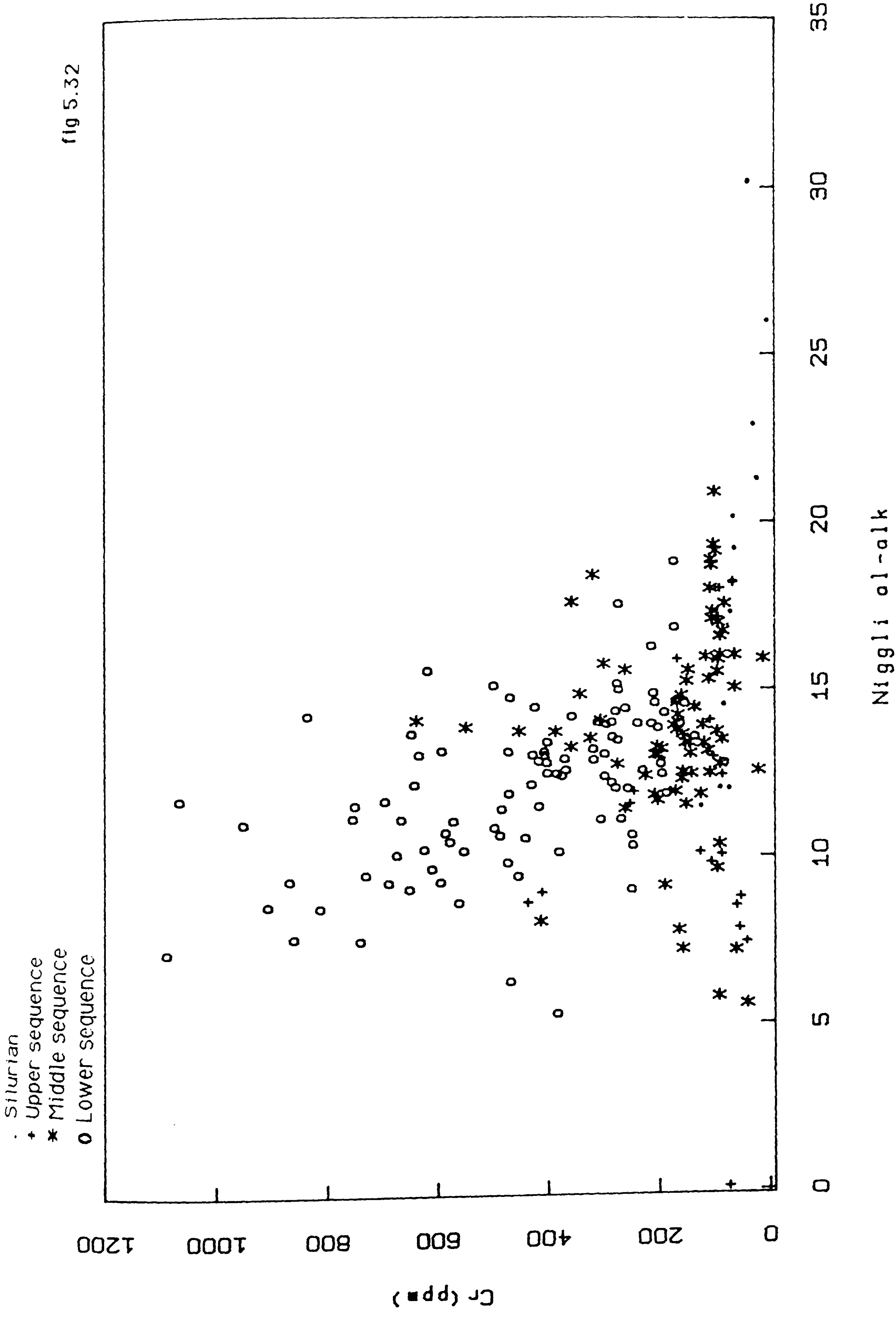

. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
Cr (ppm)
0
200
400
600
800
1000
1200
Niggli al-alk
0
5
10
15
20
25
30
35

fig 5.32

fig 5.33

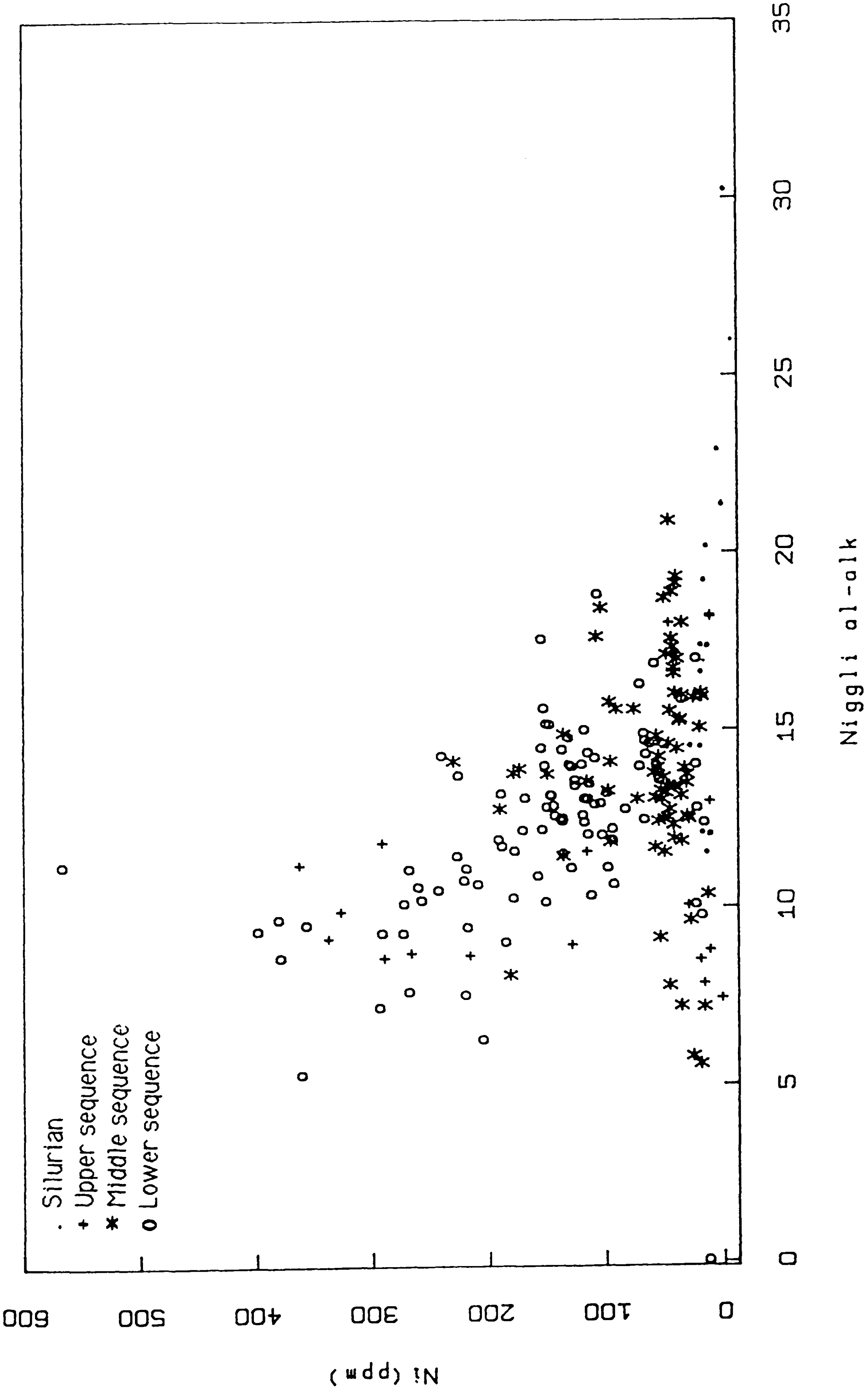

. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
Niggli al-alk
0
5
10
15
20
25
30
35
Ni (ppm)
0
100
200
300
400
500
600

fig 5.34

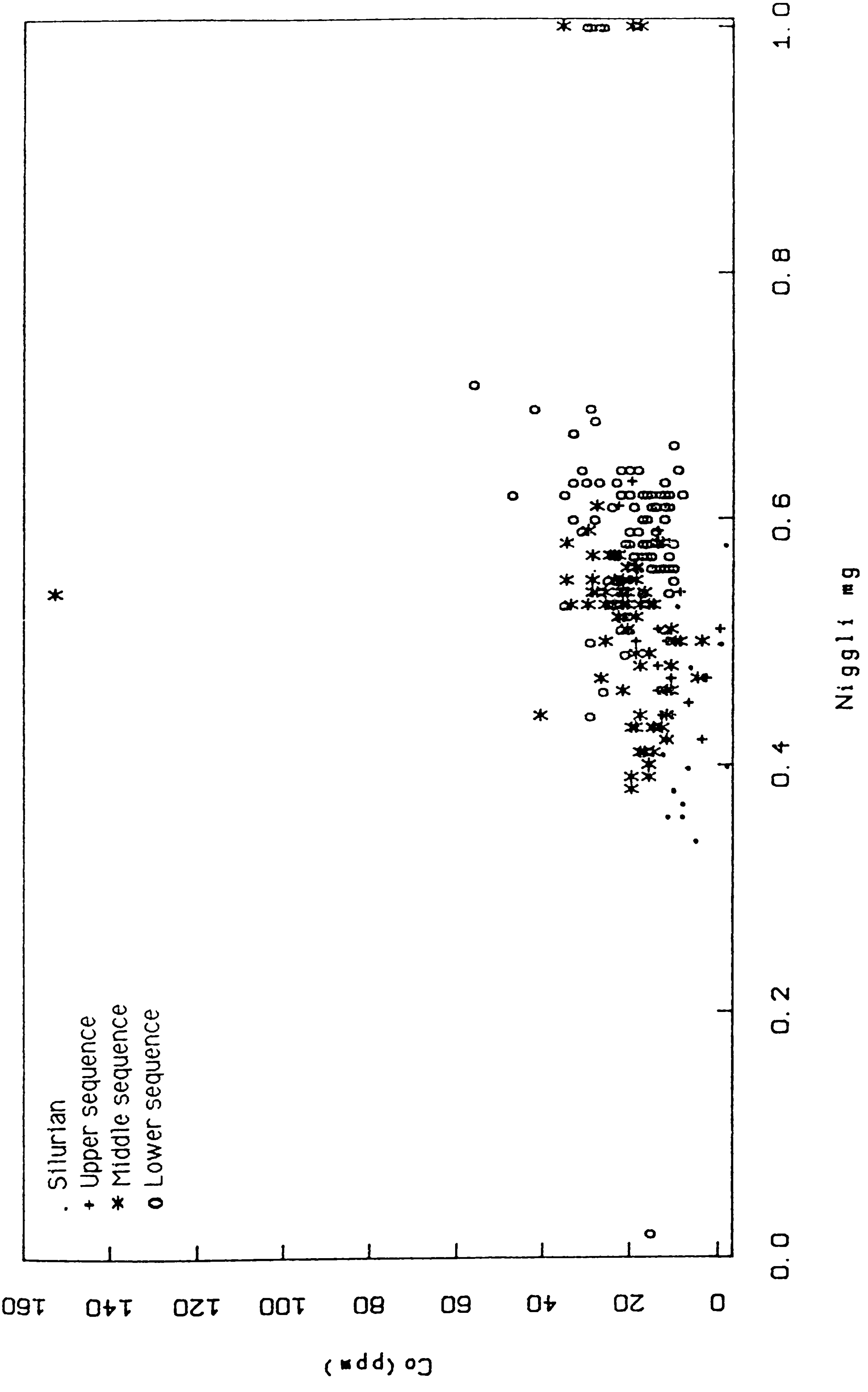

. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
Co (ppm)
0
20
40
60
80
100
120
140
160
Niggli mg
0.0
0.2
0.4
0.6
0.8
1.0

fig 5.35

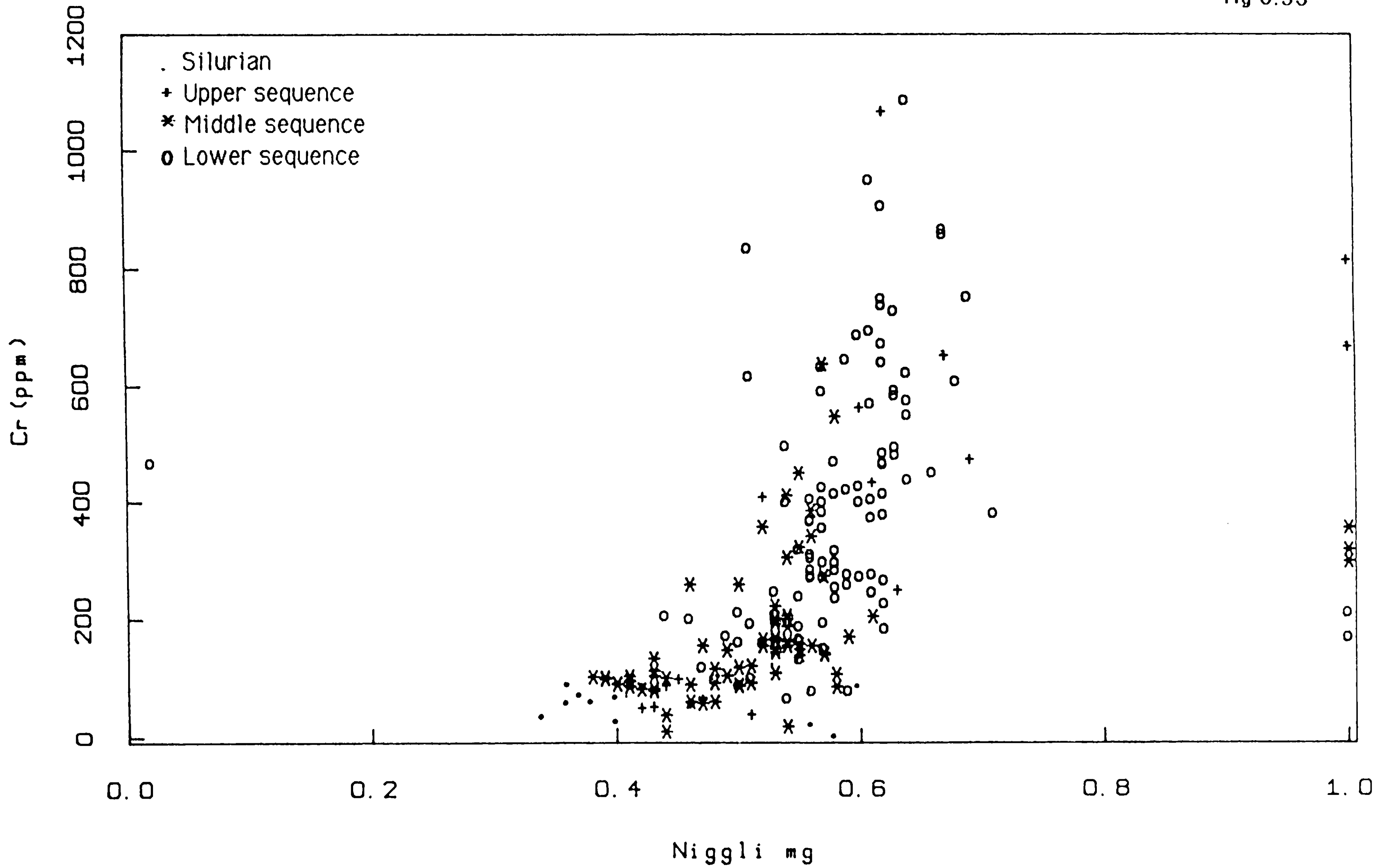

. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
Cr (ppm)
0
200
400
600
800
1000
1200
0.0
0.2
0.4
0.6
0.8
1.0
Niggli mg

fig 5.36

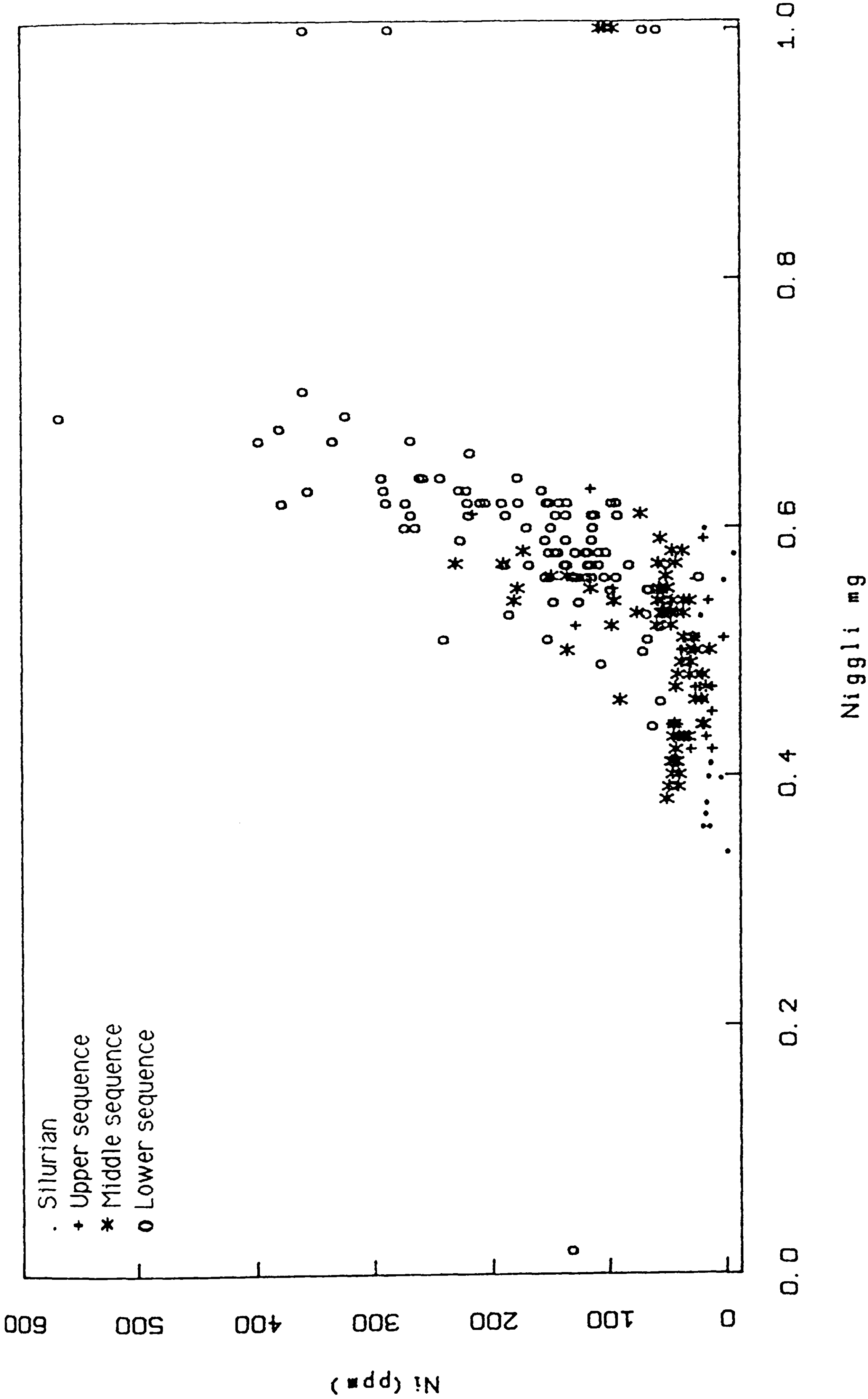
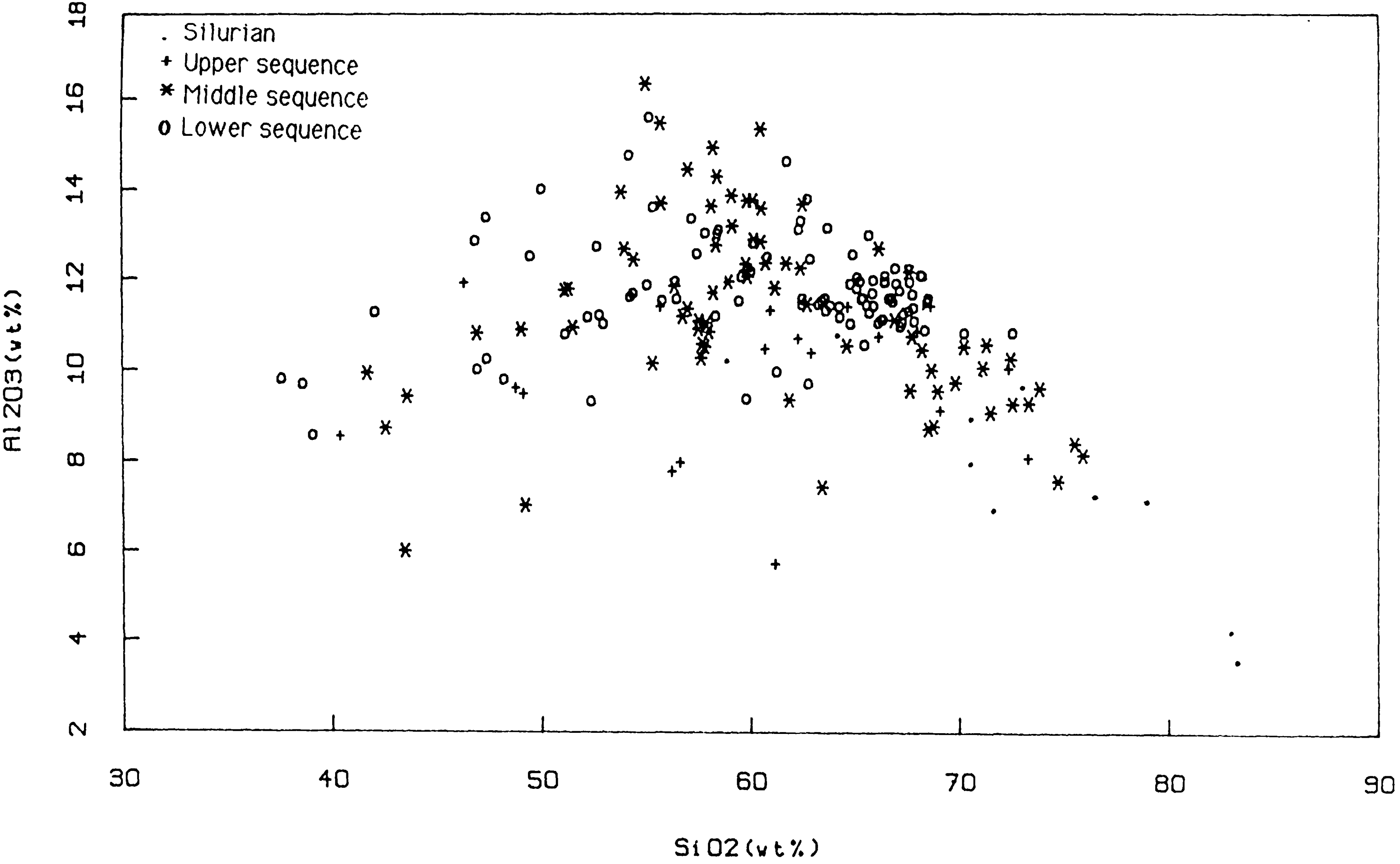
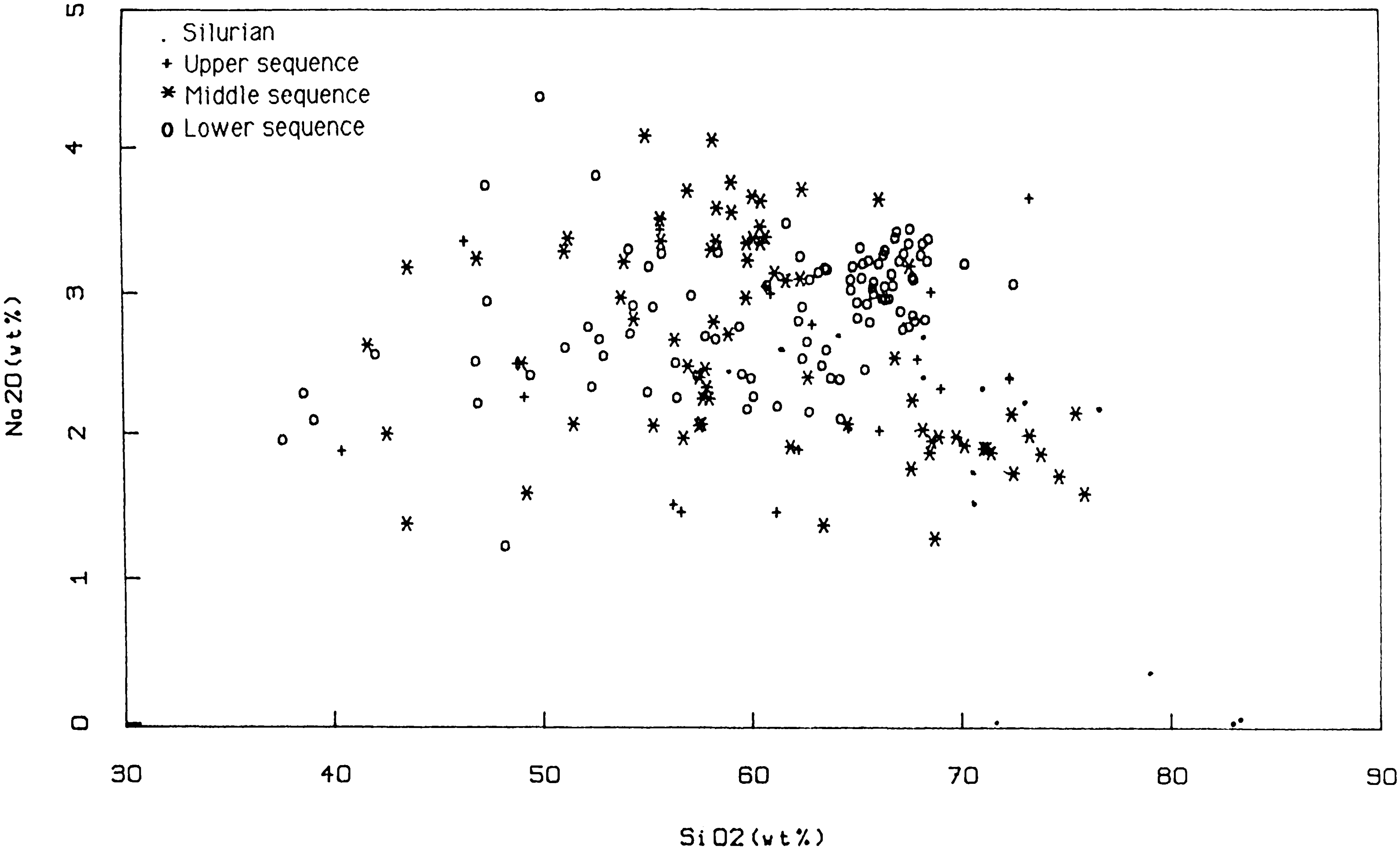

. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
Niggli mg
0.0
0.2
0.4
0.6
0.8
1.0
Ni (ppm)
0
100
200
300
400
500
600

fig 5.37



. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
Al2O3(wt%)
18
16
14
12
10
8
6
4
2
SiO2(wt%)
30
40
50
60
70
80
90

fig 5.38



. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
Na2O(wt%)
0
1
2
3
4
5
30
40
50
60
70
80
90
SiO2(wt%)

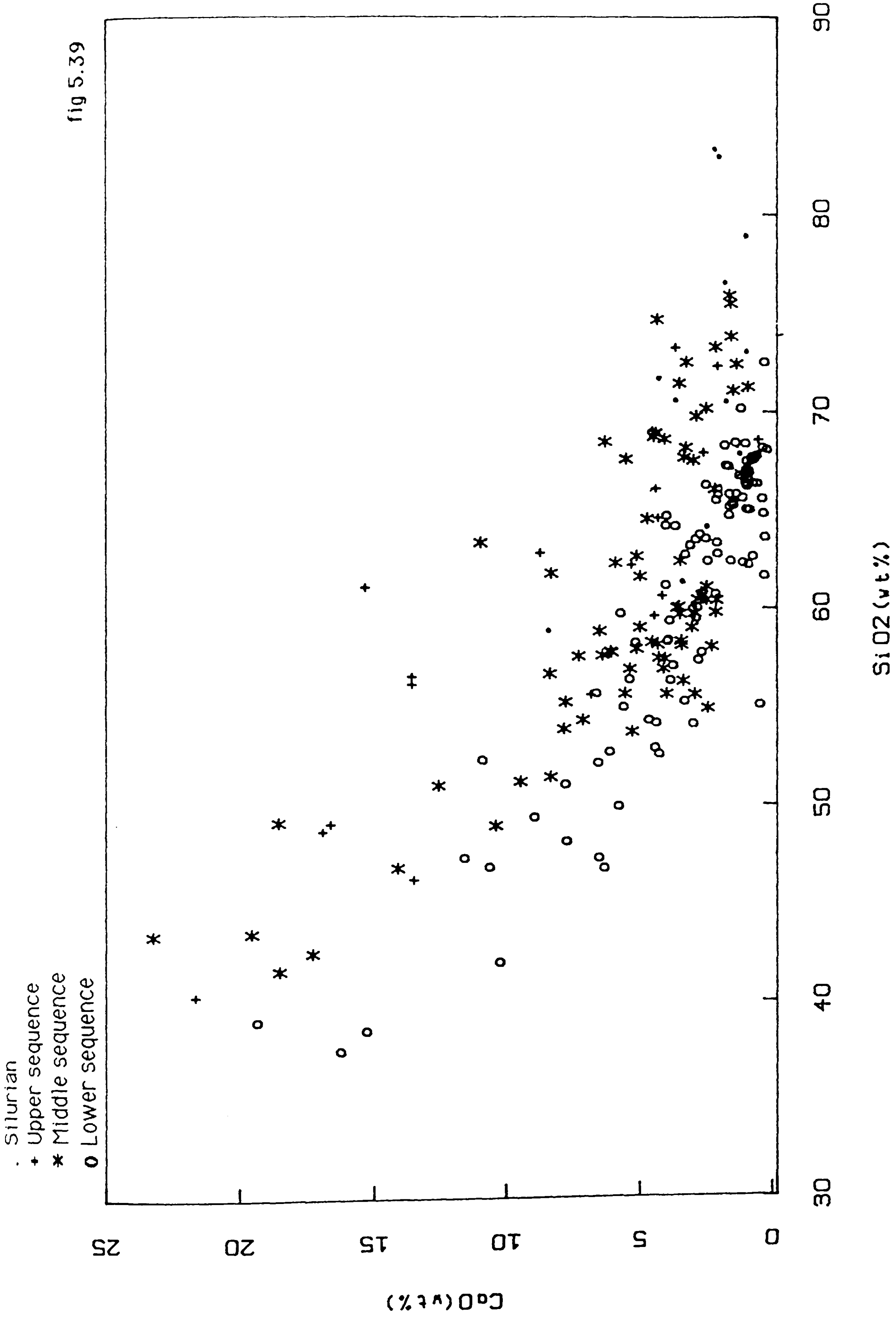
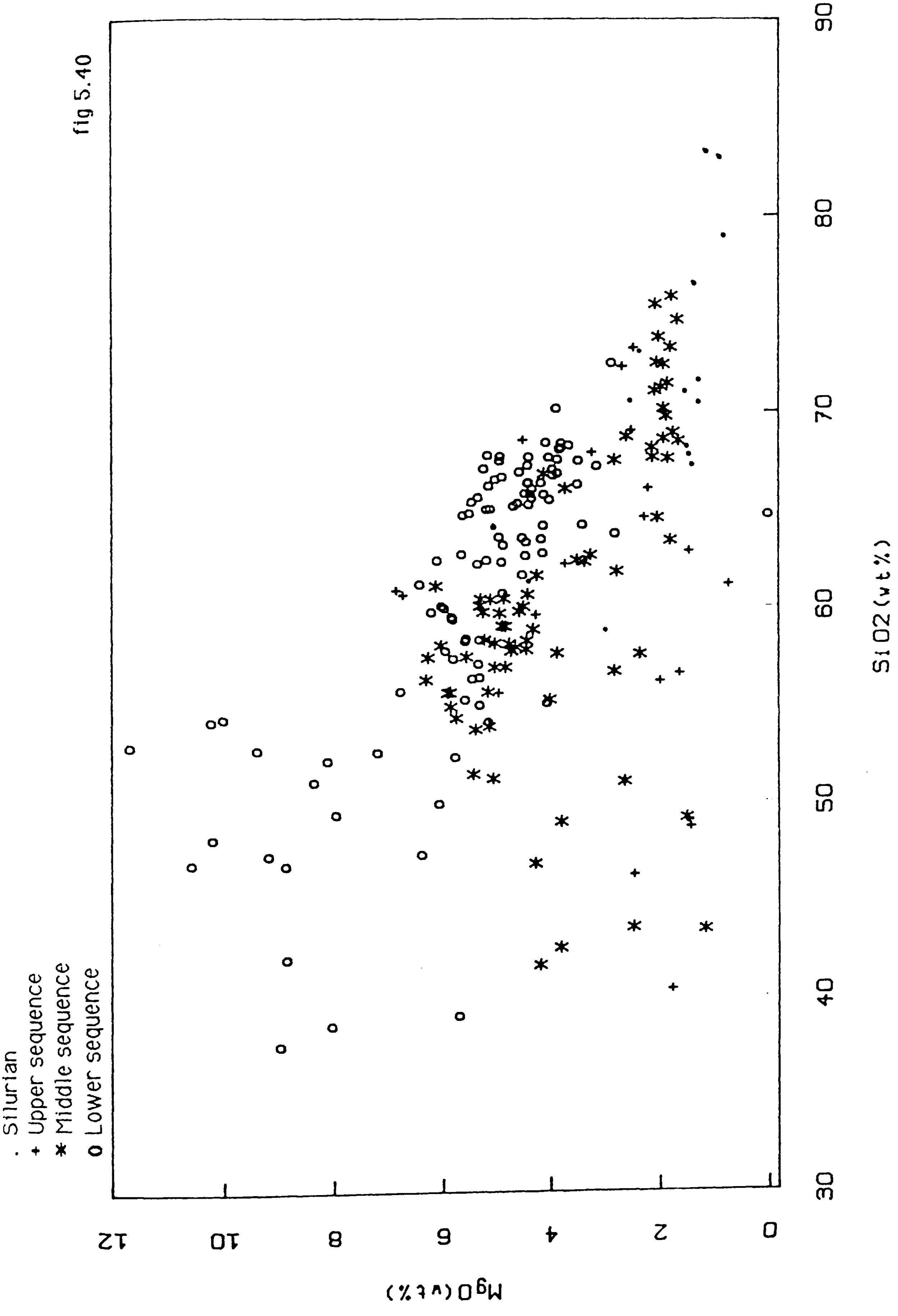


fig 5.39

. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
CaO (wt%)
0
5
10
15
20
25
SiO2 (wt%)
30
40
50
60
70
80
90

fig 5.40


. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
MgO (wt%)
0
2
4
6
8
10
12
SiO2 (wt%)
30
40
50
60
70
80
90

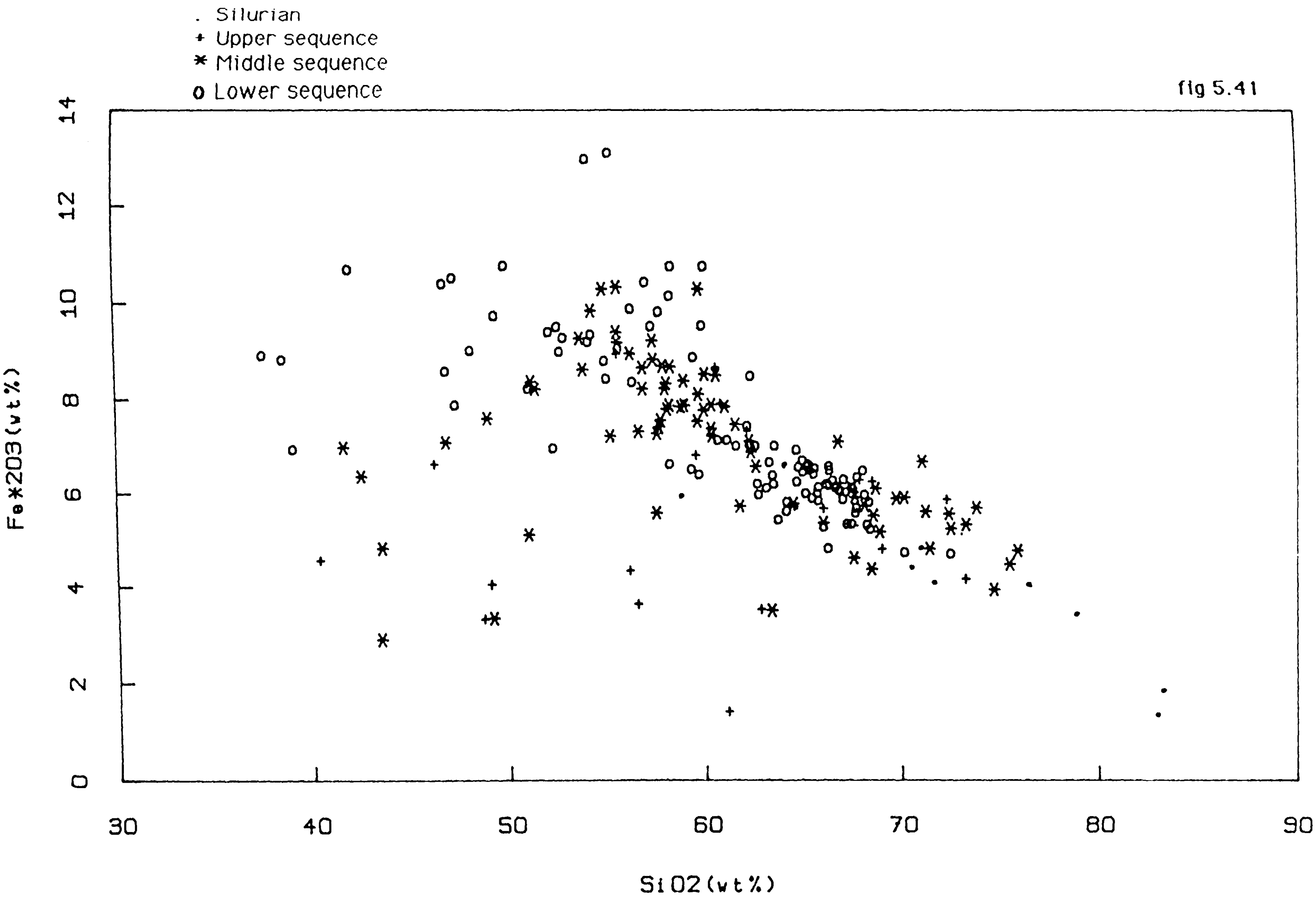


fig 5.41

. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
Fe*2O3(wt%)
0
2
4
6
8
10
12
14
SiO2(wt%)
30
40
50
60
70
80
90

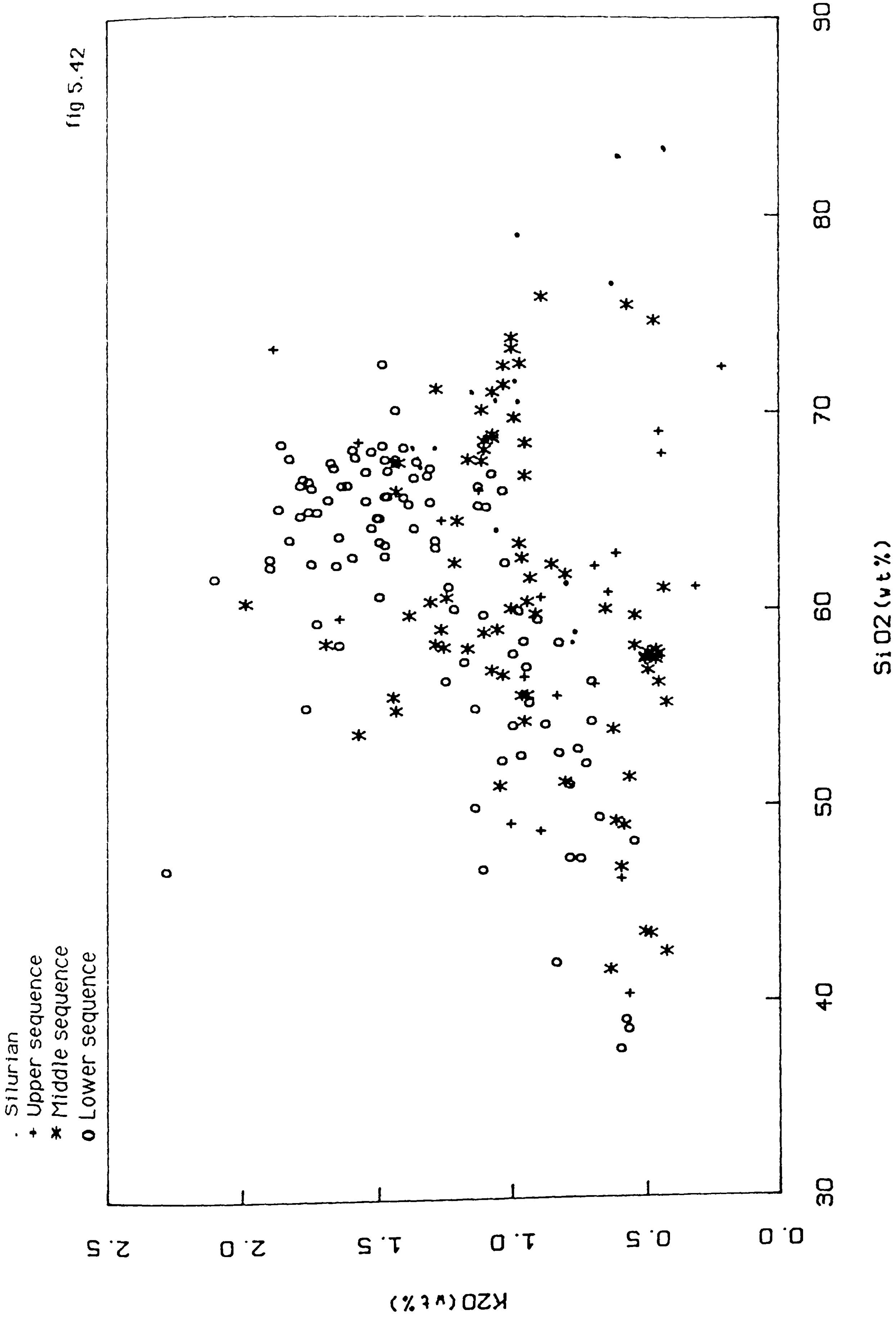

. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
K2O (wt%)
0.0
0.5
1.0
1.5
2.0
2.5
SiO2 (wt%)
30
40
50
60
70
80
90

fig 5.42

fig 5.43

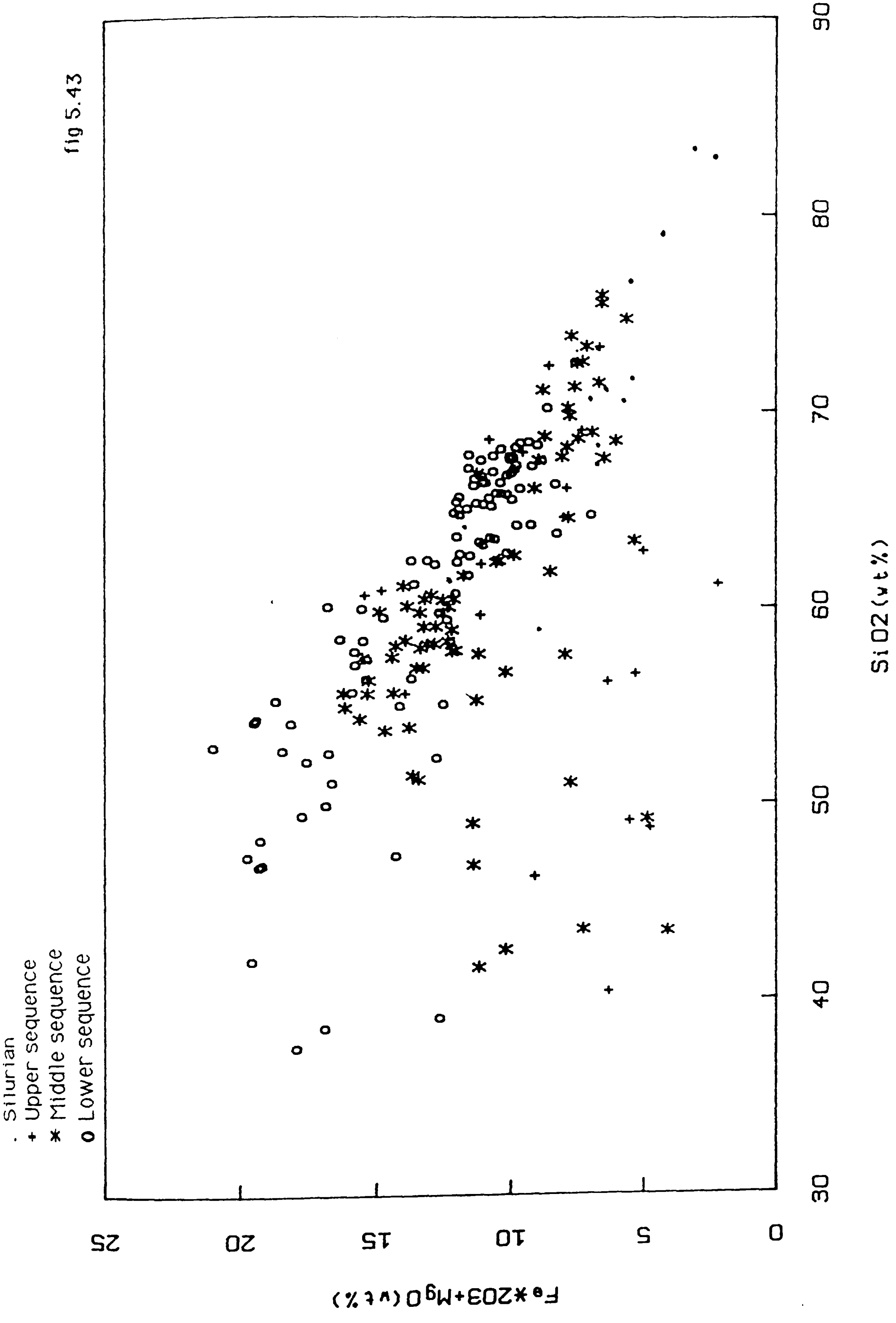

. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
SiO2(wt%)
30
40
50
60
70
80
90
Fe*2O3+MgO(wt%)
0
5
10
15
20
25

fig 5.44

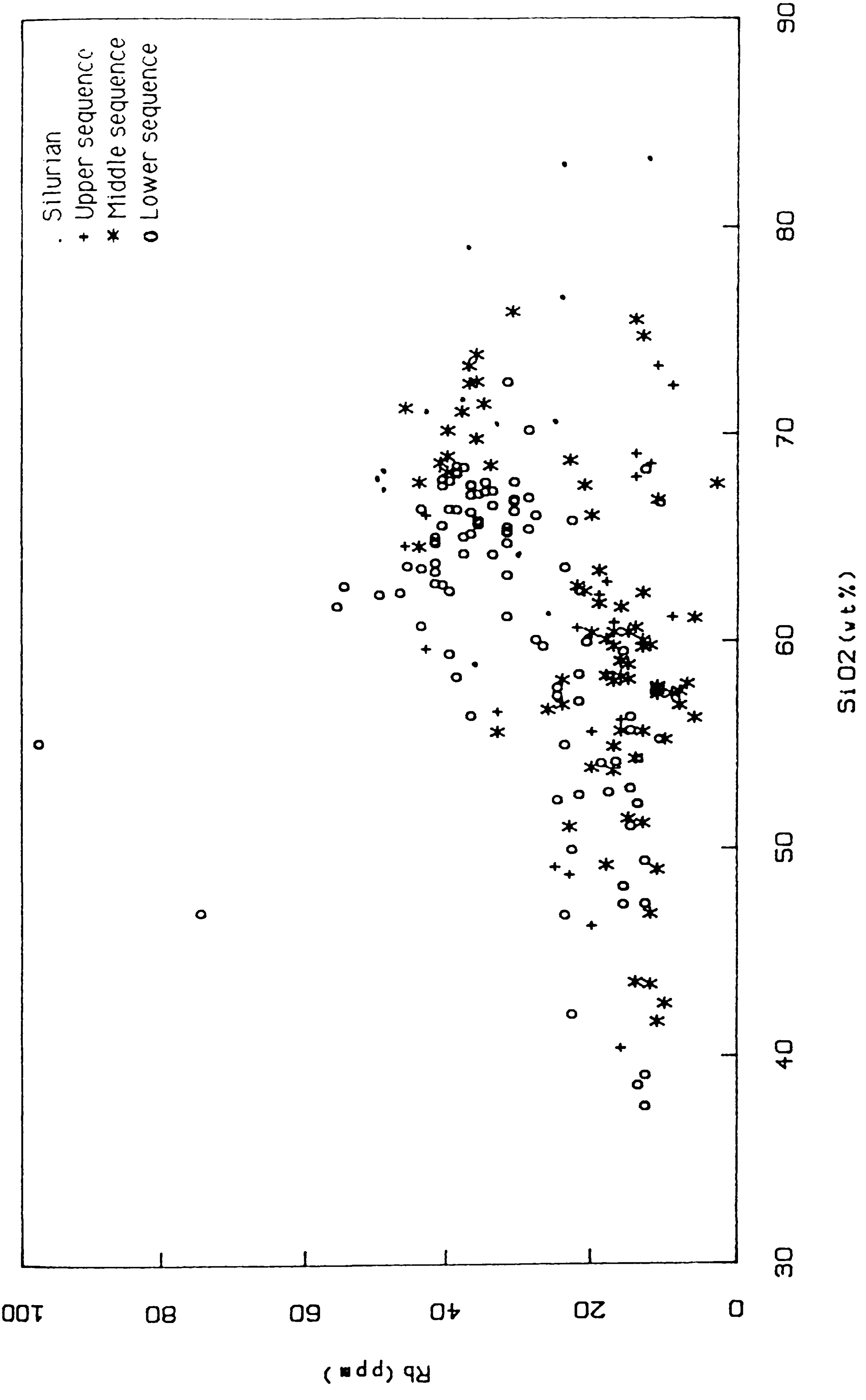

. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
SiO2 (wt%)
30
40
50
60
70
80
90
Rb (ppm)
0
20
40
60
80
100

fig 5.45

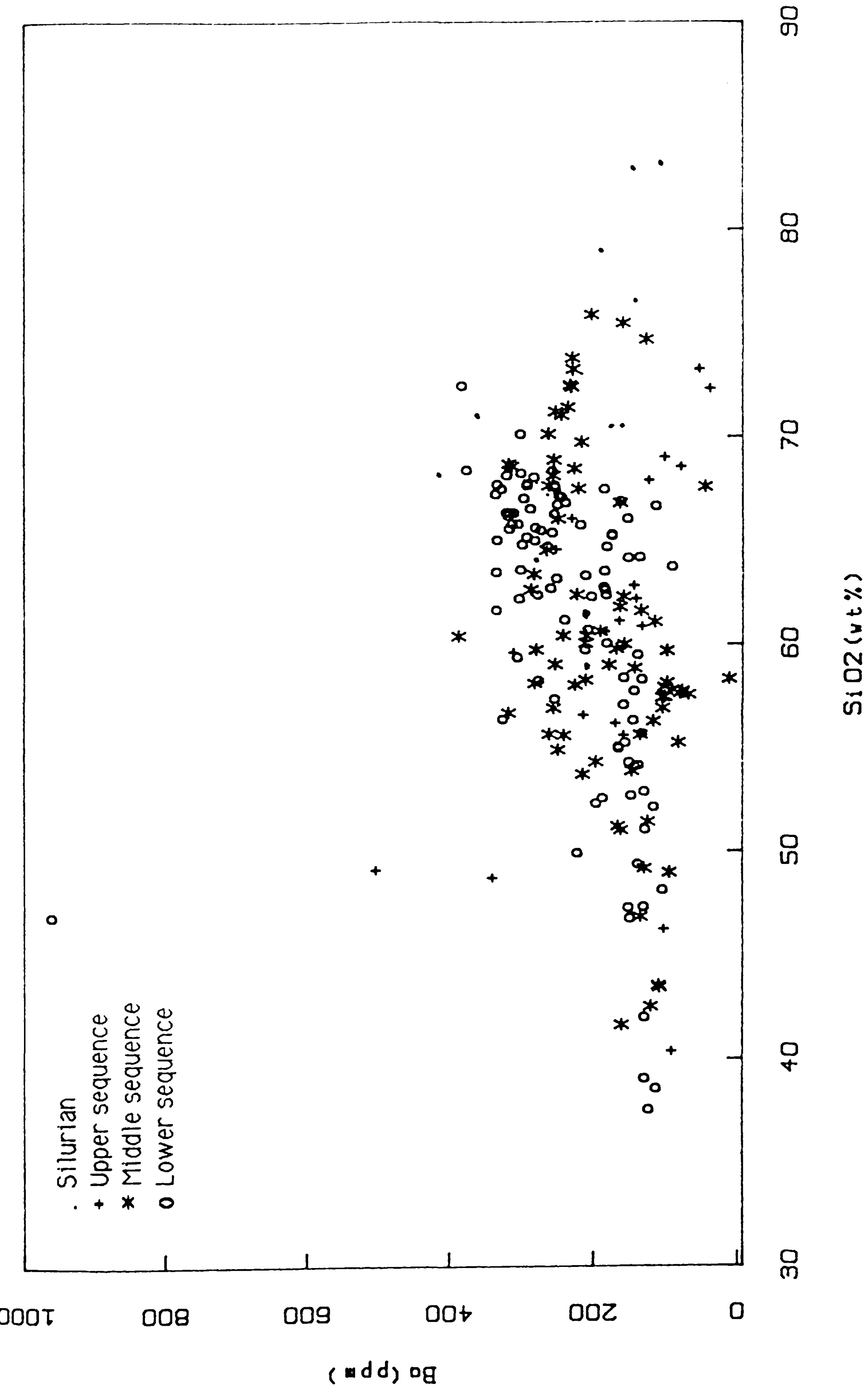
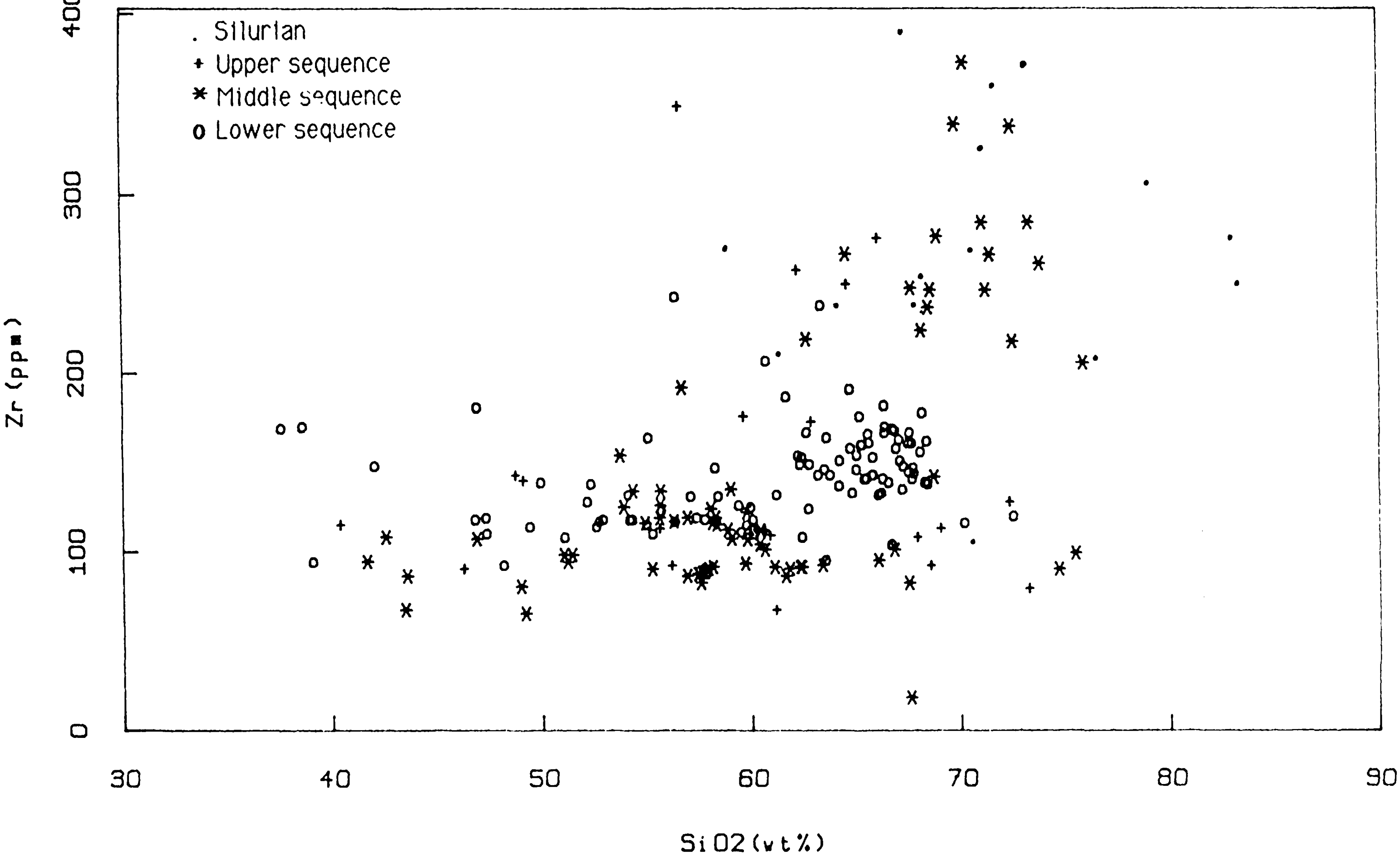
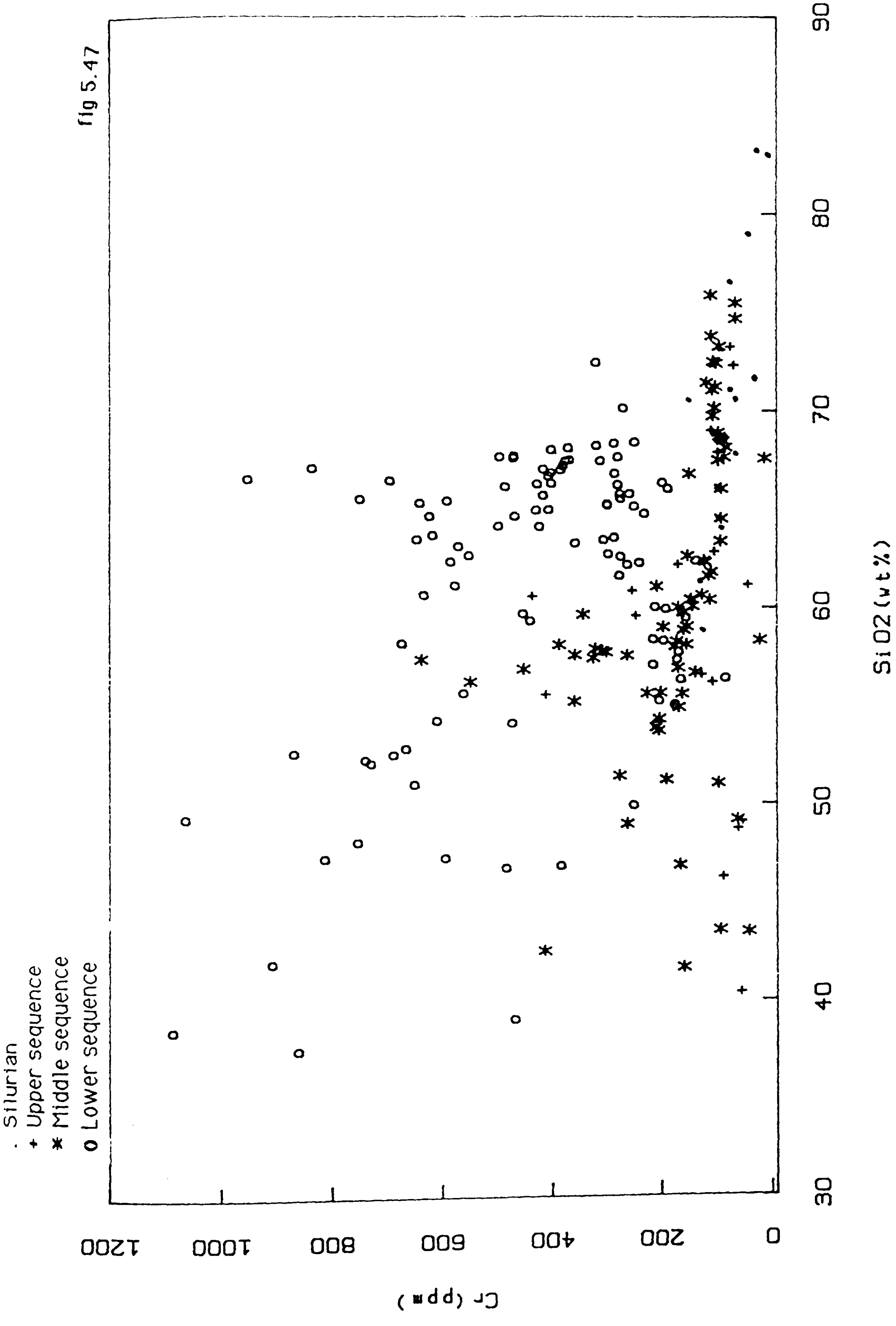

. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
Ba (ppm)
SiO2 (wt%)
0
200
400
600
800
1000
30
40
50
60
70
80
90

fig 5.46


. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
Zr (ppm)
0
100
200
300
400
SiO2 (wt%)
30
40
50
60
70
80
90



. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
Cr (ppm)
0
200
400
600
800
1000
1200
SiO2 (wt%)
30
40
50
60
70
80
90

fig 5.47

fig 5.49

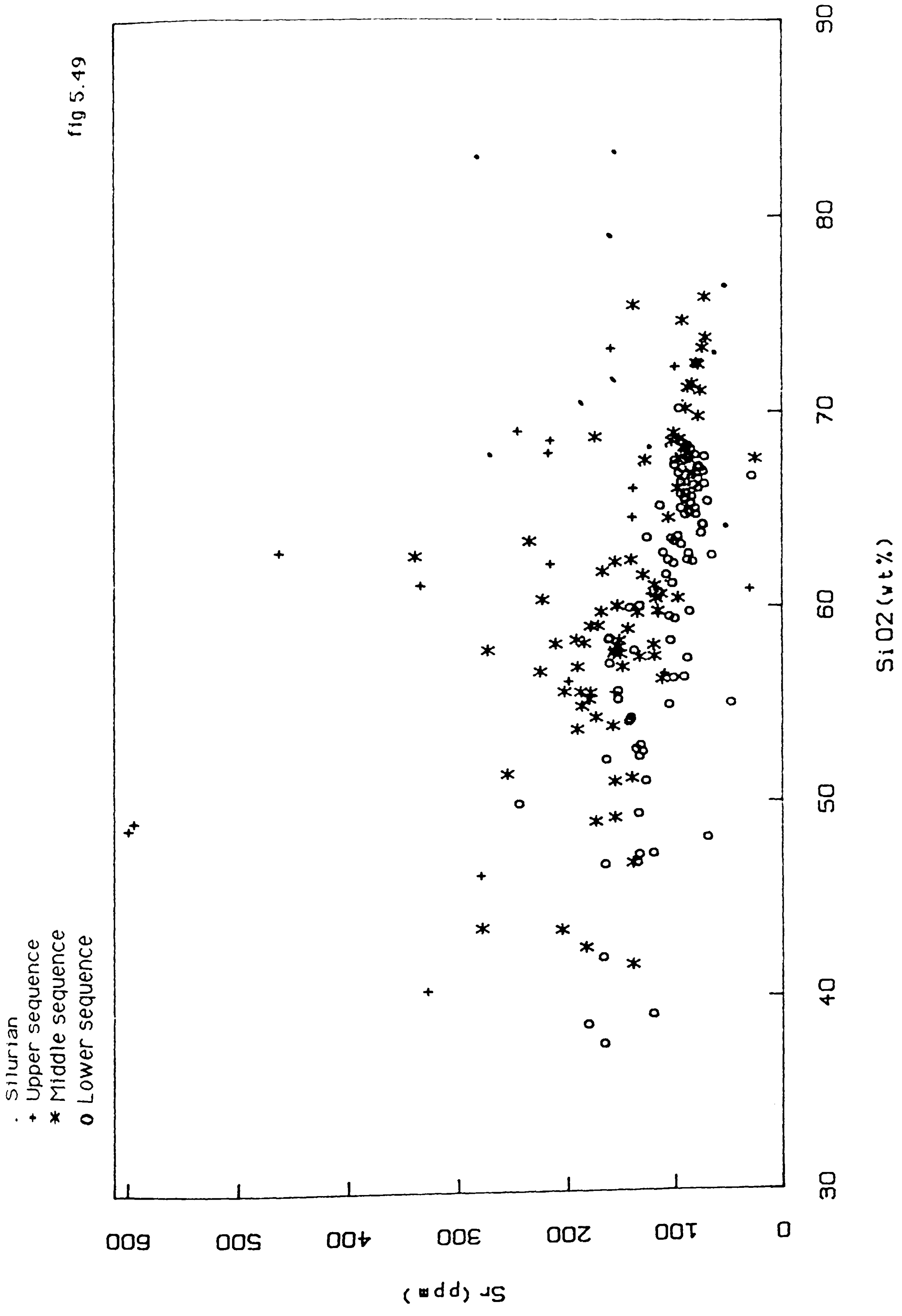
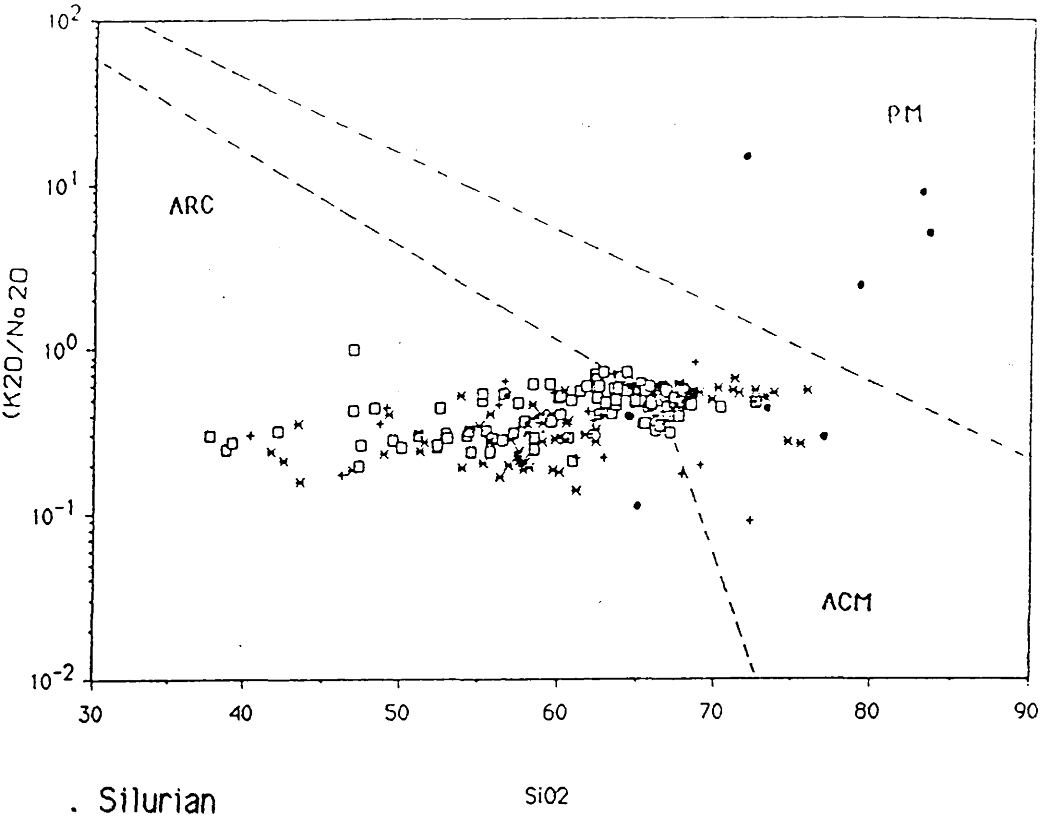

. Silurian
+ Upper sequence
* Middle sequence
o Lower sequence
SiO2 (wt%)
30
40
50
60
70
80
90
Sr (ppm)
0
100
200
300
400
500
600

fig 5.50



. Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence

fig 5.51

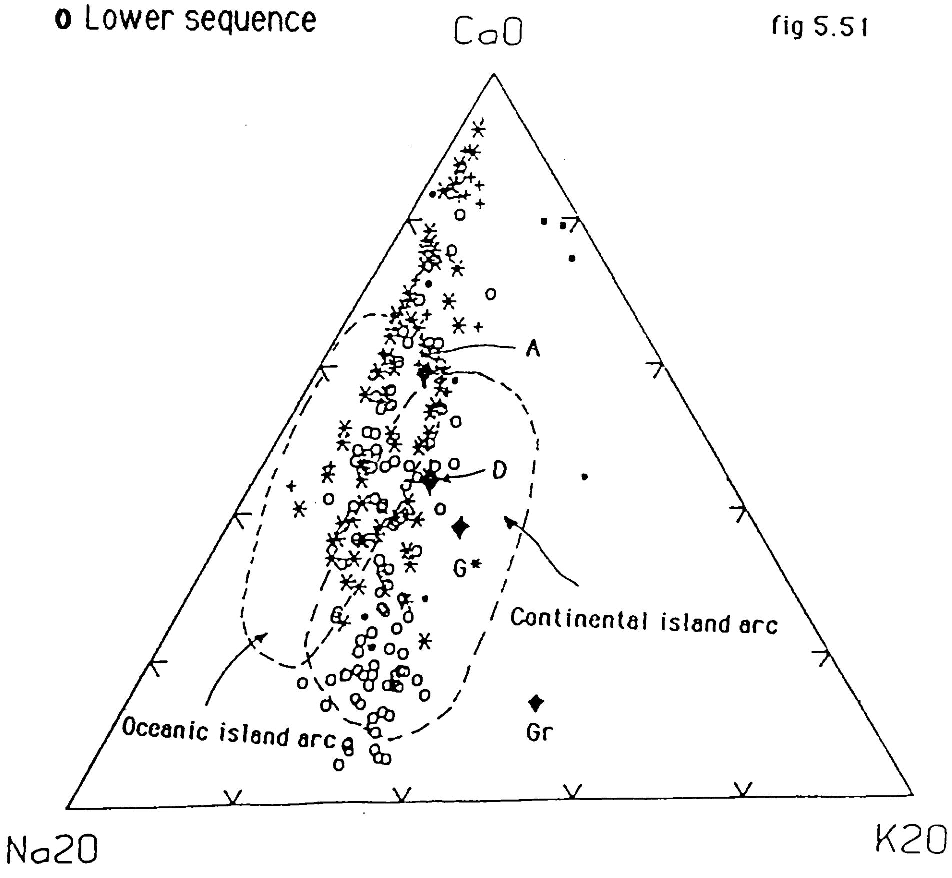


fig 5.52

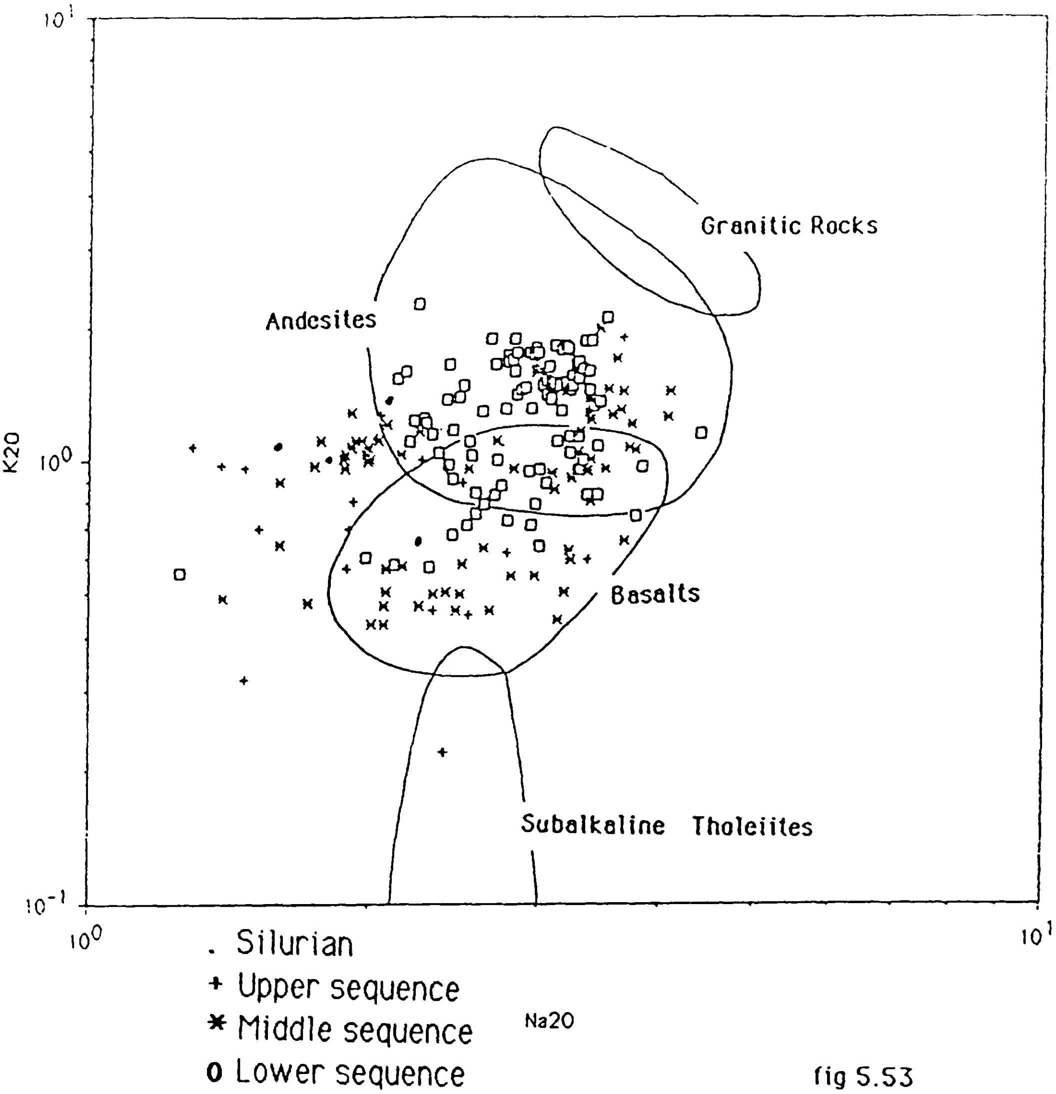


fig 5.53

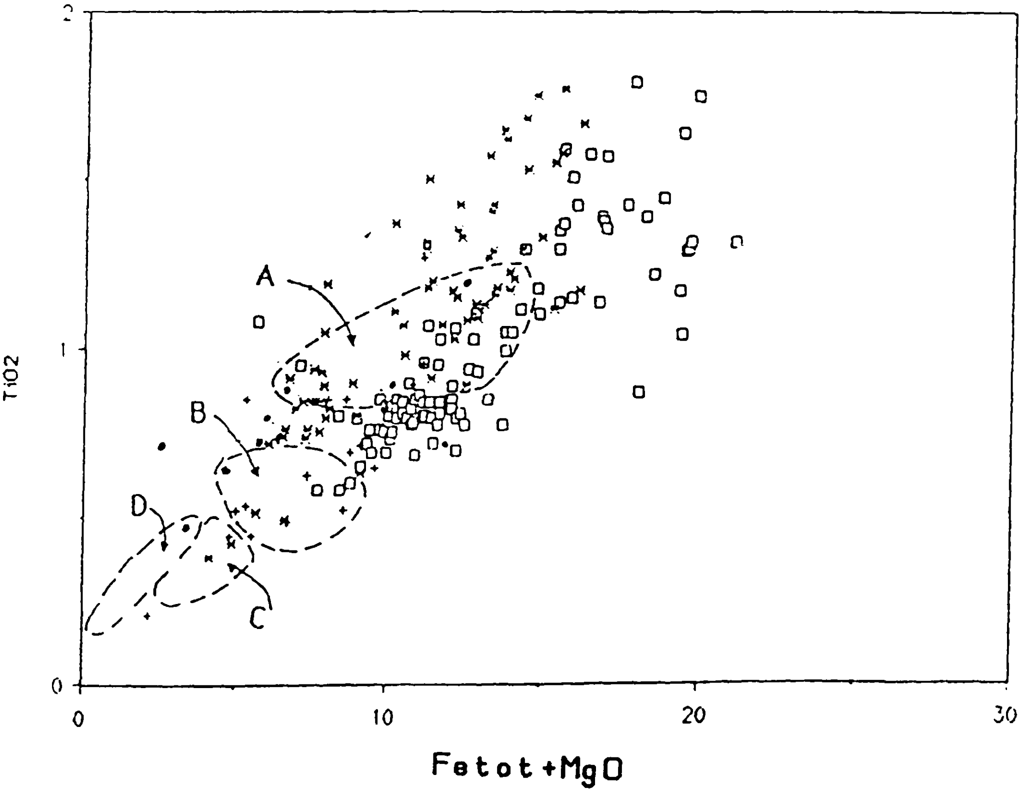


fig 5.54

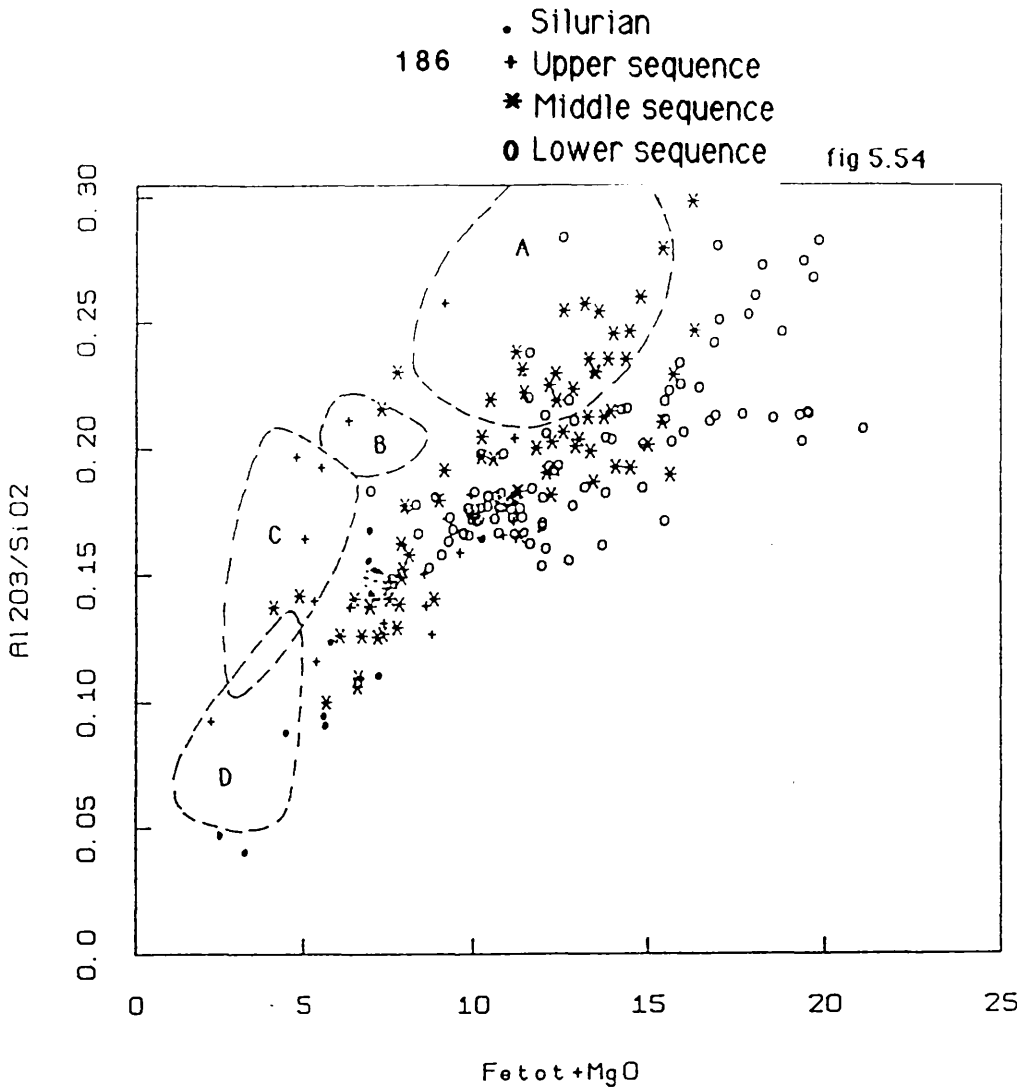


fig 5.55

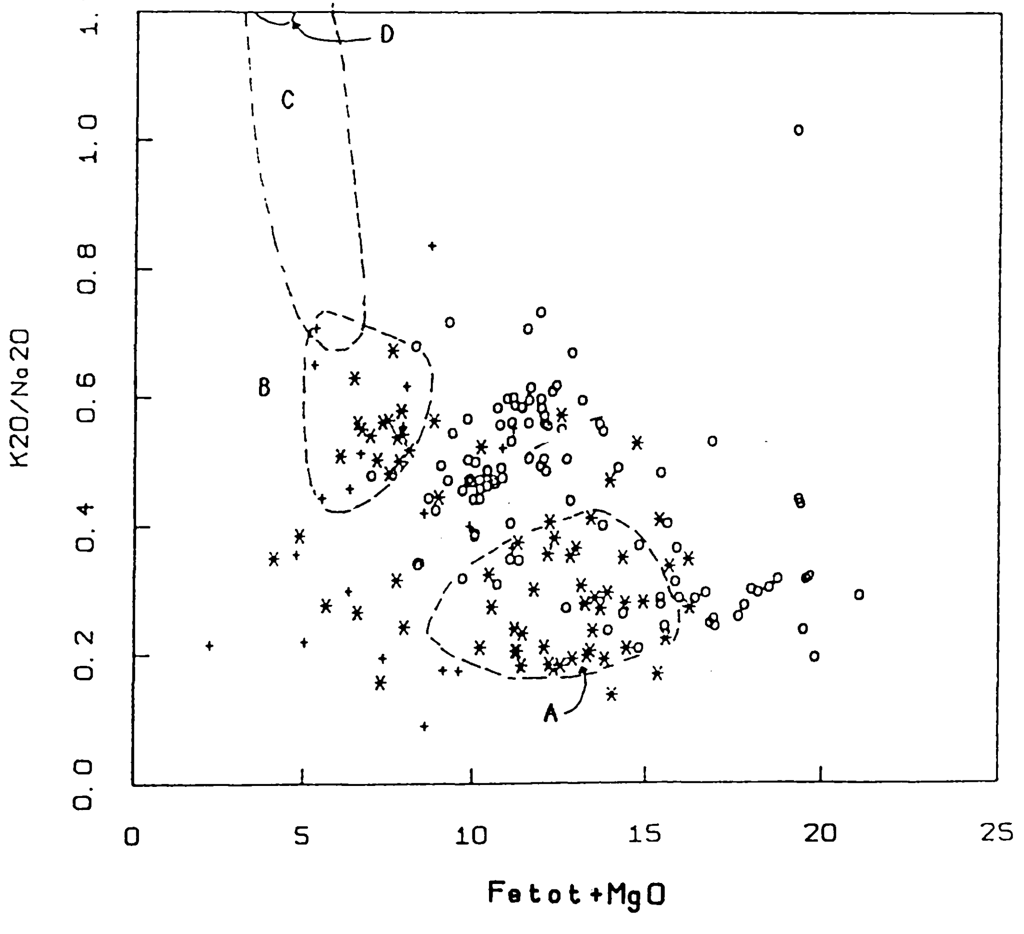


fig 5.56

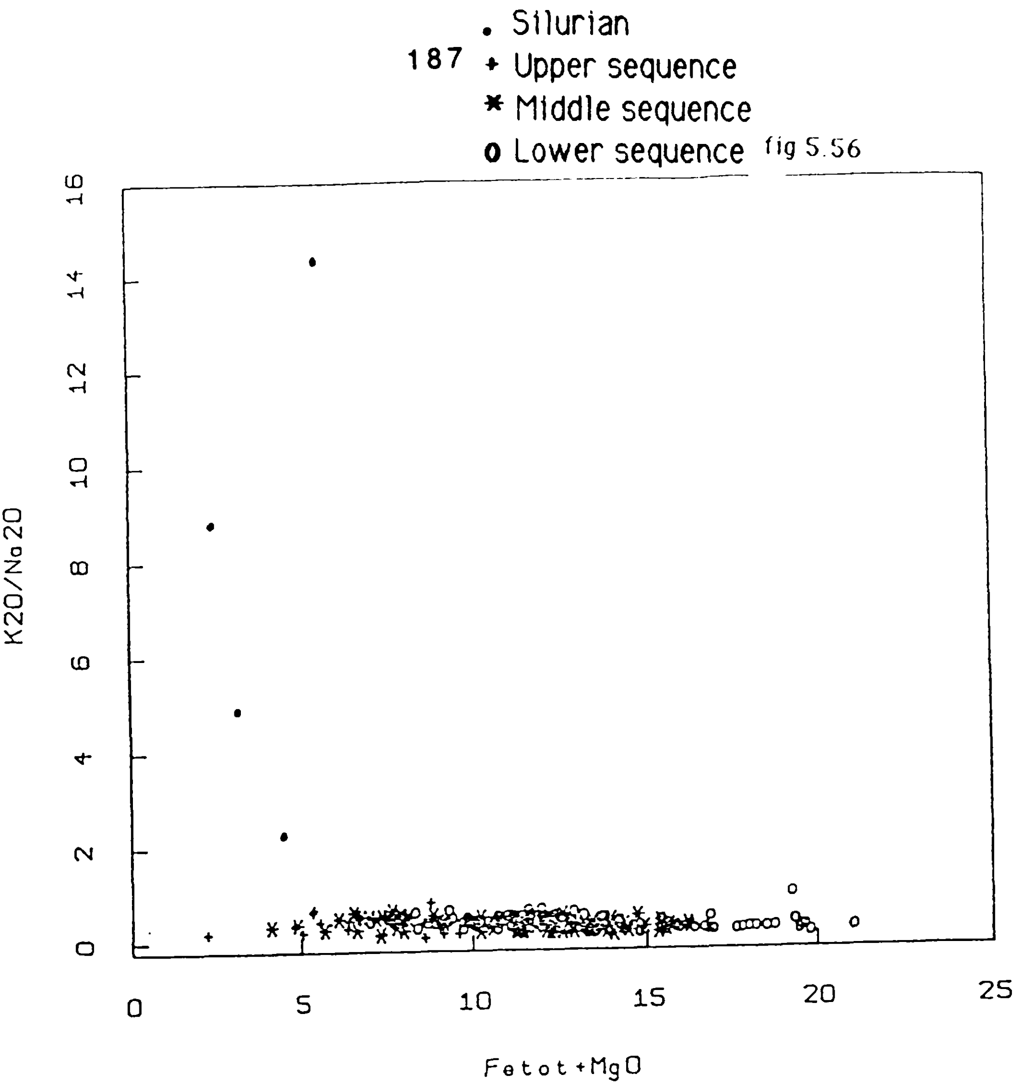


fig 5.57

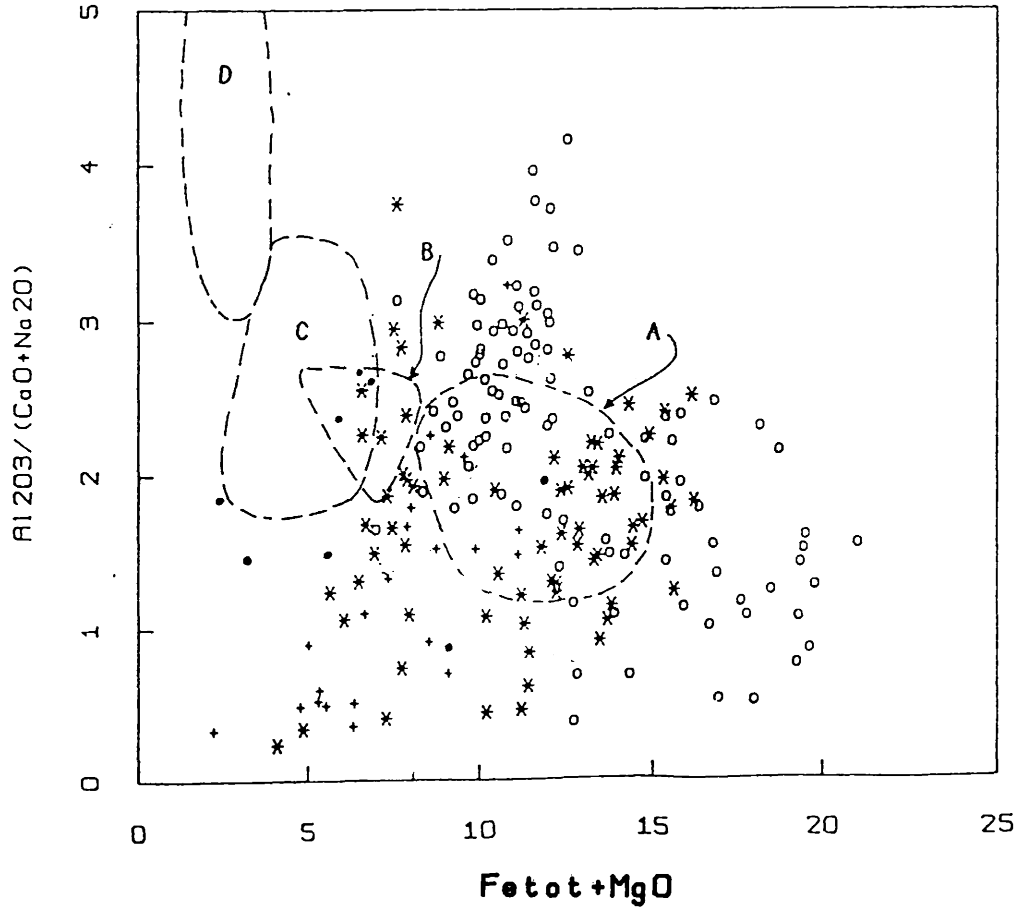
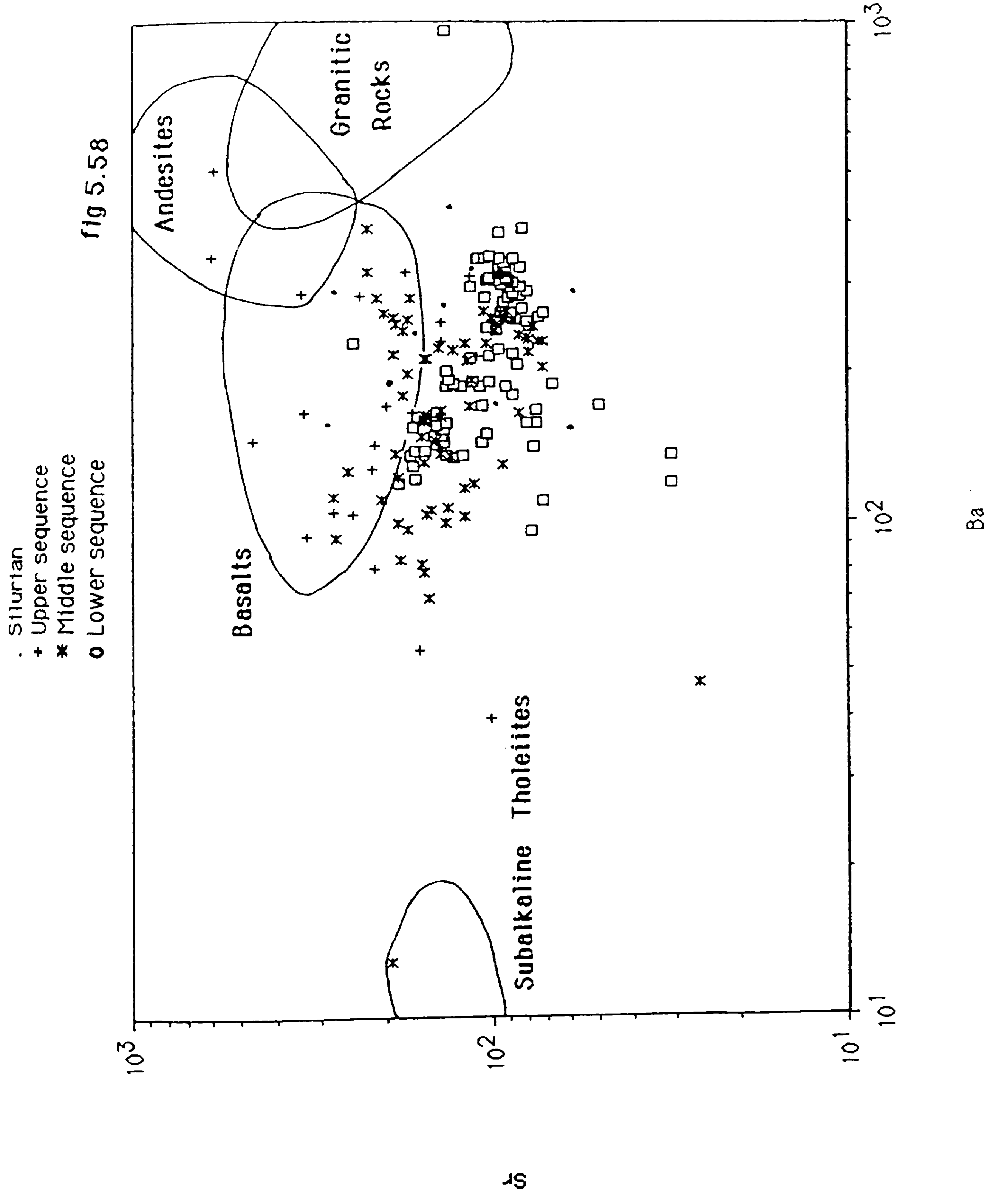


fig 5.58


· Silurian
+ Upper sequence
✱ Middle sequence
o Lower sequence
Andesites
Granitic Rocks
Basalts
Subalkaline Tholeiites
10^3
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10^1
Ba
Sr

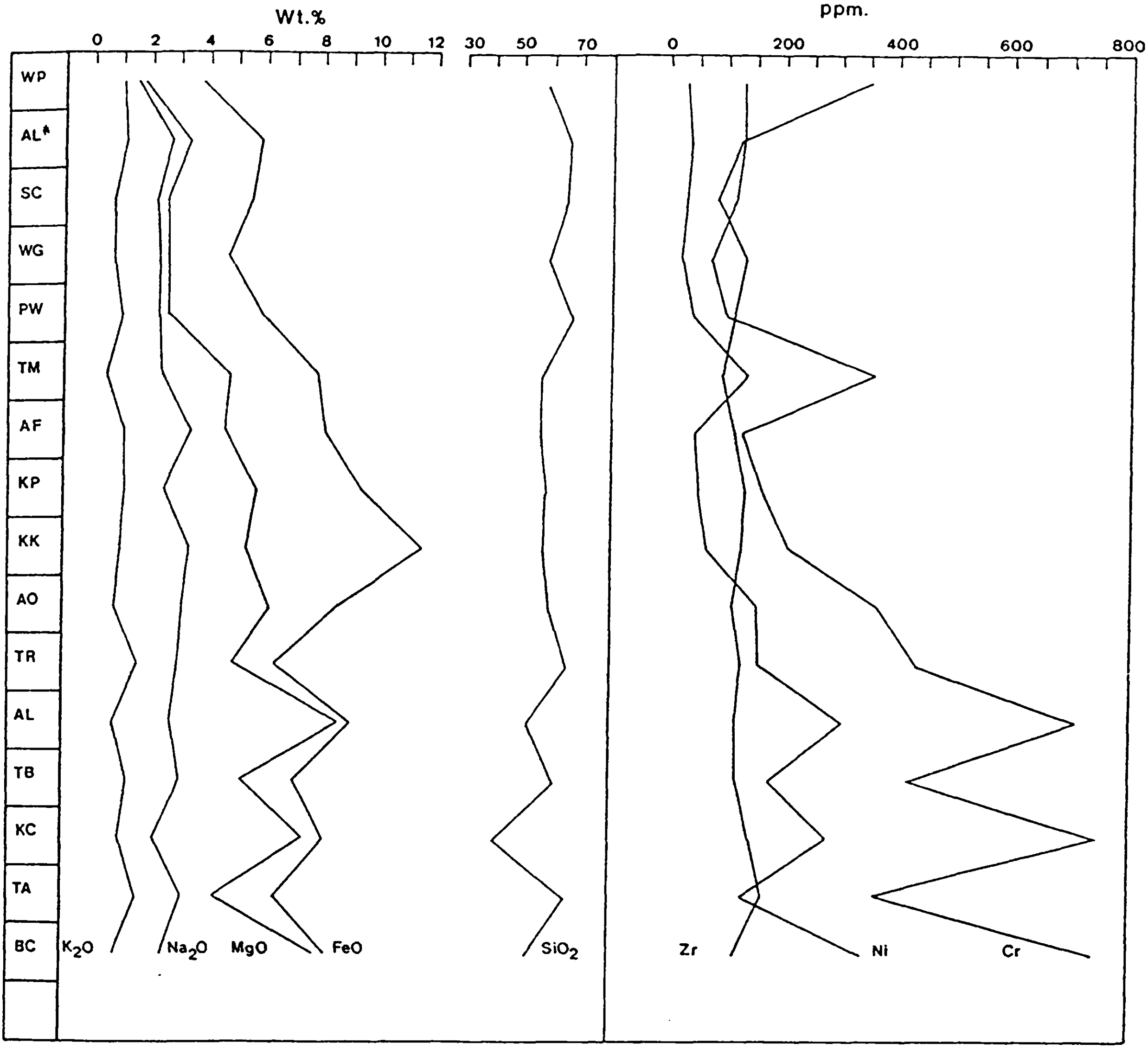


Figure 5.59: Vertical variability of some major and trace elements in the Ordovician rocks of the Girvan area.

CHAPTER SIX COMPARISON BETWEEN GIRVAN AND SOUTHERN UPLANDS

6.1-Introduction

The Southern Uplands of Scotland lies immediately to the south of the Midland Valley and is bounded on its north margin by the Southern Uplands Fault (hereafter referred to as SUF) and on its south by the Solway line. The Girvan area, which forms the main objective of the present research, is located immediately to the north west of the Southern Uplands and on the northern side of the SUF. As discussed previously (see chapter one and also below), the SUF is thought to be a terrane boundary dividing the accretionary prism of the Southern Uplands from the proximal forearc basin of the Girvan district (Bluck 1985). Whilst the dispersal patterns in the Girvan area are fairly clearly from the NW, dispersal in the Southern Uplands is far less clear. Evidence given in Kelling et al. (1987), Stone et al. (1987) and others show a wide variety of paleoflows in the Southern Uplands region. Uncertainties such as post depositional structural rotations, and deflections of turbidite flows in the trench (Leggett 1987) add greatly to the problem of determining dispersal. However, most authors accept that some, if not the bulk of the sediments there is either directly or indirectly dispersed from the NW the NW provenance of some of the Southern Uplands sediments is accepted.

However, some limitations, due mainly to the fact that all the data of Southern Uplands have to rely entirely on the published work, can complicate some of the interpretations particularly because of the number of minerals point counted and the reliability of the counting processes performed by different authors in petrography and differing analytical methods for the various elements and/or differing precisions and accuracies particularly for the trace elements in geochemistry. Further complications also arise from the fact that sampling by different authors can differ considerably but in all the investigations carried out below, it is assumed that the above mentioned complications do not substantially affect the conclusions reached.

In the sections below, a comprehensive summary to the various tectonic interpretations proposed for the Southern Uplands is first discussed followed by the differences in petrography, geochemistry and vertical variability and finally a discussion is held and inferences are drawn

6.2-Tectonic settings of Southern Uplands.

The Southern Uplands, which consist broadly of greywacke and shale with thin slivers of basic igneous rocks associated with black shales, is divided stratigraphically into three units namely: Southern, Central and Northern belts (Peach and Horne 1899; Leggett et al. 1979b; Morris 1983). The Southern Belt is composed of Wenlock greywackes and shales some of which contain graptolites (Warren 1964; Kemp 1984). The Central Belt consists of greywackes overlying a condensed Moffat Shale succession of Mid-Ordovician to Llandovery shales, ashes and cherts. In the Northern Belt, which is of Ordovician age, mafic volcanics, bedded cherts and in some places, graptolitic shales are interbedded with and underlie the greywackes.

The concept of an accretionary prism model developed progressively. Comparison of Burma with Scotland lead Mitchell and McKerrow (1975) to suggest that the greywacke sequence in the Southern Uplands was like Burma where trench and oceanic sediments are being underthrust by subduction processes. With later development of modern analogues from the Pacific (Seely et al. 1974; Karig and Sharman 1975), the model was applied with more emphasis by Mckerrow et al. (1977) and subsequently Leggett et al.(1979 (a,b), 1982) (see Figure 6.1). The region is truncated by a number of strike faults which are thought to be rotated reverse faults (e.g. Fyfe and Weir 1976, McKerrow et al. 1977, Weir 1979, Cook and Weir 1979) and Some of these reverse faults can be used to divide the Southern Uplands into 'tracts' or 'blocks', ten of which are recognized by Leggett et al. (1979) and six by Walton (1983). Some of these tracts are graphically summarized in Figure 6.2 (after Bluck 1985). Whatever the divisions, McKerrow et al. (1977) noted that the sediments within each block young to the NW but the blocks get younger to the SE.

The accretionary prism model of McKerrow et al. (1977) is supported by: (i) the association of turbidites and black shales,(ii) the opposite directions of younging of the over all succession compared with that within each block (ii) the fact that the direction of the blocks younging coincides with the direction of progressive younging in the base of the Ordovician greywacke pile. Leggett et al. (1979), Eales (1979), Leggett (1980), Leggett et al. (1982,83), Kemp et al. (1985) and others have also produced evidence to support the concept of an accretionary prism. Additional support for the accretionary prism comes from the evidence for burial and tectonic modifications to earlier slices of the accretionary prism. Silurian greywackes contain clasts of greywacke which had undergone prehnite-pumpellyite grade metamorphism and Silurian conglomerates contain fragments of cleaved black shale. These are inferred to have come from an earlier (Ordovician) accretionary prism (Bluck 1985), thus suggesting that older slices of the prism were being re-worked into younger parts such as is happening in present day regimes of this kind.

Moseley (1977-1978) was one of the first to express doubts about the model; he believed that the Iapetus Ocean had closed by the end of the Ordovician and thus like many others subsequently, had difficulty in accepting Silurian subduction of ocean floor. More recently, Anderson and Oliver (1986) Hutton and Murphy (1987) noted that the Northern Belt and the combined Central and Southern belts are two separate tectonostratigraphic terranes which were juxtaposed in the late Silurian-early Devonian. Hutton and Murphy (1987) cited evidence to show that in the central inliers of Ireland, the derivation of Llandovery sediments was from both north and south of the remnant Iapetus; by contrast, the Wenlock sediments were derived from an arc to the north and propagated across the suture. These authors believe that this arc has subsequently been cut out by strike-slip along the line of the Orlock Bridge fault at the end of the Silurian and that there is no evidence for subduction of oceanic crust after the Late Ordovician.

Evidence from some sequences which contain southerly derived tubidites with fresh andesitic detritus (which suggest an arc situated to the south of the Southern Uplands) and northerly derived turbidites which are quartz-rich, led Stone et al. (1987) to suggest a back-arc setting for the Southern Uplands with a mature continental landmass to the north and a rifted continental fragment containing an active volcanic arc to the south. They also thought that the Hawick Group and the Wenlock sequences of the Southern Belt may have been deposited in a southward-migrating foreland basin ahead of the rising thrust stack. Morris (1987) recognized a distal continental source region to the NW of the Northern Belt in the Longford-Down massif and a proximal arc source to the south, concluding that, the Northern Belt sediments were developed in a back-arc setting which closed at the end of the Ordovician (see Figure 6.4)

More recently Kelling et al.(1987) produced new sedimentological and biostratigraphical data from the Rhinns of Galloway and adjacent areas to show that a series of submarine fans developed from the northwestern margin of an assymetrical basin during the Late Ordovician and Early Silurian while pelagic facies were accumulating further to the SE. They conclude that during the Late Ordovician an active continental margin arc was juxtaposed against the Southern Uplands forearc trench; SE propagating fans were formed in a relatively narrow trench at the same time as a coarse volcanilithic sediment apron migrated northeastward as the arc was displaced relative to the trench. By Llandovery time, the forearc trench region was dominated by a variety of fan systems which were all derived from the NW. It is therefore clear that while these authors generally opt for a forearc/trench setting throughout the development of the Southern Uplands accretionary history; they added an arc to seaward during the Late Ordovician (see fig 6.3).

However, whatever the tectonic interpretation given to the Southern Uplands terranes, the main aim of this chapter is not affected and comparisons between Southern Uplands and Girvan can still be made and are given below. However, since some of the sediment (at least) is derived from the south, then a source is available to the Southern Uplands which is not seen in Girvan (where all the sediment comes from the NW)

6.3-Objective of study

Data have already been given to support the view that the Girvan sequence is part of a proximal forearc basin. On the other hand, there is less consensus over the tectonic regime in which the Southern Uplands formed as discussed above.

The main objectives of this chapter are therefore to assess:

1- If the Southern Uplands and Girvan area shared a similar or the same provenance

2- To establish if both regions showed a similar vertical change in petrography and geochemistry and could therefore belong to the same basin or dispersal systems, or otherwise be supplied with sediment from a provenance which underwent a similar kind of evolution..

3- To evaluate recent views (e.g. Elder 1988) that the SUF is a major fracture with 1500km of lateral displacement, and the Southern Uplands had a provenance which was unlike that of the Girvan .

6.4-Petrographic differences

There is no general published petrographic vertical variability of the Southern Uplands greywackes and sandstones; although both Floyd (1982) and Bluck (1985) have presented a rough correlation between different formations previously studied. Figures 6.2 and 6.5 show that it is possible to correlate petrographically similar greywackes over a wide geographical area. However, the detailed biostratigraphy is as yet poorly known, and there is still much structural complexity which is unresolved. It may be that future work may be able to demonstrate diachronism in the section, as has been done for one formation by Kelling et al. (1987).

The vertical time evolution of the Ordovician rocks have been studied by Kelling (1962), Kelling and Holroyd (1978), Floyd (1982) and Hepworth et al. (1982). Those of the Silurian rocks have also been extensively investigated by a number of authors among others Walton (1955), Warren (1963), Cook and Weir (1980), Kemp (1984), Hutton and Murphy (1987). The petrographic descriptions and vertical variability of the Ordovician suites can be best studied by summarizing one of the most up to date papers; that of Floyd (1982) on West Nithsdale especially as this work does not differ substantially from the work presented by Hepworth et al. (1982) on Bail Hill-Abington area.

In West Nithsdale, Floyd (1982) recognized five formations based on lithological and petrographical criteria obtained from detailed studies of greywackes. The description of the formations is given below in order of younging age and are portrayed in Figure 6.5 for easy matching with other formations. The petrographies of the different formations are also compared with each other in table 6.1.

1-Marchburn Formation [Llandeilo]

This formation (1300m thick) consists mainly of greywackes, laminated siltstones and grey shales with only minor amounts of conglomerate, chert and volcanic rocks. The lower parts of the succession are composed of fine-grained greywackes, laminated siltstones and shales with calcareous nodules. The beds become coarser-grained and conglomerates with small cobbles of greywackes and mudstone. This clastic sequence gives way upwards to a chert and volcanic sequence beginning with pale grey bedded cherts , followed by red chert with thin spilite lava flows and volcaniclastic rocks and ending with red cherts, sandstones and mudstone, Asecond, thinner, volcanic sequence of spilitic lavas, agglomerates and associated red cherty sandstones and mudstones follows and is best seen in Park Burn just E of Over Cairn farm. These are succeeded in turn by medium-to coarse-grained greywackes containing prominent fragments of red chert. An unrepeated succession with two volcanic horizons is supported by the presence in the intervening greywackes of many fresh pyroxene fragments.

2-Afton Formation [Caradoc]

This formation, which is about 2000 m thick, is distinguished from the previous one by its much higher quartz content, paucity of ferromagnesian minerals and absence of any chert interbedded with greywackes. Instead, it is composed chiefly of thinly-bedded greywackes interbedded with laminated siltstone and grey shale, and is characterized by the rarity of conglomerates and even coarse-grained greywackes. The greywackes are composed mainly of spilites, quartzites and mica schist rock fragments.

3-Blackcraig Formation (1500 m)[Caradoc]

The lower parts of the succession consists mainly of massive, medium to coarse-grained greywackes containing occasional patches of small pebbles. This unit is succeeded by coarse-grained greywackes and boulder conglomerates. The boulders contain acidic rock fragments with gabbros, spilites and dolerites.

4-Scar Formation (1000-2000 m)[Upper Caradoc]

The dominant lithology is medium- to coarse-grained greywacke in massive units, often enclosing pebbly patches composed of fragments of dark shale and white quartz. The rock fragments are dominated by hornblendites, andesites and rhyolites.

5- Shinnel Formation [Upper Caradoc-Lower Ashgill]

This formation (≥300 m thick) is composed of fine- to medium-grained, thiny bedded greywackes, laminated siltstones and grey shales. The greywackes, which usually display prolific small-scale ripple cross- stratification, are interbedded with massive boulder conglomerates. The boulders contain spilite and gabbro clasts, greywackes and acidic igneous rocks.

Table 6.1: Summary of the petrography of the greywackes in West Nithsdale (after Floyd 1982)

Formation	Lithic fragments	Detrital fragments
Shinnel	granodiorite, granophyre, rhyolite, felsite, spilite, quartzite, shale.	quartz (57%), feldspar, zircon, apatite.
Scar	hornblende, andesite, rhyolite, spilite glaucophane schist, garnet schist, shale.	quartz(20%), feldspar, clinopyroxene, hornblende, garnet, epidote, glaucophane, spinel.
Blackcraig	granodiorite, granophyre, diorite, gabbro, dolerite, spilite, greywacke.	quartz(33%), feldspar, clinopyroxene, epidote, hornblende.
Afton	spilite, quartzite, garnet schist, biotite, schist.	quartz(48%), feldspar, garnet, zircon.
Marchburn	Microgranite, rhyolite, felsite, andesite, gabbro, spilite, serpentinite, chert.	quartz(15%), feldspar, apatite, clinopyroxene, hornblende, spinel.

Floyd (1982) also formally compared the vertical variability of West Nithsdale with other parts of Southern Uplands of roughly similar ages. This comparison is given in table 6.2. below:

If,

* Basic-clast Division and Acid clast Division

** Upper Barren Division, Meta-clast Division and Lower Barren Division

*** Conglomeratic Division and Flaggy Division

Then:

Table 6.2 : Correlation between West Nithsdale and other Southern Uplands areas along strike (after Floyd 1982)

Rhinns of Galloway (Kelling 1961)	**NW Wigtonshire** (Welsh 1964) and SW Ayrshire	**West Nithsdale** (Floyd 1982)
Portayew Rocks	Boreland Rocks	Shinnel Formation
Portpatrick Group*	Glenwhan Rocks	Scar Formation
Galdenoch Group	Cairnerzean Rocks	Blackcraig Formation
Kirkcolm Group**	Upper Lochryan Lower	Afton Formation
Coreswall Group***	Glen App Formation (Walton 1961) Traboyack Division (Williams 1962)	Marchburn.Formatio

* Basic-clast and Acid clast Division ** Upper Barren, Meta-clast and Lower Barren *** conglomeratic Division and Flaggy Division

Kelling et al. (1987 p 801) demonstrate that a petrographically distinctive greywacke suite (with a Portpatric type petrography) gets younger in the sequence when traced to the NE. And that despite substantial lateral changes in thickness of the greywackes the petrography is generally uniform. This therefore increases the degree of confidence in the Ordovician vertical variability of Southern Uplands based on Floyd's investigation.

The Silurian rocks of the Southern Uplands are compositionally less variable than their Ordovician equivalents and can be summarized from the work of Warren (1963) on the Wenlock Rocks, Roxburghshire and Cook and Weir (1980) on Cairnsmore of Fleet, Gollaway. The work of Hutton and Murphy (1987) on similar rocks from Ireland was mostly concerned with Silurian tectonic evolution rather than stratigraphy and hence has not been considered.

Warren (1963) noted the Silurian greywackes consist of quartz, plagioclase and K-feldspars, muscovite, biotite, chlorite, opaques (magnetite, ilmenite, pyrite), garnet, zircon, tourmaline, apatite, rutile and secondary carbonate (calcite, dolomite, ankerite). The rock fragments present are given below in table 6.3. It should be noted however, that acidic igneous rock fragments are the most dominant components in the coarse-grained greywackes. Cook and Weir(1980) showed the Silurian rocks of Cairnsmore of Fleet to be to composed of turbidites of dominantly acidic igneous rocks with only witth rare lithic greywackes. Thick sequences of interbedded and ungraded arenites and argillites are also typical of these .rocks.

Table 6.3: rocks fragments present in the Wenlock Rocks, Roxburghshire (after Warren 1963)

sedimentary

chert, shale and siltstone, greywacke, arkose, limestone.

metamorphic

vein quartz, quartzite, chlorite and mica-schist, chloritite.

Igneous

granite(or granodiorite), granophyre, quartz keratophyre, spilite, rhyolite, quartz porphyry, keratophyre, andesite.

From the work of Warren (1963) and Walton (1955) (abundance of acid lavas) and Cook and Weir (1980) (abundance of granitic rocks) it became clear that more differentiated magmatic material was introduced to Southern Uplands through Silurian times.

Inspection of table 6.1 shows that the low quartz contents in the Marchburn Formation (15%) rise significantly in the Afton Formation (48%) and Blackcraig Formation (33%) before tending to decline in the Scar Formation (20%). Quartz then rises sharply to 57% in the Shinnel Formation which should be compared to 15% in the Marchburn Formation. This therefore suggests that, in general terms, although quartz tends to fluctuate in the Scar Formation, it generally rises with younging age during the Ordovician times. The case of the Silurian rocks is more complex and only very few point counts are available from the Wenlock Rocks (Warren, 1963) which show that the quartz contents range from 8.9% to 31.9% suggesting diminution of quartz in passing from Ordovician to Silurian rocks, but probably this trend is caused by the small sample size studied by Warren (1963) and hence are thought unreliable.

Basic rock fragments are also present in some of the Ordovician rocks (e.g. Marchburn and Blackcraig formations) but the Shinnel Formations and Silurian rocks are poor in basic rock fragments and the opposite is true for the acidic rock fragments which therefore indicates that there is an increase in the degree of acidity in passing from Ordovician to Silurian times.

The other important aspect of the Southern Uplands is the presence of metamorphic rock fragments. These are represented by grains of quartzite, quartz-, chlorite-mica-schists, garnet, staurolite and glaucophane schists (Kelling 1962, Warren 1963, Holroyd 1978, Floyd 1982). This therefore suggests contributions from low to medium regionally metamorphosed terranes. However, the presence of blue-schist fragments suggests a provenance in high pressure-low temperature metamorphic rocks such as those now present at Ballantrae (Bluck 1985). Sanders and Morris (1978) and Yardley et al. (1982) have postulated a regional blue-schist facies development over parts of the Dalradian outcrop. However, Bluck (1983, 1984, 1985) and Watson (1984) both thought the Dalradian rocks to be a very unlikely source because they believe the Highland Border Complex was situated between the Dalradian and Southern Uplands outcrops during Ordovician times especially as the rocks Highland Border Complex are themselves free of blue-schist-detritus Bluck (1985) suggested a new source which he believed to have been located in the Midland Valley of Scotland at least during Ordovician and Silurian times.

Comparison of chapter four with the previous summary clearly suggests that there are some similarities and differences in the petrography and vertical variability between Girvan and the Southern Uplands. (1) Both terranes share many lithic fragments and detrital minerals. These include mafic and ultramafic, dolerite, andesite, granodiorite, rhyolite, granite, granophyre, chert, quartzite, quartz, feldspar, epidote, spinel, zircon, apatite, and ± garnet. (2) They do not share glaucophane and blue-schist fragments. (3) Both show a vertical change in composition from Ordovician to Silurian: (a) Mafic and ultramafic clasts are common in the lower sequence in both areas; (b) Acidic clasts get more common upward in the sequence; (c) quartz becomes more common upward. (4) The vertical increase in granitic rock fragments recorded in the Silurian of the Southern Uplands is not seen in the Girvan district but this may be due to the fact that only the Llandovery rocks have been studied. A comparison between the two areas is made more difficult by the fact that some of the greywackes in the Southern Uplands come from the south.

The QFL diagram as illustrated in Figure 6.6 shows that the Ordovician and Silurian rocks from the two areas plot distinctly from each other indicating different sources. Much of the Ordovician rocks of the Southern Uplands were derived from undissected magmatic arc compared to a fairly dissected and mixed magmatic arc for similar rocks from Girvan; although it is very interesting to note that some data do overlap with each other.

From the above points the following inferences are drawn:

1-Both regions shared a fairly similar type of source terrane which had mafic and ultramafic (probably ophiolitic) component; a volcanic-plutonic component (probably an arc) and a basement component.

The ophiolitic component could have come from the widespread c 480 Ma obducted ophiolite sheets which typified the southern Laurentian margin from the Appalachais to Norway (Dunning and Krogh 1985). In this case the position of the Southern Uplands relative to its source could be anywhere along the Laurentian margin.

The presence of arc detritus offers no less a constraint to the relative positions of the Girvan and Southern uplands sequences. Arc-type detritus typifies the greywackes of Ireland (Sanders and Morris 1978) and Lower Paleozoic rocks in Central Newfoundland and Gasp have arc type rocks or have a provenance in arcs (Hiscott et al. 1986). Either the sequence at Girvan or the Southern Uplands could therefore acquire arc detritus from the width of this orogen.

The distribution of basement detritus is equally uncertain. Detritus from the basement which is probably not of Dalradian Origin in the Southern Uplands (Kelley and Bluck 1989), and basement detritus appears in greywackes from Ireland (Sanders and Morris 1978) and from Central Newfoundland (Colman-Sadd and Swindon 1984). In all the places listed above, the basement detritus is mixed with arc and ophiolitic sediment as at Girvan and within the Southern Uplands.

2-Both regions generally evolved in the same way. From basic rocks dominated by low quartz to acid rocks dominated to high quartz greywackes.

3-However, there are sufficient numbers of important differences to suggest that both regions may not have shared exactly the same source. These include the the blue- and glaucophane-schists being absent from the Girvan sequence, the greywackes of rather were derived from the north whereas those of Southern Uplands were derived from a source to the south.

6.5-Geochemical differences

Much of the work carried out on Southern Uplands dealt mainly with the petrography of the rocks and only very few workers (e.g. Alsayegh 1971, Floyd 1975, Haughton 1988) paid special attention to the importance of the geochemistry in solving tectonic problems. As discussed above, from the work of Alsayegh 1971, Floyd 1982 and Bluck 1985, it is now clear that lateral changes in Southern Uplands are insignificant and therefore a geochemical study from one or two areas would clarify the geochemical trends within Southern Uplands including the geochemical vertical variability in passing from the Ordovician to Silurian times.

The most intensive geochemical (major and trace elements only) investigation undertaken on Southern Uplands was that of Alsayegh (1971). A total of 303 samples of greywackes and sandstones were collected from the Lower Paleozoic with most of the sampling from the Upper Ordovician rocks in the Rhinns of Galloway. The rest of the sampling was from four traverses running roughly parallel to the Rhinns of Galloway, perpendicular to the strike of the area and 5-15 km apart from each other. Sample locations, their petrography and whole rock geochemistry as well as the exact location of the traverses are not discussed here but can be found in Alsayegh (1971). In the sections below, an attempt is made to investigate the geochemistry of the Southern Uplands rocks as a guide to the provenance areas and tectonic settings because this kind of work has not been done due to the late appearance of some methods (Bhatia 1983, Van de Kamp and Leake 1985, Roser and Korsch 1986). The geochemical vertical variability is also considered.

6.5.1-Major and trace elements differences

Comparison of Figure 6.7 to 6.11 with their equivalents in Figures 5.50 and 5.53-57 in Chapter 5 show that the lowest and highest SiO2 contents are found in rocks from Girvan compared to their age equivalents in Southern Uplands thus reflecting greater heterogeneity in terms of their silica contents. Southern Uplands greywackes also generally have higher -but narrower range- Al2O3/SiO2 ratios and this trend is expected because of their general tendency to be lower in silica but richer in alumina compared to those from Girvan. Further, Girvan greywackes have much lower Al2O3/(CaO+Na2O) ratios than those from the Southern, Uplands which reflects a smaller range in composition in terms of alumina-rich components, The similar range of Fetot+MgO suggests that both suites are rich in basic and ultrabasic components, particularly the Ordovician rocks compared to the Silurian greywackes in both areas. It is also to be noted that both the Ordovician and Silurian rocks of the Southern Uplands have very high K2O/Na2O ratios compared to Girvan. This trend in probably related to the abundance of metamorphic rock fragments which are dominantly biotite- and muscovite-rich fragments (Alsayegh 1971, Floyd 1982).

It is unfortunate that the most important mafic elements (e.g. Cr, Ni, Co) have not been determined by Alsayegh (1971) but the available data as can be seen from table 6.4, show that there are some differences between Girvan and Southern Uplands greywackes of similar ages. Caradoc rocks of Girvan are lower in K, Rb, Ba, and to a lesser extent Zr and Sr but they tend to be richer in Ca compared to their equivalents in the Southern Uplands. Those rocks deposited during the Ashgill at Girvan are also poorer in K, Fe, Mg, Rb, Ba, Ga and to a lesser extent La, Ce and Y and again they are richer in Ca relative to those deposited in Southern Uplands. During the Llandovery, the Girvan rocks remain poorer in K, Rb, Mg, and also Ca but become richer in SiO2 compared to those of Southern Uplands. While Ca is thought to be related to calcite-rich cements, the enrichment of the Southern Uplands greywackes in K, Rb, Ba, La, Ce etc is clearly related to the presence of metamorphic rock fragments. The remaining elements are inconclusive because they are statistically insignificant.(i.e. very large standard deviations).

6.6-Differences in tectonic settings based on geochemical evidence

This step has not been previously investigated and therefore the data of Alsayegh (1971) have been used to reconstruct the tectonic settings of Southern Uplands sediments based on whole rock geochemistry. Comparison of these tectonic fields with those of Girvan is then discussed. For this purpose, Southern Uplands data have been reported on the plots suggested by Bhatia (1983) and Roser and Korsch (1986) (Figures 6.7-11) which have already been explained in Chapter 5. It should be mentioned that 75 Southern Uplands Wenlock greywackes (from Alsayegh 1971) are also included in the plots.

From Figure 6.7 it is clear that almost all of the data fall between active continental margin (ACM) and passive margin (PM) with only 12 Silurian and one Ordovician greywacke falling in the oceanic island arc field (ARC). This trend is also highlighted by the Bhatia's diagram of K2O/Na2O versus Fetot+MgO (see Figure 6.10) where, contrary to the other plots, all data plot outside the fields of ARC and CA. These trends can be caused in two ways; either the tectonic fields proposed by Roser and Korsch (1986) on the K2O/Na2O versus SiO2 diagram cannot be compared to Bhatia's diagrams or else the diagram is realistic but the trends exhibited are caused by the presence of some K-rich components in the Southern Uplands greywackes. The first possibility is extremely unlikely because as shown in Chapter 5 both, Bhatia (1983) and Roser and Korsch (1986) tectonic fields agree with each other and there is no explanation why these fields agree in one area but not in others. Further, even on the K2O/Na2O versus Fetot+MgO diagram of Bhatia's (1983), the data plot outside the ARC field which therefore still suggests good agreements between the two proposals. The only tenable explanation therefore, is that Southern Uplands greywackes are composed almost entirely of material derived from a magmatic arc.

Figure 6.12 shows that there is a positive correlation between TiO2 and K2O which indicates that much of K is held in biotite and probably also muscovite where present rather than dominantly held in K-feldspar. This indicates that the particularly high K2O/Na2O of the Southern Uplands greywackes (almost twice higher than those from Girvan) is due to the abundance of metamorphic rock fragments which are dominantly mica-schists (Alsayegh 1971, Floyd 1982). If 30-40% of K is subtracted from the total K assuming it is coming in metamorphic biotite and muscovite, then much of the data would fall between ARC and ACM. It can therefore be concluded that the magmatic arc material introduced to Southern Uplands during Ordovician and Silurian times was accompanied by ACM material in both times. The contribution from ACM does not seem to be supported by any of Bhatia's diagrams because none or only insignificantly few points do plot inside the ACM, PM or CA fields. This is expected because addition of metamorphic rock fragments particularly as mica-schists does not influence heavily the Al2O3, SiO2, CaO and Na2O compared to K2O.

It has been shown in Chapter 5 that even Bhatia's tectonic fields are not too realistic because of the small sample size used and their relative homogeneity. However, despite the just mentioned complications, it is very interesting to note that a large number of samples do indeed fall within the ARC field of Bhatia (1983) which suggests substantial contributions from magmatic arc material in both Ordovician and Silurian times. More importantly, a much larger number of samples do fall inside the the forearc field of van de Kamp and Leake (1985) derived from the greywackes of the Mesozoic of the Great Valley Sequence which supports the growing consensus that Southern Uplands rocks were deposited in forearc accretionary prism rather than in backarc regions.

There is no published geochemical guides to identify accretionary prisms based on whole rock geochemistry evidence but from the summary given exceptionally higher K20/Na20 ratios are probably the most diagnostic evidence can be deduced from Southern Uplands

Table 6.4: Geochemical comparison between Girvan and Southern Uplands.(values given betwen parentheses are actual wt% before recalculation to 100% on volatile-free basis)

GIRVAN

	1.Lland		2 L.Ashg		3. Carad		4 Llan	
	x	σ	x	σ	x	σ	x	σ
SiO_2	75.85	6.93	67.43	8.89	64.73	8.12	64.37	7.43
TiO_2	0.84	0.12	0.76	0.17	1.08	0.37	0.98	0.28
Al_2O_3	9.67	2.50	10.65	1.65	12.34	2.07	12.50	1.14
Fetot	5.24	1.63	5.63	1.47	7.12	1.7	7.9	1.80
MnO	0.08	0.02	0.20	0.15	0.15	0.14	0.2	0.63
MgO	2.40	1.30	2.70	0.93	4.14	1.51	5.80	1.88
CaO	2.78	1.92	9.12	5.97	5.90	4.62	3.63	3.50
Na_2O	1.94	1.02	2.46	0.64	2.90	0.72	3.07	0.45
K_2O	1.08	0.28	0.94	0.45	1.0	0.35	1.40	0.39
P_2O_5	0.12	0.02	0.09	0.06	0.12	0.03	0.15	0.19
Total	100		100		100		100	

SOUTHERN UPLANDS

	5 Carad		6 Ashg		7 Llandov	
	x	σ	x	σ	x	σ
SiO_2	64.09 (60.3)	4.6	59.04 (54.29)	2.43	60.62 (55.22)	2.93
TiO_2	1.17 (1.1)	0.2	1.00 (0.92)	0.13	0.77 (0.70)	0.12
Al_2O_3	13.92 (13.1)	1.8	13.61 (12.52)	1.09	11.69 (10.65)	1.54
Fetot	8.28 (7.79)	1.21	8.46 (7.78)	1.02	6.02 (5.48)	0.9
MnO	0.03 (0.03)	0.02	0.03 (0.03)	2.02	0.02 (0.02)	0.02
MgO	5.44 (5.12)	1.5	8.38 (7.71)	0.01	5.36 (4.88)	0.86
CaO	2.23 (2.1)	1.3	4.63 (4.26)	1.65	11.30 (10.29)	2.86
Na_2O	2.55 (2.4)	0.5	2.53 (2.33)	0.51	1.96 (1.79)	0.5
K_2O	2.12 (2.0)	0.6	2.15 (1.98)	0.58	2.10 (1.91)	0.41
P_2O_5	0.17 (0.16)	0.03	0.17 (0.04)	0.04	0.16 (0.15)	0.03
Total	100		100		100	

cntd

Table 6.4: Continued

GIRVAN

	1 Llandov		2 L Ashg.		3 Carado-		4 Llv-Lland	
	x	σ	x	σ	x	σ	x	σ
Rb	35	10	21	11	20	11	31	13
Ba	242	82	190	116	183	73	233	104
Sr	145	68	249	144	143	50	107	33
Zr	274	71	151	74	140	76	144	27
Ga	11	3	10	2	14	8	12	2
La	21	7	14	5	20	29	16	10
Ce	43	15	28	14	32	32	27	25
Y	26	10	26	7	30	25	26	3

SOUTHERN UPLANDS

	5 Carad		6 Ashg		7 Llandov	
	x	σ	x	σ	x	σ
Rb	63	19	50	14	75	17
Ba	645	270	659	237	257	74
Sr	316	240	370	149	131	45
Zr	278	94	190	52	248	65
Ga	17	2	17	2	14	2
La	33	10	21	6	24	3
Ce	66	20	44	10	56	8
Y	24	4	18	3	24	3

1 = average of 16 Llandovery samples (Girvan)
2 = average of 22 Lower Ashgill samples (Girvan)
3 = average of 72 Caradoc samples (Girvan)
4 = average of 102 Lower Llanvirn-Llandeilo samples (Girvan)
5 = average of 111 Caradoc samples from Alsayegh (1971) (Southern Uplands)
6 = average of 31 Ashgill samples " " " (Southern Uplands)
7 = average of 53 Llandovery samples " " (Southern Uplands)
x = average and σ = standard deviations.

It became clear therefore, that from the discussion given above and table 6.5 given below that the major differences as regards the tectonic settings of Southern Uplands and Girvan reside in the tectonic fields derived from the diagrams of K2O/Na2O versus SiO2 of Roser and Korsch (1986) and K2O/Na2O versus Fetot+MgO of Bhatia (1983). Southern Uplands data plot mainly between ACM and PM while those from Girvan plot between ARC and ACM and these differences are attributed to contributions mainly from metamorphic rock fragments to the former. on the K2O/Na2O versus Fetot+MgO, practically none of Southern Uplands data plot inside any of the four fields while many samples of Girvan plot inside the ARC and CA and these trends are also caused by the relative differences in their K2O/Na2O ratios.

Table 6.5: Comparison of Bhatia's parameters of Girvan with those of Southern Uplands

	1		2		3		4	
	x	σ	x	σ	x	σ	x	σ
Fetot+MgO	10.18	2.95	11.62	3.13	10.4	1.4	13.5	2.7
TiO2	0.95	0.32	0.94	0.3	0.7	0.12	1.0	0.2
Al2O3/SiO2	0.18	0.04	0.19	0.03	0.2	0.0	0.2	0.0
K2O/Na2O	0.37	0.15	0.41	0.14	1.1	0.3	4.3	0.7
Al2O3/ (CaO+Na2O)	1.6	0.70	1.92	0.76	1.0	0.4	3.0	1.1

Key to Table 6.5

1 = average of 16 Llandovery samples (Girvan)

2 = average of 94 Caradoc-Ashgill samples(Girvan)

3 = average of 53 Llandovery samples (from Alseygh 1971) [Southen Uplands]

4 = average of 142 Caradoc-Ashgill samples (from Alsayegh 1971) [Southen Uplands]

x = mean values and σ = standard deviations

6.7-Differences in the chemical vertical variability

Inspection of the table given above as 6.4 and Figures 6.15-16 show that both Girvan and Southern Uplands greywackes exhibit similar trends in Al, Fe, Mg and Na but not Si and Ca. The Ordovician greywackes of the Southern Uplands tend to be richer in Si Than the Silurian rocks compared to Girvan where Si increases systematically whereas Ca tends to rise in Ashgill then decline in Llandovery. The tendency of Fe and Mg to increase in the Southern Uplands Silurian rocks suggests possible contribution from mafic-rich sources; In contrast to those at Girvan where much of the contributions were from quartz-rich sources. The ratio K2O/Na2O decreases significantly in Southern Uplands in passing from Caradoc to Llandovery which indicates diminishing metamorphic contributions. The ratio remains practically unchanged in Girvan probably because unroofing and erosion of metamorphic terranes were insignificant at all ages.

The trace elements as can be seen from Figure 6.16 and table 6.4 also show some similarities and differences. While Rb, Ce, La, Ga, and Y and to a lesser extent Zr generally show both similar trends and concentrations, Sr and Ba differ substantially in both areas. Both Sr and Ba are lower and tend to decrease with younging age in Southern Uplands than in Girvan.

6.8-Discussion and conclusions

From the investigations carried out above, it became clear that a number of differences and silmilarities exist between Girvan and Southern Uplands in petrography, geochemistry, tectonic settings and vertical variability.

There is a similarity between the sediments in the Southern Uplands and the Girvan area. Both are dominated by volcanic lithic fragments, both have detritus from plutonic acid sources, and both have metamorphic basement clasts. When represented on a QFL diagram, both terranesindicate deriviation from an arc terrane. In terms of trends through time, both show a change to a greater abundance of acid rock fragments and quartz in younger rocks.

Geochemically, the rocks from both terranes plot mostly within the field of greywackes with some falling the field of lithic arenites of Pettijohn et al. (1972) (see Figures 6.13-14). However, four Silurian rocks from Girvan which are particularly Si-rich plot distinctly from the rest of the samples suggesting greater heterogeneity in terms of their silica contents. However, one of the major chemical differences between Girvan and Southern Uplands is exhibited by the elements, CaO, Rb, Ba, Ce, Sr and the K2O/Na2O ratios. While the enrichment in Ca and hence Sr is attributed to the abundance of secondary carbonates in the matrix of the greywackes from Southern Uplands, the high K2O/Na2O ratios and hence Rb, Ba and Ce are attributed to the presence and abundance of metamorphic rock fragments.

There are also notable differences between rocks from the same regions. The Southern Uplands greywackes are particularly rich in metamorphic rock fragments compared to their equivalents at Girvan. In addition, blue-and glaucophane schists are present in the former but totally absent from the latter. Further, when represented on the QFL triangular diagrams, the Southern Uplands rocks fall well within the field of Undissected magmatic arc compared to a fairly dissected, transitional and mixed magmatic arc material at Girvan.

As regard the tectonic settings as deduced from the geochemistry, all the conclusions remain rather equivocal because the same data plot within different fields when using different plots. On the K2O/Na2O versus SiO2 the Southern Uplands greywackes plot dominantly in the ACM field with the remaining samples falling whithin the ARC and PM fields. This contrasts with those from Girvan which plot mostly within the ARC field with only few samples plotting in the ACM field. However, on the TiO2, Al2O3/SiO2 and Al2O3/(CaO+Na2O) versus Fetot+MgO all data from both terranes fall within and around the ARC fields but not in the ACM, CA and PM. Although these can be regarded as differences and similarities between Girvan and Southern Uplands, the question whether they were both deposited in similar tectonic settings remains unanswered. However, it seems very likely that more material derived from ACM contributed to Southern Uplands than to Girvan.

The main differences in the vertical variabilities between the two terranes are the enrichement in SiO2 of the Silurian rocks compared to the Ordovician at Girvan but similar values or slightly lower in the Silurian rocks of Southern Uplands. This disagrees with deductions reached from the petrography where quartz is higher in the Silurian rocks compared to the Ordovician rocks in both Girvan and the Southern Uplands. In the latter the statistically significant differences between the Ordovician and Silurian greywackes reside in their Ca and Sr contents with the Ordovician greywackes being poorer in Ca and unexpectedly richer in Sr and Ba compared to the Silurian rocks which is not shared by the Girvan greywackes. The remaining elements generally show similar trends.

From the above discussion, the following conclusions can be drawn:

1. Both the Southern Uplands and the Girvan sequence probably shared a provenance in an arc regime which was dissected to expose source batholiths and basement.
2. This arc-like source extended laterally at least as far as the width of the Southern Uplands-Longford Down belt of turbidites- a width of some 300 km.
3. For the Southern Uplands at least, this arc-like source changed in time to become more acidic.
4. If it is accepted that the Girvan sequence was deposited in a proximal forearc, and the Southern Uplands is a trench then on the basis of the data available it seems probable that they were not part of the same dispersal system. There may be many reasons for this:

(a) That a southerly source has been active in the Southern Uplands and yielded a substantial volume of debris N. In this case, both basins did not share a similar dispersal and therefore could not had a similar source (Fig 6.17A).

(b) That between the forearc basin and the trench there may have been an extensive outerarc rise which may have contributed sediments to the trench. These components like blue-schist may have been produced in this way (Fig 6.17B).

(c) That there was substantial axial flow into the trench. Paleoflow data produced by many workers is summarized by Kelling et al. (1987) who indicates that much of the sediment in the Southern Uplands may have an 'axial' dispersal. However, unlike the axial system seen in, for example, the Sunda trench (Moore et al. (1982) where the sediment which is dispersed axially is quite distinctive from the sediment dispersed laterally, both axial and lateral sources are the same in the Southern Uplands. This might indicate an ultimate source in arc followed by lateral transportation along the trench axis. In this case the composition of the accretionary prism (Southern Uplands) sediment will be determined by a larger provenance than for the forearc at Girvan.

(d) If the above possibilities are discounted, then there may be a case to be made for the SUF to have a substantial displacement bringing together basins with different provenance areas (Fig 6.17C).

Deciding between the four possibilities is very difficult on account that indeed more detailed field, petrographic and geochemical studies are still needed particularly on the Southern Uplands area. However, in view of the large similarities between the two areas as discussed above and the fact that Southern Uplands, like Girvan, was probably deposited in a proximity to arc make the view of 1500 km lateral displacement (Elder 1988) very improbable. It therefore seems likely that the possibility (a) is the most acceptable ofthe four, although the possibilities (b) and (c) cannot be totally ruled out

Key to Figures 6.1-17

Figure 6.1: Paleogeography of Southern Uplands during Caradoc and Wenlock times(after McKerrow et al. 1977).

Figure 6.2: Diagramatic view of the Southern Uplands accretionary prism and trench complex during Ordovician times (after Bluck 1985). CG=Coreswall Group; KG=Kirkcolm Group; PG=Portpatrick Group; PR=Portayew Rocks; TB=Traboyack Division; LR=Loch Ryan Rocks; C=Cairnerzean Rocks; GW=Glenwhean Rocks; BR=Boreland Rocks; MF=Marchburn Formation; AF=Afton Formation; BC=Blackcraig Formation; SF=Scar Formation; SHF=Shinnel Formation; CF=Crawfordjohn Formation; AF=Abington Formation; EF=Elvan Formation, GF=Glencapple Formation; HBFZ=Highland Boundary Fault zone; SUF=Southern Uplands Fault; SL=Solway Line.

Figure 6.3:Paleography of SW Southern Upland during Ordovician and Silurian times after McKerrow et al. (1987)[forearc theory]. AFL=Afton Lobe (Blackcraig Formation); BB=Ballygrot Block; CL=Corsewall Group Lobe ; CnL=Carsphairn Lobe ; FF=Finnalaghta Formation; GG=Gowna Group; GaG=Galdenoch Group; LF=Lakhan Formation; ML=Marchburn Formation Lobe ; PG=Portpatrick Group; PL=Portslogan Lobe (Kirkcolm Group); PR=Potayew Rocks; ScF=Scar Formation; ShF=Shinnel Formation; ABb=Ardwell Bay beds; AM=Alticry Member; CM=Chippermore Member; ChM=Chair Member; CFM=Cairnie Finnart Member; DM=Duniehinnie Member; DPM=Daw Point Member; DrM=Drumblair Member; FBF=Float Bay member; GF=Garheugh Formation; GPF=Grennan Point Formation; KF=Kilfillan

Formation; MHF=Money Head Formation; PLF=Port Logan Formation; SBb=Stirking Bight beds. (Numbers 1,2,3 etc=earlier accreted tectono-stratigraphic tracts)

Figure 6.4: Paleogeography of the Northern Belt of the Southern Uplands during late Ordovician and early Silurian times (after Morris 1987)[backarc theory].

Figure 6.5: Time stratigraphical diagram showing proposed stratigraphic correlation of the greywackes within West Nithsdale and part of the Central Belt (After Floyd 1982).

Figure 6.6: QFL diagrams of Southern Uplands greywackes (after Morris 1987). The field of the Girvan greywackes is also for comparison

Figure 6.7: SiO2 vs K2O/Na2O of S. Uplands to decipher the provenance areas and tectonic settings (ARC = Oceanic Island Arc, ACM = Continental Island Arc, PM = Passive Margins)

Figures 6.8-11: Scatter diagrams of S. Uplands of Fetot+MgO vs TiO2, Al2O3/SiO2, K2O/Na2O, Al2O3/(CaO+Na2O) respectively. They are used to decipher the provenance areas and tectonic settings (ARC= Oceanic Island Arc, CA = Continental Island Arc, ACM = Active Continental Margin, PM = Passive Margins). Dotted fields outline composition of forearc greywackes from the Mezozoic Great Valley Sequence, California (From Van de Kamp and Leake 1985).

Figure 6.12: Scatter diagram of Ti versus K2O.

Figure 6.13-14: Scatter diagrams of log Na2O/K2O versus log SiO2/Al2O3. The fields of greywacke, lithic arenites, arkose, subarkose and sublithic arenites of both Girvan and Southern Uplands after Pettijohn et al. (1972) are also shown.

Figure 6.15-16: Geochemical comparison between Girvan and Southern Uplands (6.15 for major and 6.16 for trace)

Figure 6.17: Possible relationships between Girvan and Southern Uplands during Ordovician and Silurian times. G=Girvan; S.U=Southern Uplands; SUF=Southern Uplands Fault, S.T=Southern terranes as the likely source for the Southern Uplands greywackes.

Fig 6.1

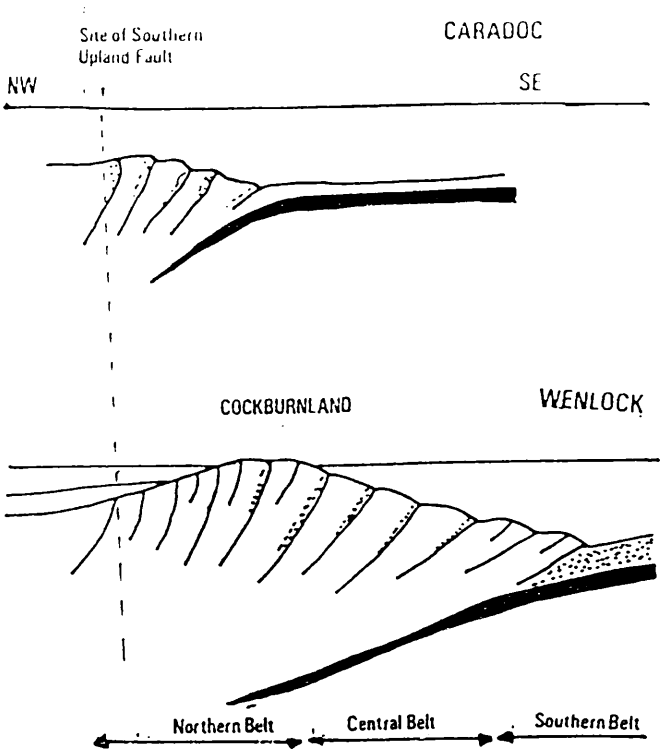

Site of Southern
Upland Fault
CARADOC
NW
SE
COCKBURNLAND
WENLOCK
Northern Belt
Central Belt
Southern Belt

Fig 6.2.

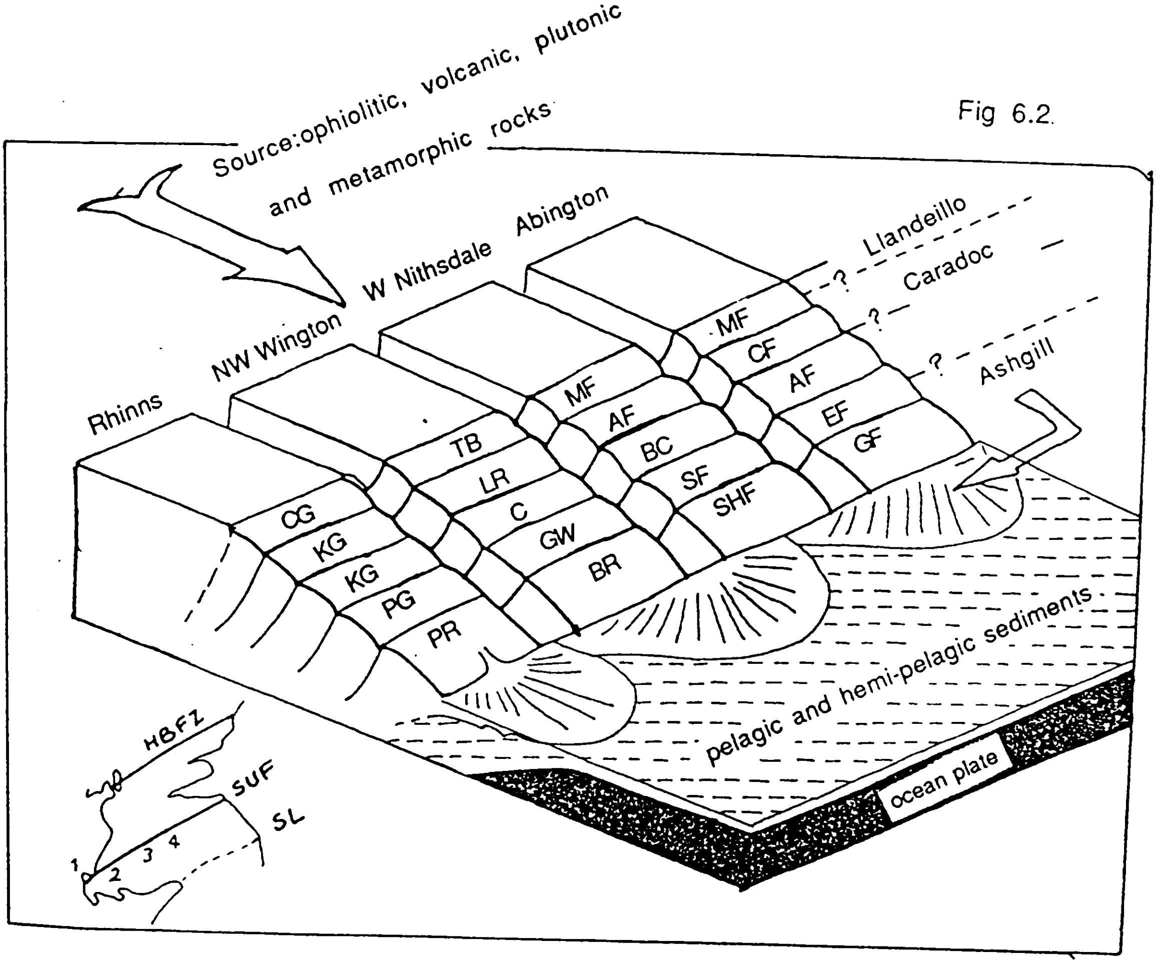

Source:ophiolitic, volcanic, plutonic
and metamorphic rocks
Rhinns
NW Wington
W Nithsdale
Abington
Llandeillo
Caradoc
Ashgill
?
?
?
MF
CF
AF
EF
GF
MF
AF
BC
SF
SHF
TB
LR
C
GW
BR
CG
KG
KG
PG
PR
pelagic and hemi-pelagic sediments
ocean plate
HBFZ
SUF
SL
1
2
3
4

Fig 6.3

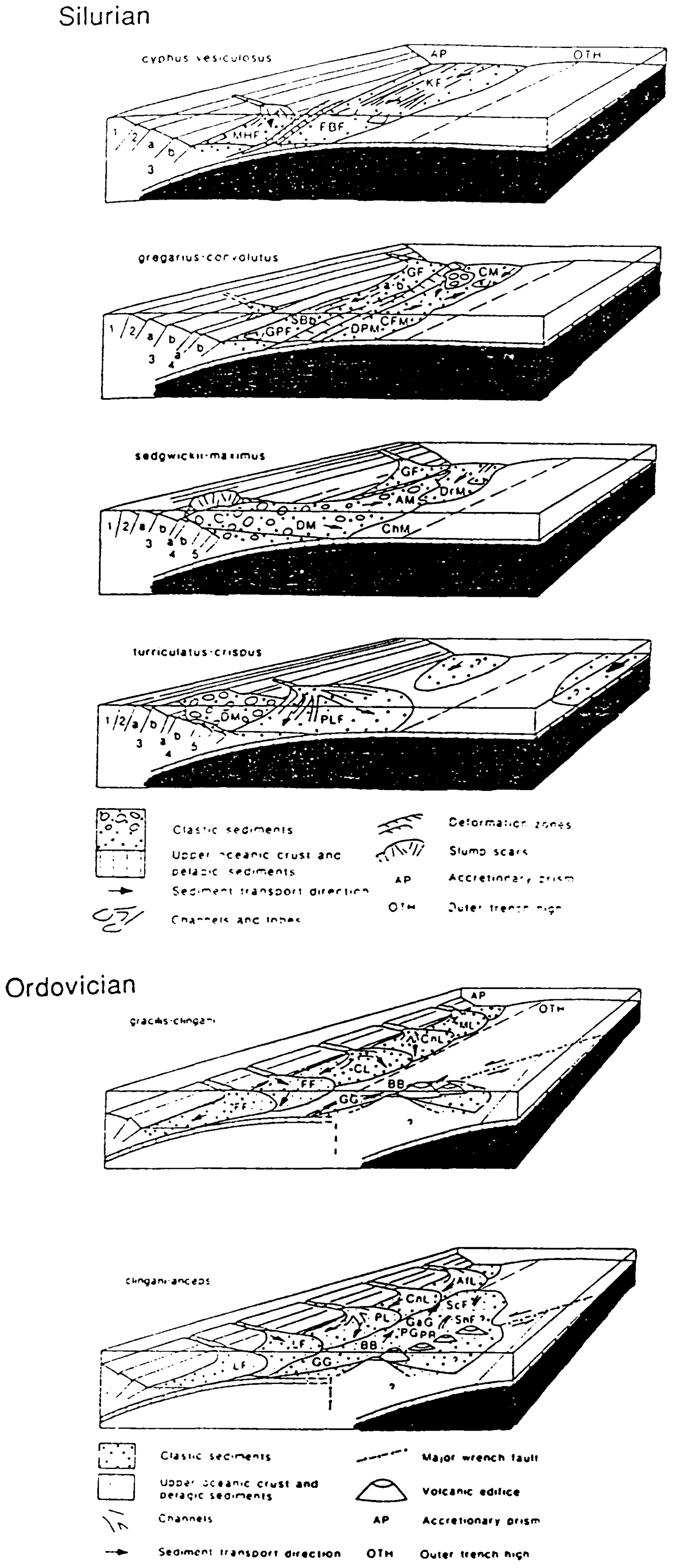

Silurian
cyphus-vesiculosus
AP
OTH
KF
FBF
MHF
1
2
a
b
3
gregarius-convolutus
GF
CM
a-b
SBb
GPF
DPM
CFM
1
2
a
b
3
a
4
b
sedgwickii-maximus
GF
DrM
AM
DM
ChM
1
2
a
b
3
a
b
4
5
turriculatus-crispus
DM
PLF
1
2
a
b
3
a
b
4
5
Clastic sediments
Upper oceanic crust and pelagic sediments
Sediment transport direction
Channels and lobes
Deformation zones
Slump scars
AP
Accretionary prism
OTH
Outer trench high
Ordovician
gracilis-clingani
AP
OTH
ML
CnL
CL
FF
BB
GG
FF
?
clingani-anceps
AtL
CnL
ScF
PL
GaG
SnF
PG
PR
LF
BB
LF
GG
?
Clastic sediments
Upper oceanic crust and pelagic sediments
Channels
Sediment transport direction
Major wrench fault
Volcanic edifice
AP
Accretionary prism
OTH
Outer trench high

Fig 6.4

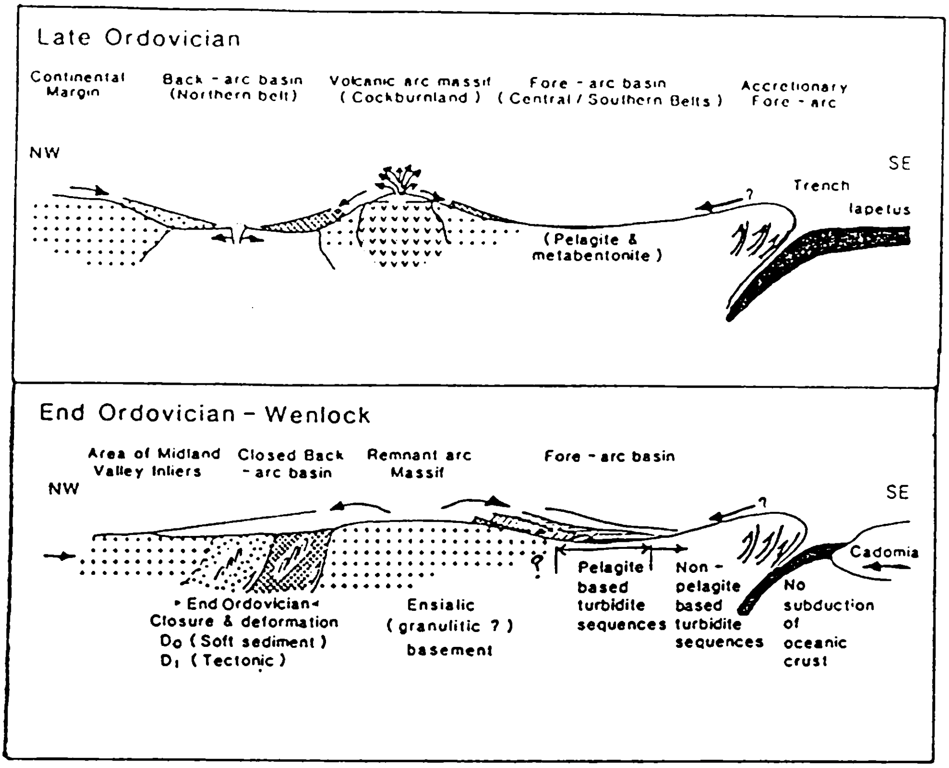

Late Ordovician
Continental Margin
Back - arc basin (Northern belt)
Volcanic arc massif (Cockburnland)
Fore - arc basin (Central / Southern Belts)
Accretionary Fore - arc
NW
SE
Trench
Iapetus
?
(Pelagite & metabentonite)
End Ordovician - Wenlock
Area of Midland Valley Inliers
Closed Back - arc basin
Remnant arc Massif
Fore - arc basin
NW
SE
?
?
Cadomia
▸ End Ordovician ◂ Closure & deformation
D0 (Soft sediment)
D1 (Tectonic)
Ensialic (granulitic ?) basement
Pelagite based turbidite sequences
Non - pelagite based turbidite sequences
No subduction of oceanic crust

Fig 6.5

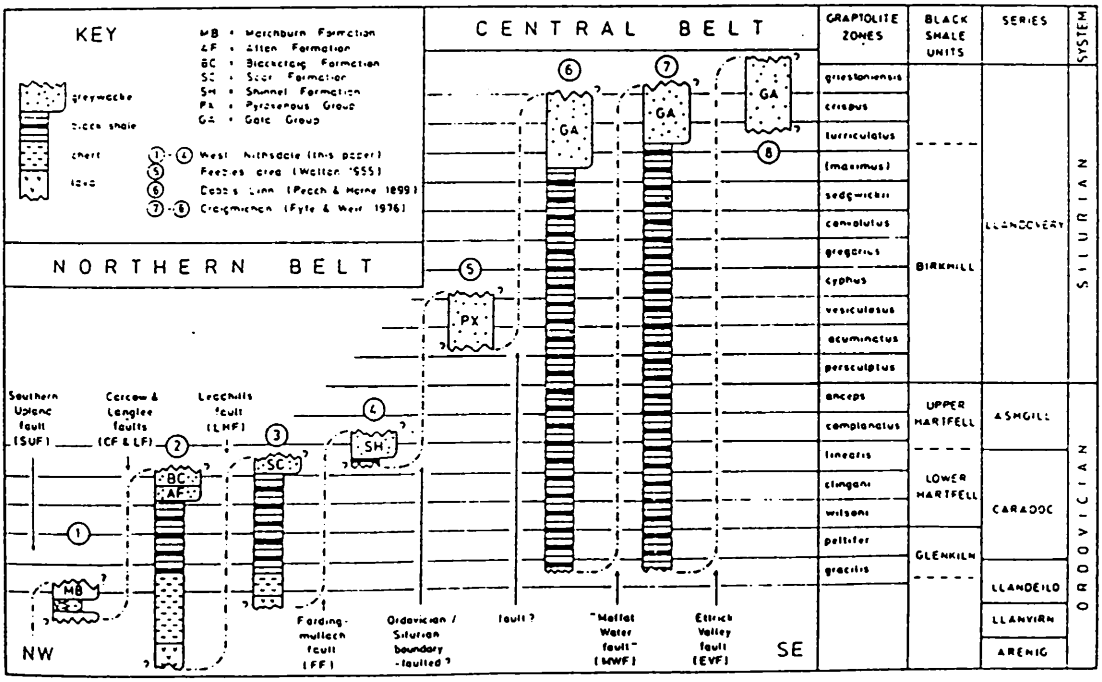

KEY
greywacke
black shale
chert
lava
MB · Marchburn Formation
AF · Afton Formation
BC · Blackcraig Formation
SC · Scar Formation
SH · Shinnel Formation
PX · Pyroxenous Group
GA · Gala Group
①-④ West Nithsdale (this paper)
⑤ Peebles area (Walton 1955)
⑥ Dobb's Linn (Peach & Horne 1899)
⑦-⑧ Craigmichan (Fyfe & Weir 1976)
NORTHERN BELT
CENTRAL BELT
GRAPTOLITE ZONES
BLACK SHALE UNITS
SERIES
SYSTEM
griestoniensis
crispus
turriculatus
(maximus)
sedgwickii
convolutus
gregarius
cyphus
vesiculosus
acuminatus
persculptus
anceps
complanatus
linearis
clingani
wilsoni
peltifer
gracilis
BIRKHILL
UPPER HARTFELL
LOWER HARTFELL
GLENKILN
LLANDOVERY
ASHGILL
CARADOC
LLANDEILO
LLANVIRN
ARENIG
SILURIAN
ORDOVICIAN
①
②
③
④
⑤
⑥
⑦
⑧
MB
BC
AF
SC
SH
PX
GA
GA
GA
?
Southern Upland fault (SUF)
Carcow & Langlee faults (CF & LF)
Leadhills fault (LHF)
Fardingmullach fault (FF)
Ordovician / Silurian boundary -faulted ?
fault ?
"Moffat Water fault" (MWF)
Ettrick Valley fault (EVF)
NW
SE

Fig 6.6

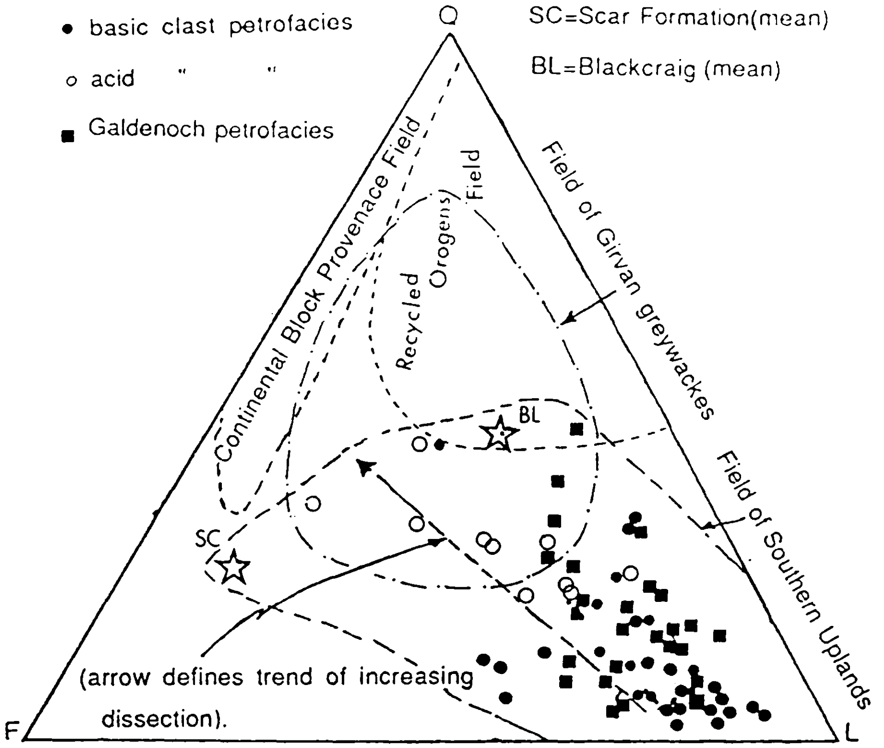

● basic clast petrofacies
o acid " "
■ Galdenoch petrofacies
SC=Scar Formation(mean)
BL=Blackcraig (mean)
Q
F
L
Continental Block Provenace Field
Recycled Orogens Field
Field of Girvan greywackes
Field of Southern Uplands
BL
SC
(arrow defines trend of increasing dissection).

Fig 6.7

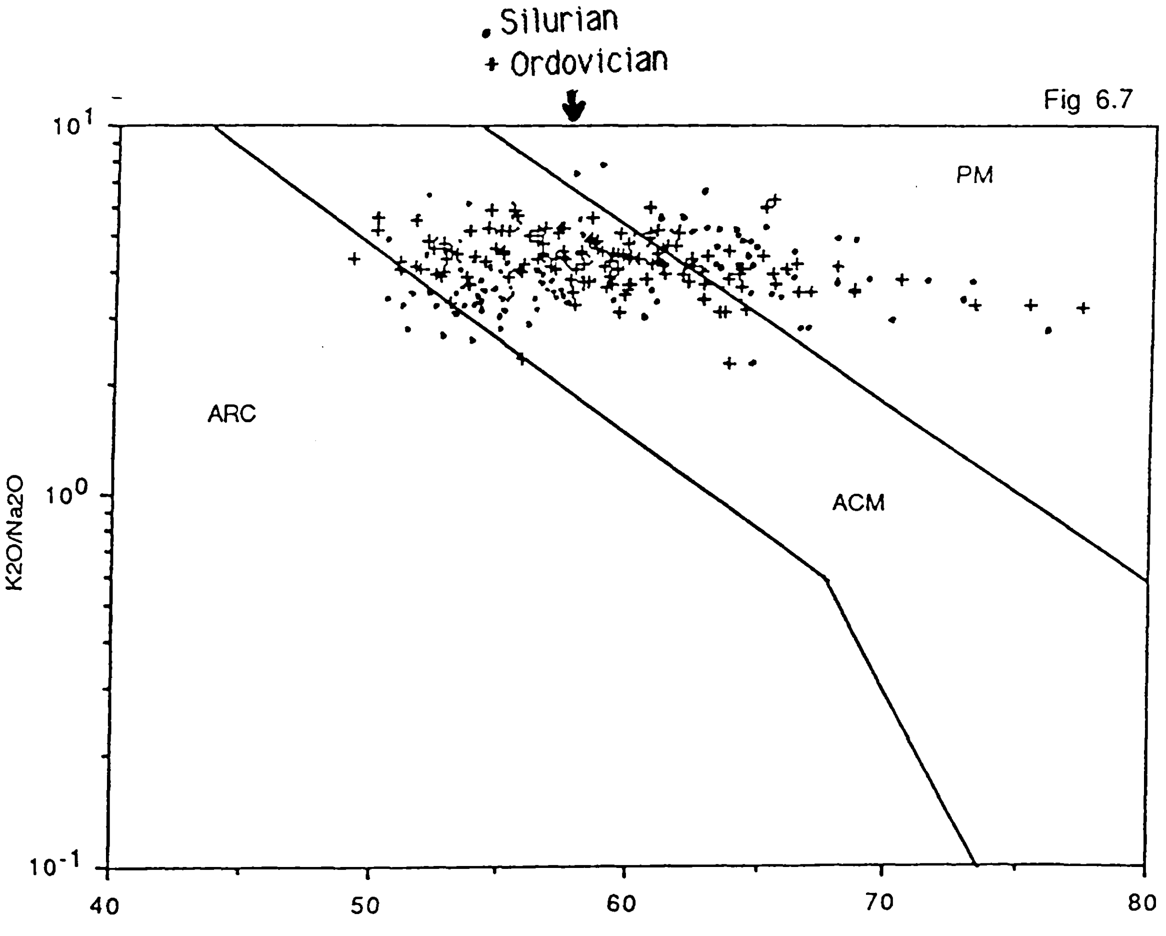
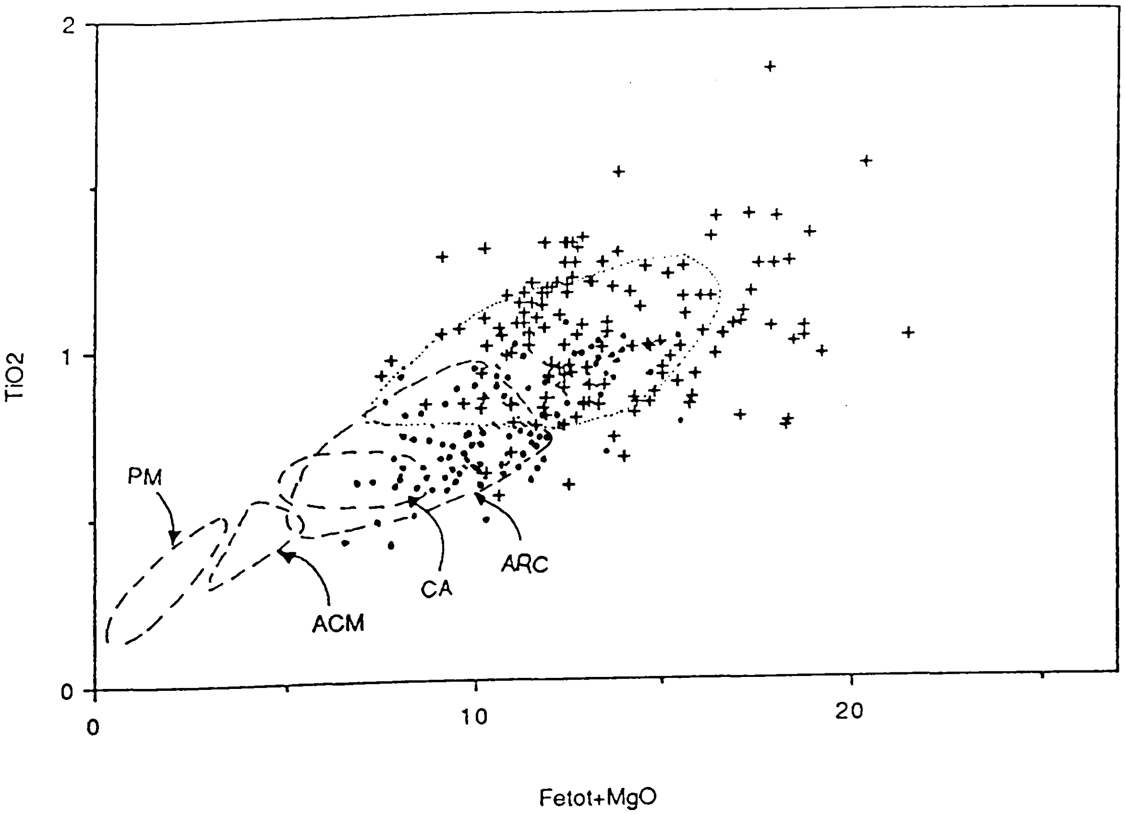

• Silurian
+ Ordovician
10^1
10^0
10^{-1}
K2O/Na2O
40
50
60
70
80
SiO2
PM
ARC
ACM

Fig 6.8



• Silurian
+ ordovician

Fig 6.9

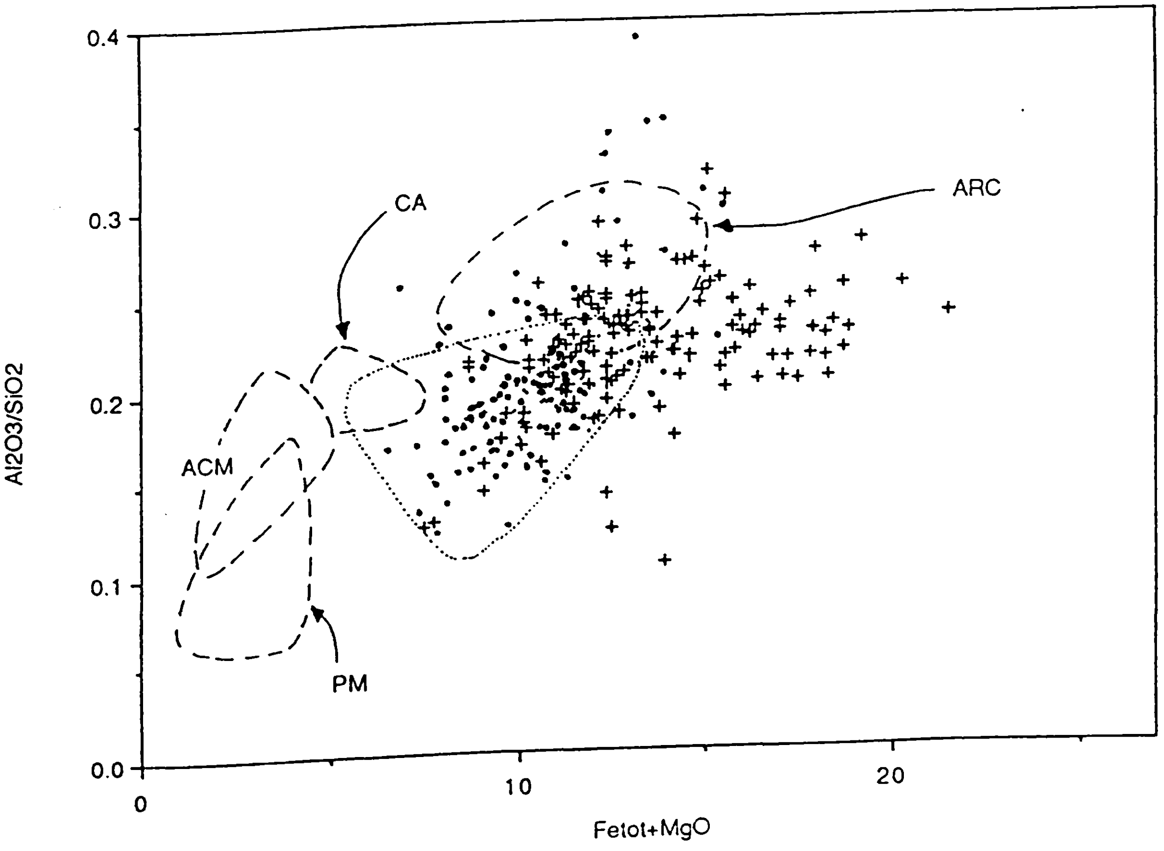


Fig 6.10

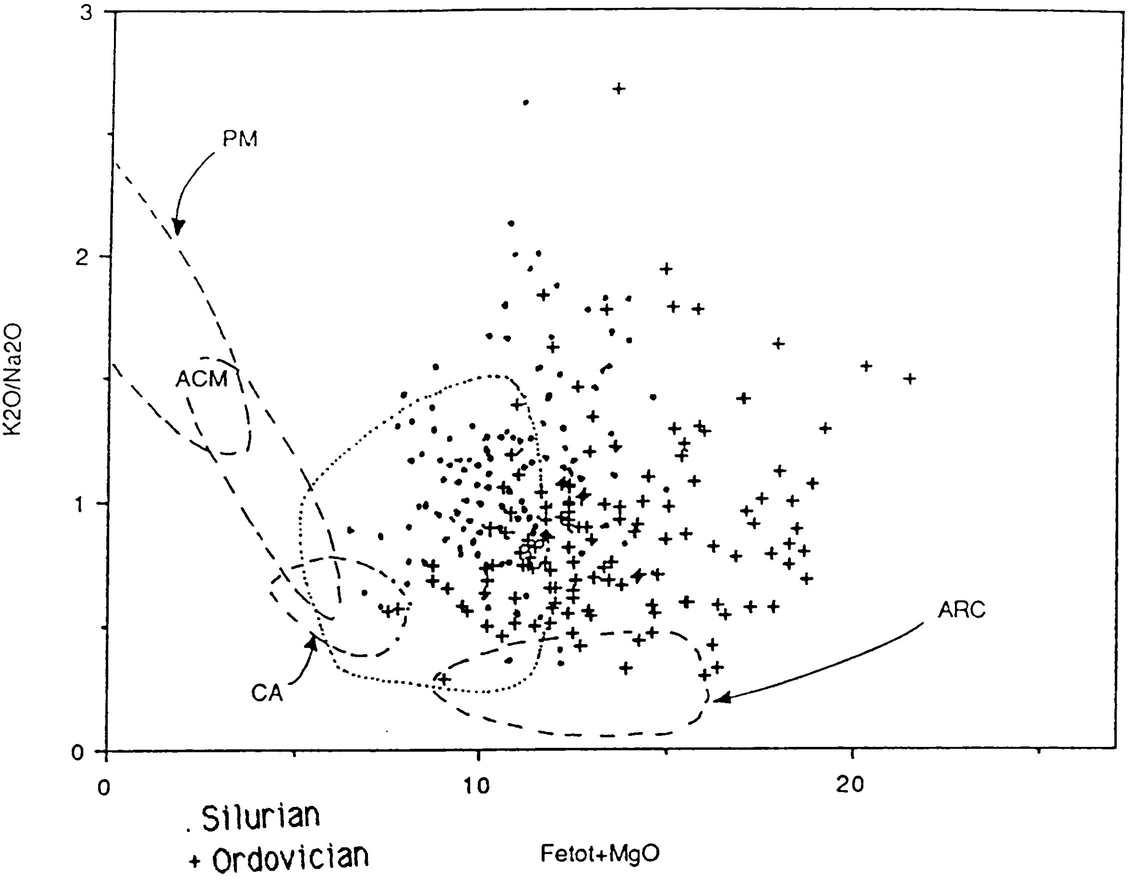


Fig 6.11

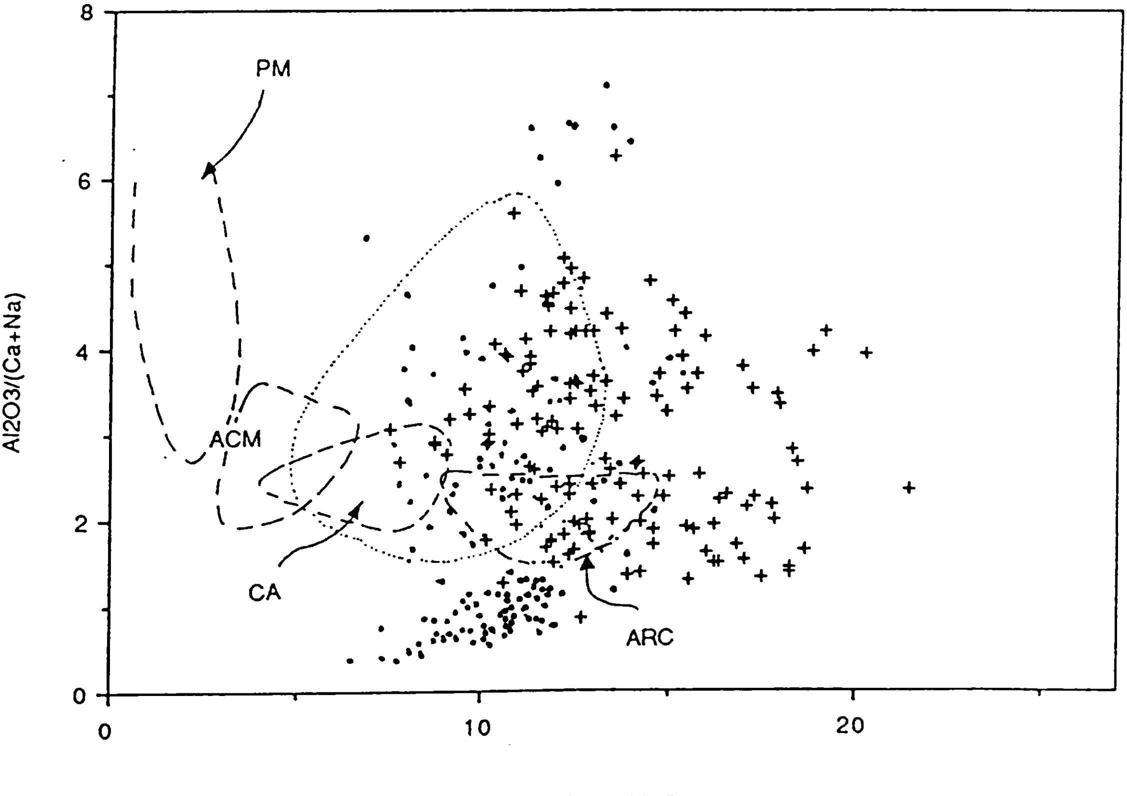


Fig 6.12

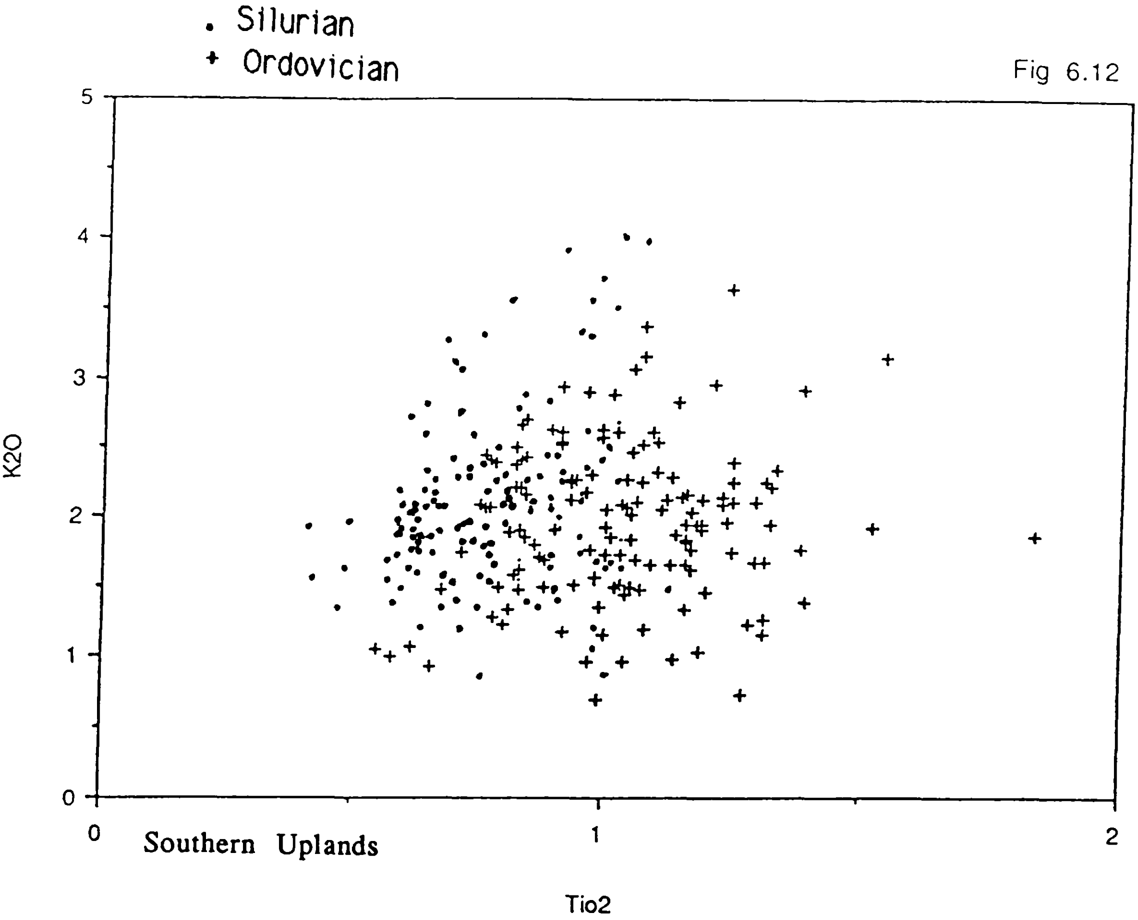
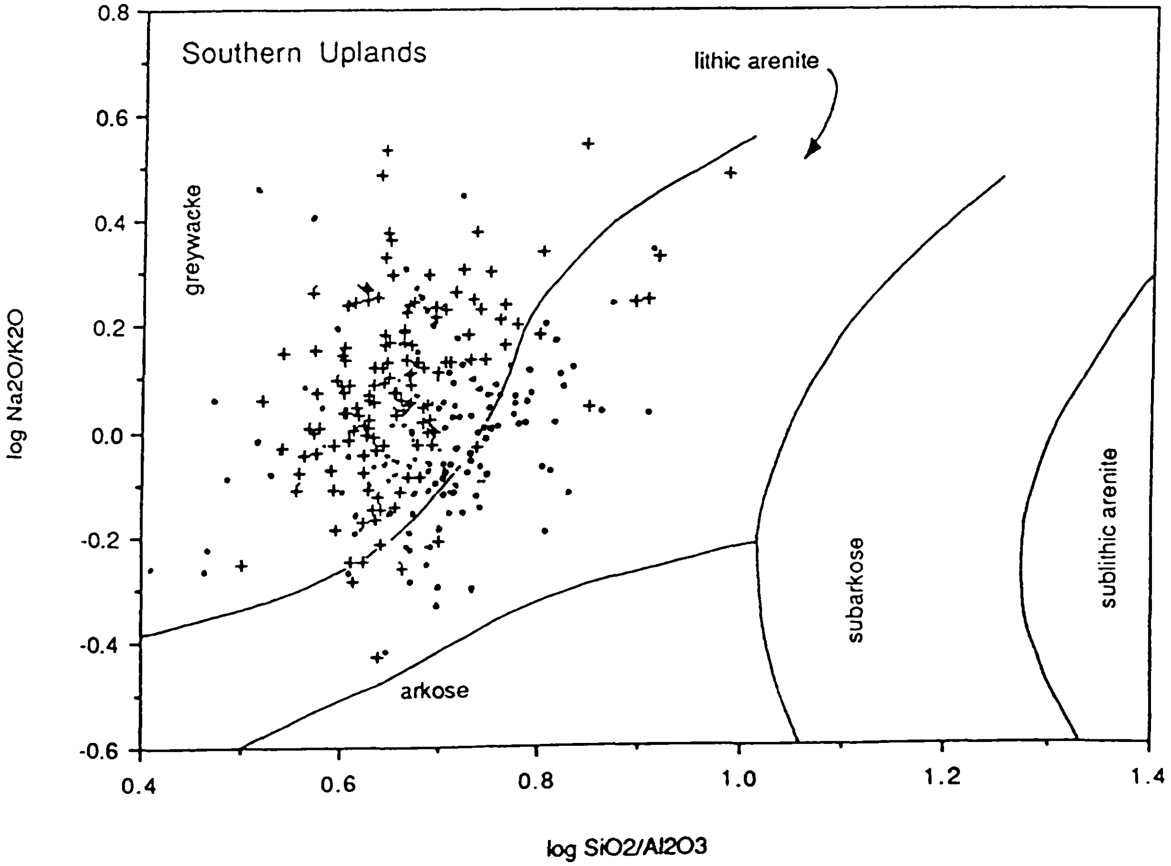


Fig 6.13



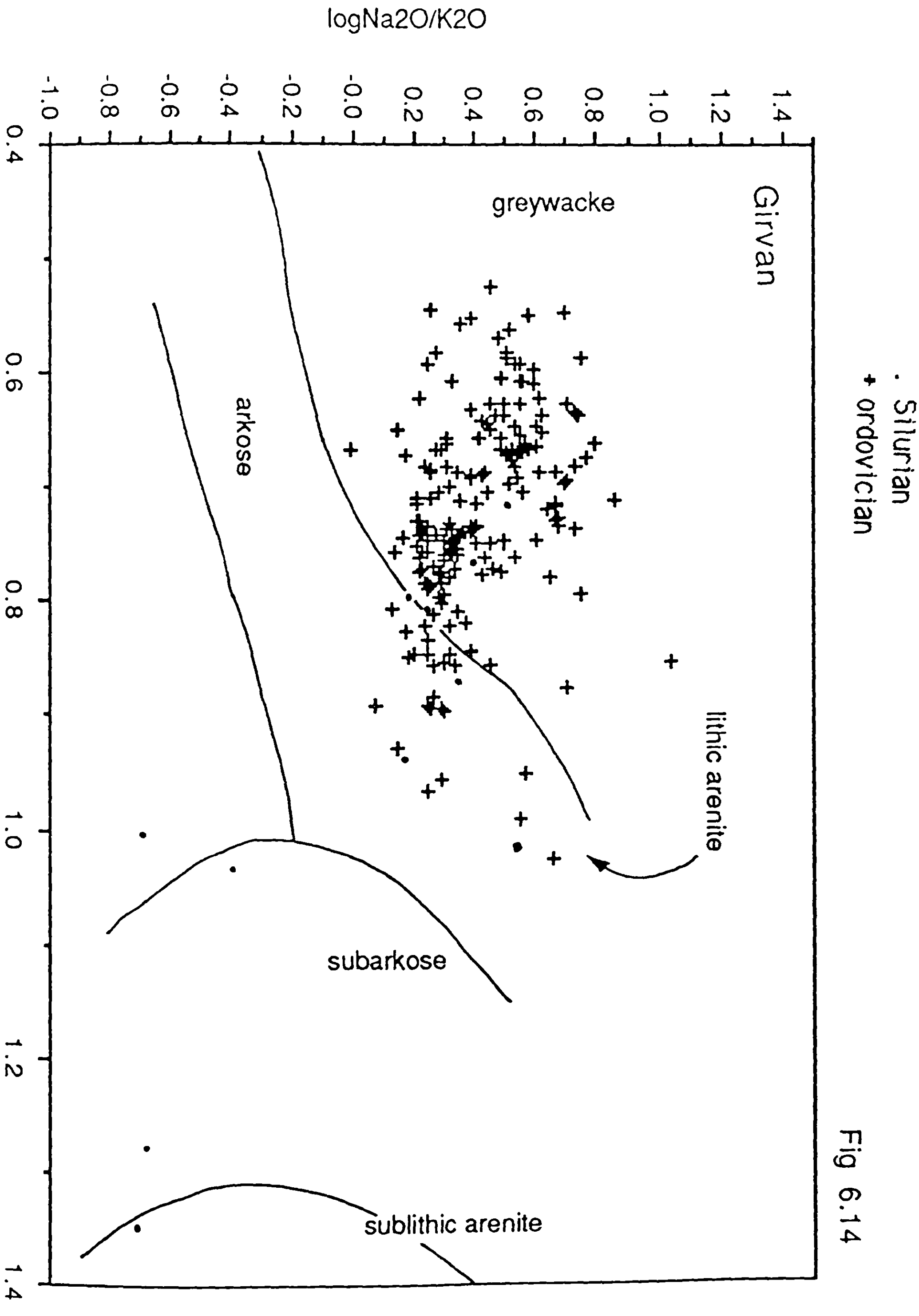

Girvan
. Silurian
+ ordovician
logNa2O/K2O
-1.0
-0.8
-0.6
-0.4
-0.2
-0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
logSiO2/Al2O3
0.4
0.6
0.8
1.0
1.2
1.4
greywacke
arkose
lithic arenite
subarkose
sublithic arenite

Fig 6.14

Fig 6.15

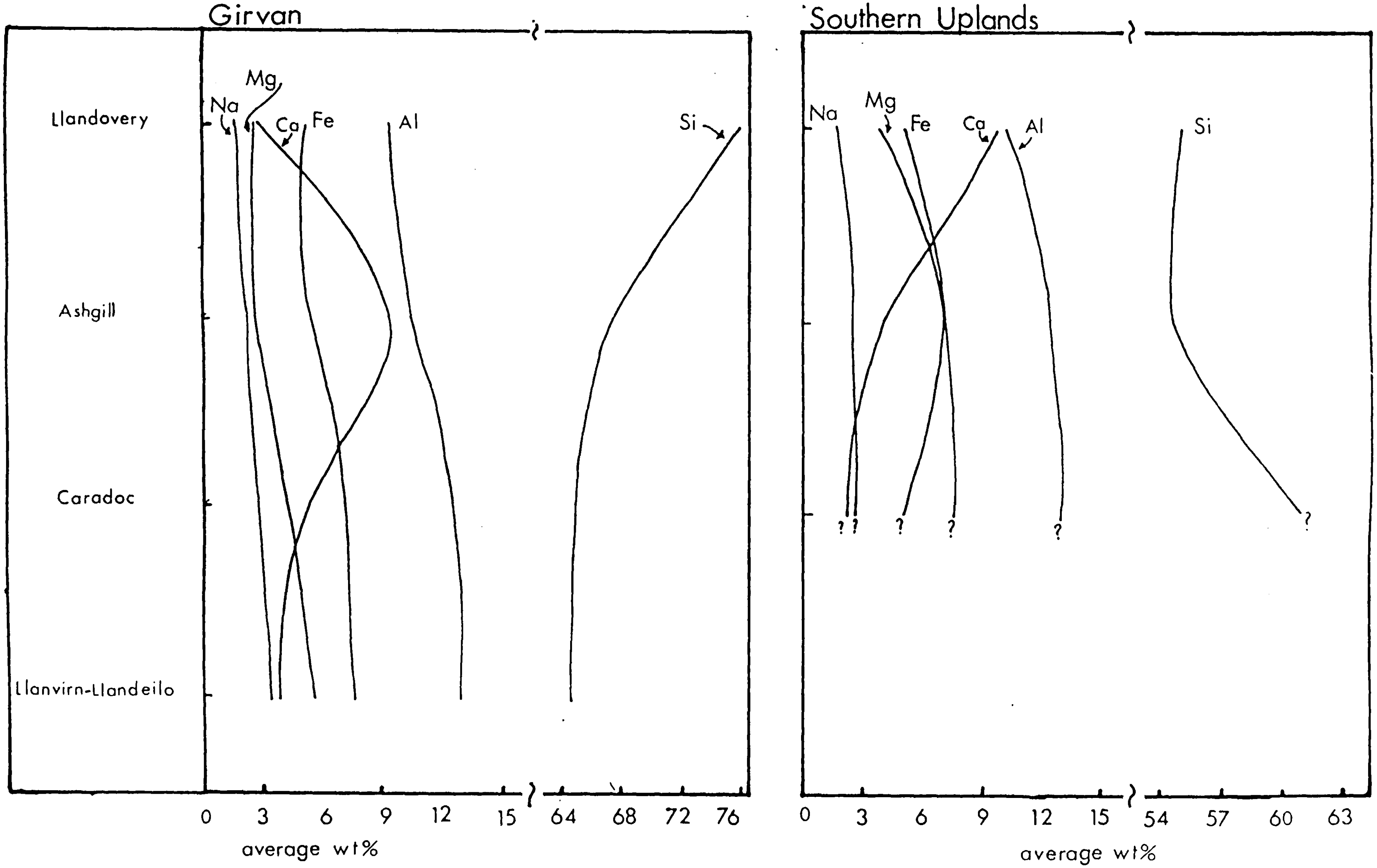

Girvan
Southern Uplands
Llandovery
Ashgill
Caradoc
Llanvirn-Llandeilo
Na
Mg
Ca
Fe
Al
Si
?
0
3
6
9
12
15
64
68
72
76
54
57
60
63
average wt%

Fig 6.16

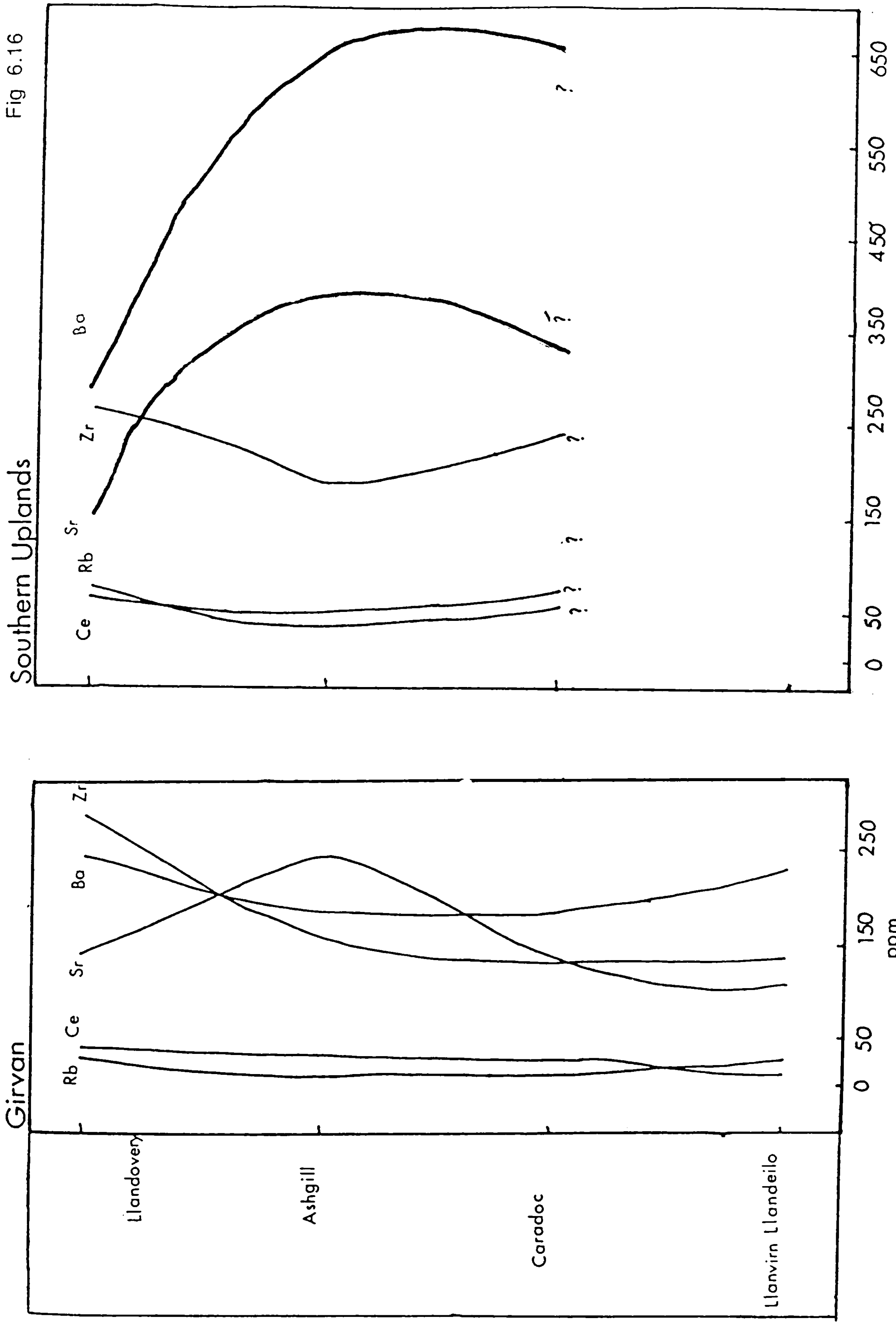
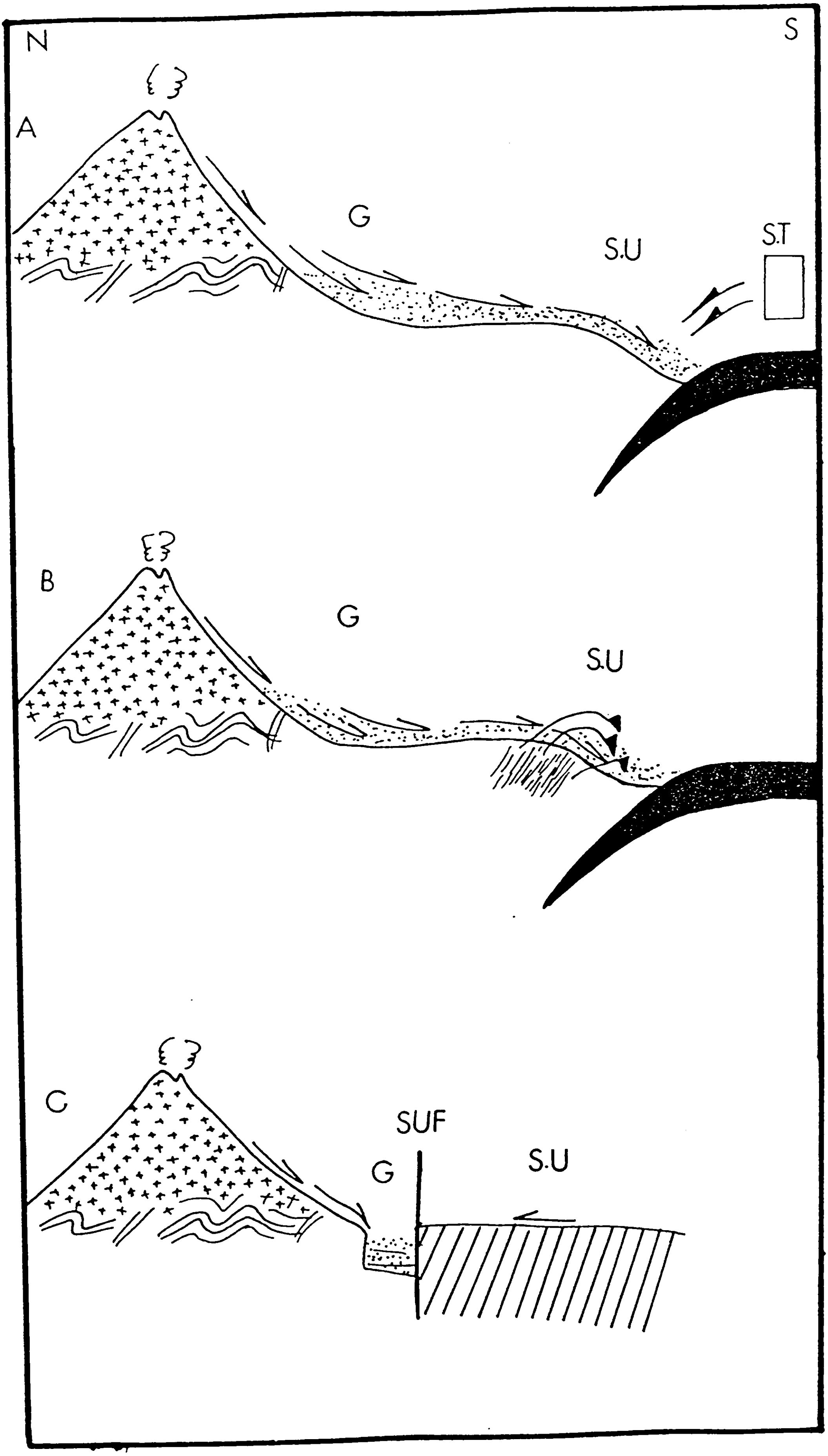

Southern Uplands
Ba
Zr
Sr
Rb
Ce
?
?
?
?
?
?
650
550
450
350
250
150
50
0
ppm
Girvan
Zr
Ba
Sr
Ce
Rb
250
150
50
0
ppm
Llandovery
Ashgill
Caradoc
Llanvirn Llandeilo

Fig 6.17



CHAPTER SEVEN THE SIGNIFICANCE OF THE PETROGRAPHY AND GEOCHEMISTRY AT GIRVAN ON THE EVOLUTION OF THE CALEDONIDES

7.1 Introduction

Since the early work of Dewey (1969, 1971), there has been significant changes in the understanding of the evolution of the Caledonides of Scotland. One of the main thrusts in Caledonian research was to interpret the relationships between the three tectono-stratigraphic units; Dalradian, Midland Valley and Southern Uplands blocks which are separated from each other by the Southern Uplands and Highland Boundary faults (Fig 7.1). The Midland Valley is flanked to the north by the Dalradian sequence of Precambrian sedimentary and relatively minor volcanic rocks. Anderton (1985) suggested that the sedimentological evolution of the Dalradian block reflects the lithospheric stretching which gave rise subsequently to the Cambrian Iapetus Ocean. To the south, is the Southern Uplands block which itself comprises a number of fault-bounded segments or tracts of Llandeilo to Wenlock age. Below, the various tectonic models proposed to explain the evolution of the Scottish Caledonides are first discussed and then the implications of the present data on the previous models are presented.

The main aim of this chapter is therefore to interpret the results of petrography and geochemistry at Girvan in terms of the evolution of the Caledonides.

7.2-Various models for the Caledonian evolution.

The development of plate-tectonic concepts in the late 1960's in conjunction with Wilson's (1966) suggestion of a proto-Atlantic ocean led to many interpretations of the British Caledonides through plate-tectonic processes. Those tectonic models proposed for the Girvan area are detailed in chapter one whereas those suggested for the Southern Uplands are discussed in chapter six. In this section, the overall evolution of the whole Southern Scotland is considered in terms of Caledonian evolution rather than considering each part separately. Despite many tectonic models being proposed for the Scottish Caledonides all of which are rather controversial, they can be summarized in three main models namely: (1)-Leggett et al. and Yardley et al.; (2)-Bluck and (3)-Stone et al. models.

Leggett (1980), Yardley et al.(1982) and Leggett et al. (1982, 1983) believed that the Midland Valley was a forearc region dividing the Southern Highlands (arc basement) from the Southern Uplands (trench-accretionary prism) in Ordovician and Silurian times (Fig 7.2). It was flanked by the Southern Highlands to the NW and a rising upper trench slope break (Cockburnland) to the SE.

An alternative model proposed mainly by Bluck (1983, 1984, 1985) and shared by Longman et al.(1979); Van Breeman and Bluck (1981), envisaged the Midland Valley as an arc-inter-arc terrane during the Ordovician and Silurian times (Fig 7.3) with the arc to have been flanked to N by a marginal basin in which rocks of the Highland Border Complex formed (Bluck.1984). To the S in the Llanvirn-Ashgill sequence at Girvan, a proximal forearc is preserved in which boulders of granitic and volcanic detritus accumulated. The author argued that the presence of a proximal forearc sequence in the southwestern margin of the Midland Valley demands an Ordovician arc to the immediate N of it (in the Midland Valley) and a forearc to the south of it (in the position of the Southern Uplands). He suggested that a trench sequence and coeval proximal forearc basin sequences lie adjacent to each other in southern Scotland and hence a complete forearc basin is missing. The Southern Uplands accretionary prism is thought to have been thrust over the continental crust of the Midland Valley and may also have been thrust over the missing forearc basin.

The most up to date tectonic model is that of Stone et al. (1987) His work in the Southern Uplands suggests a backarc and foreland thrust duplex model for the Southern Upland terranes. The arguments given and which are partly or wholly shared by Welsh (1964), Morris (1979) being that: (a) the contrasting nature and direction of the greywacke provenance from SE (oceanward in a forearc setting) of mature quartzoses and fresh andesitic detritus and (b) an extensive syn-tectonic dyke swarm in which mantle-derived lamprophyres are prominent (Fig 7.4).On the basis of these data, an arc source south of the present Southern Uplands is suggested. The Southern Uplands are considered to be a backarc basin, and a subduction zone is thought to exist to the south beyond the arc.

7.3 Tectonic evaluation of the Girvan sequence

Deciding between the three main models discussed above depends largely on the interpretation of the Llanvirn-Ashgill sequence at Girvan; the stratigraphy of which can be found in Williams (1962), Ingham (1978) and Ince (1984).

7.3.1-Previous ideas

Yardley et al. (1982) considered the whole of the Midland Valley, including Girvan, to have been a forearc basin throughout Ordovician and Silurian times. The arc, in this view, was founded on the Dalradian metamorphic basement. Its remnants are now to be seen in the older gabbros and the c 470 Ma granites of the NE Dalradian outcrops. Geochemical considerations (Leake 1989), have indeed shown that basic intrusions into the Dalradian elsewhere have a chemistry which matches that of arc rocks.

The Girvan sequence in this view is simply seen as an exposure of a much more extensive forearc basin which covered most of the Midland Valley.

In the alternative view of Stone et al. (1987) the Girvan area is thought to be part of the backarc basin (Fig. 7.4). It is positioned on the cratonic side of the basin, being subjected to faulting presumably as the crust was extended.

Bluck (1985) envisaged the Girvan sequence forming in a proximal forearc basin in which uplift of the arc produced contemporous faults which allowed an arc to rise in the N and basin to sink in the S. The Midland Valley was seen as the site of the arc; and the Girvan sequence as the site of the proximal forearc. The rocks which were deposited in fan-deltas and associated environments dispersing sediment from N contain granitic clasts of similar age to the sedimentary rocks in which they were deposited. The presence of andesite, rhyolite and quartz porphyry clasts in the conglomerate and associated sandstones and greywackes,field and structural constraints led Bluck to suggest a proximal forearc region for Girvan. On this evidence the contemporary arc massif should be to the north, and since some of the clasts are greater than 2 m in diameter then it should be fairly proximal. This led Bluck to conclude that the arc was located in the Midland Valley.

Yardley et al. (1982) considered the whole of the Midland Valley including Girvan to have been a forearc basin throughout the Ordovician and Silurian times. The arc, in this view, is situated in the Dalradian block to the N. Erosion of this arc was thought to supply the Girvan area as well as elsewhere. The paucity of metamorphic detritus, and the fact that during Ordovician times the Dalradian block suffered its maximum uplift, does not lend much support for this theory.

7.3.2 Present results

The sequence of rocks at Girvan comprises coarse conglomerates banked-up against contemporaneously active faults. These conglomerates were deposited in fan-deltas which interfingered, on their basin side, with turbidites. The conglomerates are dispersed from the N and NW, and contain an abundance of igneous clasts.

Detailed petrographic and geochemical studies of the Girvan greywackes as discussed in chapters four and five respectively suggest that the material deposited was derived from basic , ultrabasic and volcanic rocks through to the most differentiated acidic rocks during the Ordovician times. By Ashgill and Llandovery times, contributions from basic, ultrabasic and some of the volcanic components have become less significant but more quartz-rich recycled material was more and more introduced to the area. On the basis of evidence presented elsewhere and in chapters four, five and six, the following points can be made

1. The conglomerates at Girvan have clasts ranging up to 3 m in diameter and were deposited in fan-deltas (Bluck 1983; Ince 1984). For reasons of coarse grain-size, environment of deposition (fan deltas are proximal type sediments) and structural control they are thought to be proximal deposits. Since the turbidites collected for this thesis can be traced laterally into these conglomerates, the turbidites are also considered to be proximal.

2. The compositions of the conglomerates and interfingering turbidites are dominated by igneous detritus. This includes mafic and ultramafic clasts with a probable origin in the Ballantrae complex; acid-intermediate effusive rocks; granites, with cooling ages which show they were intruded at the time of sedimentation (Longman et al. 1979); and abundance of granophyric debris which suggests high level plutonism. Petrographically, the sandstones plot in the fields of transitional through dissected to mixed arc, and the chemistry also defines them as arc-type rocks.

From the evidence of composition it is clear that these rocks source in arc terrane. Combining the reasoning here with 1 above , then the arc was situated immediately to the NW.

3-By early Silurian times, this arc may have become insignificant or even stopped, and the basement or mature sedimentary basins, probably not associated with it, dominated the record.

4-By comparison, and despite its variability, the Southern Uplands has the petrography and chemistry of a forearc or backarc deposit.

5-Despite a general similarity in the evolutionary history of the Southern Uplands and the Girvan area, there are sufficient difference to suggest that both areas did not share a common history.

It should be mentioned that despite some difficulties mainly related to disagreements between the various tectonic fields proposed based on the geochemistry, geochemical re-investigation of Southern Uplands rocks clearly suggest proximal to an arc environment.

7.4 Implication of the present data on the available models

The data and direct inferences made from them in 7.2-3 together with the data presented in chapters four, five and six have a substantial bearing on the plate tectonic setting of Southern Scotland.

The models of Leggett et al. (1982) and Yardley et al. (1982) which require an arc within the Dalradian block and a forearc basin in the Midland Valley to the immediate south, are not supported by the evidence supported here. Consideration of grain size etc lead to the conclusion that the arc source was within the Midland Valley, and not beyond it.

It follows, however, that if there was indeed an arc in the Dalradian block, then two arcs existed along the Laurentian margin.

The models of Stone et al. (1987) requiring an arc to the south of Southern Uplands is again contradicted by the evidence presented here. It is the main conclusion of this thesis that the area now to the N. of Southern Uplands was arc-forearc region, and an accretionary prism would be anticipated to have existed to the south. Once again, if the idea of Stone et al. (1987) lead to the conclusion that there is an arc to the south , there is a 'double arc' problem in the Caledonides. However, Kelly and Bluck (1989) point out that the detritus which is dispersed from the south is older than the age of the sediment and may therefore belong to an inert arc massif.

The Southern Uplands ploted data show that they also belong to a forearc setting, and in a general sense share a volcanic and metamorphic basement provenance with the Girvan sequence. However, in detail there are sufficient differences to suggest that both could not have shared the source area.

The concept that the Caledonides comprises a series of terranes each with an individual history and each with a history distinct from each other may provide a solution to the multi-arc problem as well as the problem of provenance of the Southern Uplands sediments.

Key to Figures 7.1-4

Figure 7.1: Geological sketch map of N. Scotland showing the three major tectono-stratigraphic units.

Figure 7.2: Tectonic model of the Scottish Caledonides after Leggett et al. (1982-83) and Yardley et al.(1982).

Figure 7.3: Tectonic model of the Scottish Caledonides after Bluck (1985)

Figure 7.4: Tectonic model of the Scottish Caledonides after Stone el al (1987).

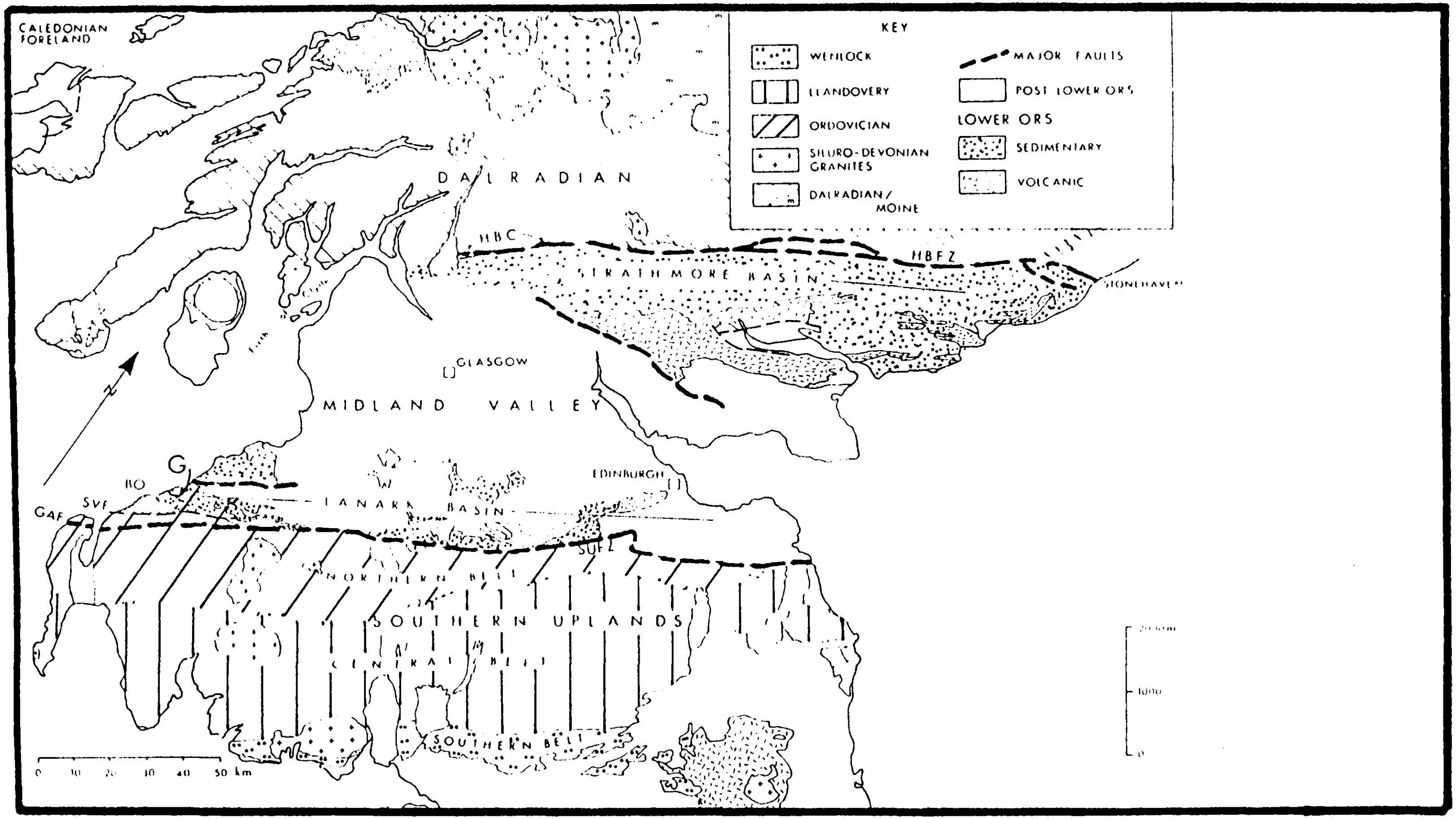
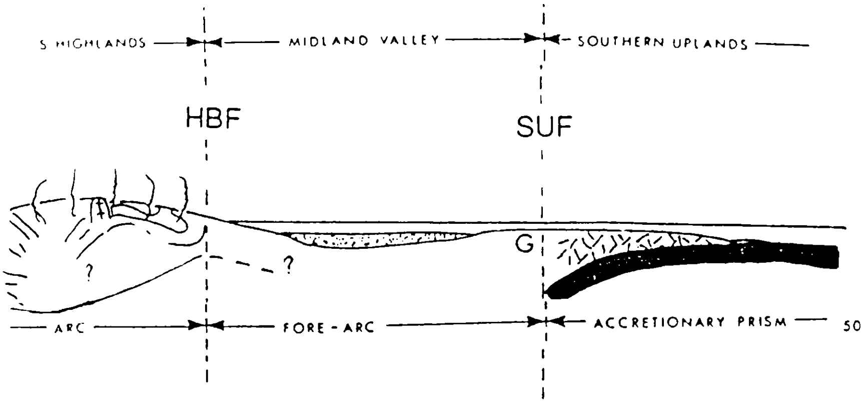


Fig 7.1: Geological sketch map of N Scotland showing the three major tectono-stratigraphic units (see text for explanation).

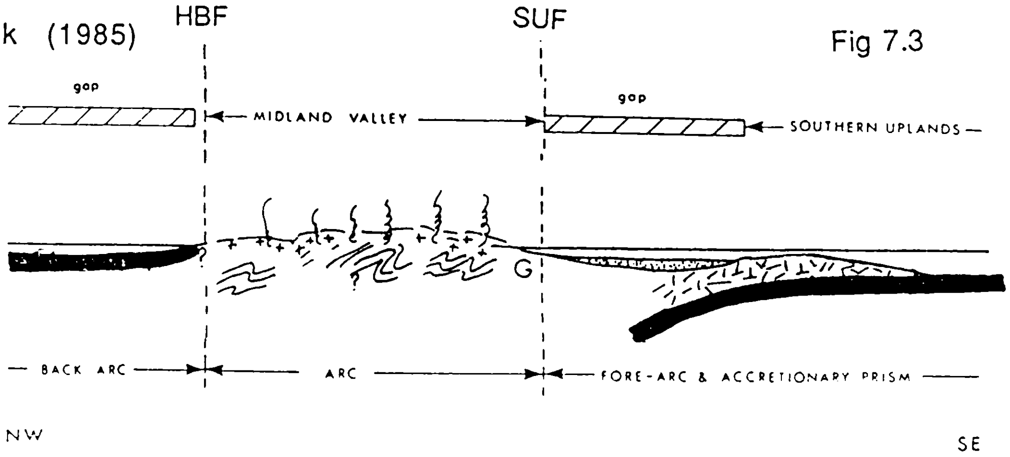
Legget et al. (1982,83) and Yardley et al. (1982)

Fig 7.2



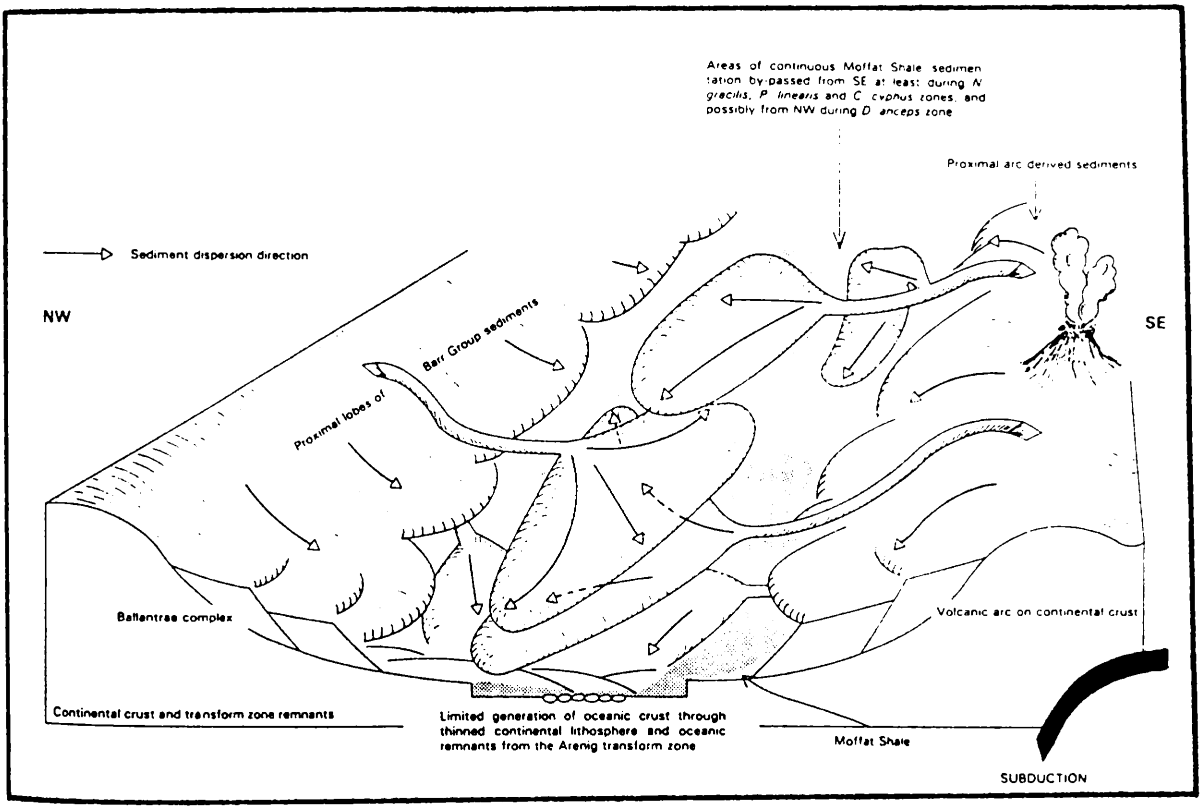
Bluck (1985)

Fig 7.3



Stone et al. (1987)

Fig 7.4



CHAPTER EIGHT SUMMARY AND CONCLUSIONS

Detailed studies of the Girvan area greywackes show that these rocks exhibit great petrographic and chemical variations and show systematic changes in passing from Upper Llanvirn through to Llandovery age

Petrographic studies of greywackes in the Girvan area show them to have formed in a forearc setting. The lower part of the sequence (Llanvirn and Llandeilo) is dominated by basic and ultrabasic (gabbro, spilite, serpentinite, dolerite) rock fragments with various minor proportions of rhyolite, granite-granodiorite (usually hornblende-bearing) fragments. The petrography indicates the uplifting and unroofing of a major igneous complex. Apart from the mafic and ultramafic rock fragments and minerals, which are thought to have derived from the obducted Ballantrae complex, there are intermediate and acidic rock fragments as well as granites and granophyres. Granitic clasts from the coarser parts of the sequence have yielded Rb/Sr ages of between 593 ± 28 Ma and 451 ± 8 Ma (Longman et al. 1979) and have petrographic and chemical affinities of high level intrusions. Based on conglomerate clast studies, Bluck (1983) also noted that some of the clasts are mineralogically dissimilar to those now exposed at Ballantrae and as a consequence he linked these rocks to other phases of granitic intrusions of ages of between 590 Ma and 450 Ma. It is therefore likely that the source as this time comprised an obducted ophiolite upon which was founded an igneous complex. This complex comprised acidic rocks and associated plutons, some of which may have been sufficiently high level to be granophyric.

The mineralogy of the Llanvirn-Llandeilo greywackes as given above continues into the Caradoc rocks, but the succeeding Lower Ashgill sandstones and greywackes tend to be richer in acidic rock fragments, quartz (which may be of sedimentary origin) and probably also some sedimentary quartz-rich material.

The progressive changes in the composition of the greywackes with younging age is attributed mainly to the evolution in the composition of the magmatic arc which was founded on an obducted ophiolite. The abnormally quartz-rich nature of the Ashgill greywackes suggests addition of recycled sedimentary material during this time and this recycled orogen, quartz-rich material is particularly enhanced during Llandovery. Basic and ultrabasic rock fragments are totally absent in these Llandovery rocks and even the acidic components became scarce with the rocks being composed almost entirely of recycled orogenic material.

The reason for this change to a recycled orogen type source are uncertain. Possibilities are that a pause in arc activity has permitted drainage to reach back into the craton and tap source of quartz-rich sediment or has allowed erosion to expose the root zones of the arc. There is also the possibility that a new source was emplaced by structural events, but this possibility cannot be tested by the data presented here.

Detailed geochemical studies also showed important features both as regards the vertical variability, provenance areas and tectonic settings. In passing from the Upper Llanvirn to Llandovery, those compatible elements which are commonly enriched in mafic and ultramafic rocks (e.g Mg, Fe, Cr, Ni, Co) tend to decrease with younging age whereas those incompatible elements (e.g, K, Rb, Zr) and Si generally increase thus strongly supporting conclusions reached from the petrography. As deduced from Harker-type diagrams, these chemical changes are related to a normal evolution in the magmatic arc but also to some addition of sedimentary and little metasedimentary components particularly during Llandovery.

The tectonic setting of the Girvan sequence can be deduced again from both the petrography and geochemistry. The petrography shows that the Ordovician greywackes-forming material was derived from transitional through dissected to mixed magmatic arc regimes and by Llandovery, almost pure recycled orogenic quartz-rich material was introduced to the area. Detailed modal analyses of the rocks suggest forearc deposition settings for the Girvan area greywackes which therefore excludes interarc settings as suggested by Bluck (1983) and includes forearc settings as suggested by Leggett et al. (1982, 83) and Yardley et al. (1982)

Despite disagreements between different tectonic fields proposed by different authors particularly those suggested by Bhatia (1983) and Roser and Korsch (1986), the chemistry shows that there is a general agreement in that the Ordovician rocks were derived from a magmatic arc and probably deposited in forearc settings. It is also found that the Llandovery rocks included some silica-rich sediments and hence supporting the petrography.

The relationships between Girvan and Southern Uplands as discussed in chapters six and seven show that there are a number of similarities and differences as regards petrography, geochemistry and vertical variability. The Southern Uplands greywackes are particularly rich in the total metamorphic rock fragments compared to their equivalents at Girvan. Glaucophane-schists are also present in the former but are totally absent from the latter. On the QFL diagram, although the rocks from the two areas sometimes overlap with each other, the Southern Uplands greywacke-forming material was probably derived from an undissected magmatic arc compared to a fairly dissected magmatic arc material for the Girvan rocks. Geochemically, the Southern Uplands rocks are also richer in Ca, Rb, Ba, Ce Sr and K2O/Na2O ratio than those from Girvan but the enrichment in these elements are attributed to the abundance of carbonate for Ca and Sr and metamorphic rock fragments for the remaining elements. Although the petrography suggests that the quartz content increases with younging age in both areas,the chemistry shows that this is true only for the Girvan rocks. Also the Llandovery rocks of Southern Uplands are richer in Ca compared to the Ordovician greywackes which is not shared by the rocks at Girvan. However, Both petrographic and geochemical evidence show that both areas were deposited in proximity to arc.

This implies that: (1) The proximal forearc at Girvan belongs to a different provenance area than the accretionary prism region of the Southern Uplands with (a) That a southerly source has been active in the Southern Uplands and yielded a substantial volume of debris N. In this case, both basins did not share a similar dispersal and therefore could not had a similar source and (b) That between the forearc basin and the trench there may have been an extensive outerarc rise which may have contributed sediments to the trench.

These components like blue-schist may have been produced in this way. (2) The Southern Uplands Fault has a substantial displacement bringing together basins with different provenance areas and tectonic settings.

APPENDICES

Appendix one: Results of point counting

Silurian

	S1	S2	S3	S4	S5	S6	S7	S8	S9	HQ1
Q	71	71	77	73	70	74	78	78	76	74
L	10	13	10	11	14	8	6	6	10	13
F	19	16	13	16	16	18	16	16	14	13
Qm	56	65	65	65	62	68	65	65	63	61
Lt	25	19	22	19	22	14	19	19	23	26

							upper sequence		
	HQ2	HQ3	HQ4	HC1	HC2	HC3	AL*1	AL*2	AL*3
Q	75	76	78	80	83	84	80	68	78
L	12	10	10	9	8	6	10	10	15
F	13	14	12	11	9	10	10	22	7
Qm	60	70	65	52	78	78	78	62	71
Lt	27	16	23	37	13	12	12	16	22

	AL*4	AL*5	AL*6	WG1	WG2	WG3	WG4	WG5	WG6	WG7
Q	80	79	78	47	61	56	52	53	61	67
L	8	12	15	47	34	27	26	22	12	21
F	12	9	7	6	5	17	22	25	27	12
Qm	73	74	74	74	77	46	48	41	42	54
Lt	15	17	19	20	18	37	30	34	31	34

		middle sequence						
	WG8	PW1	PW2	PW3	PW4	PW5	PW6	PW7
Q	69	83	85	57	61	61	46	67
L	22	6	5	5	3	8	5	12
F	9	11	10	38	36	31	49	21
Qm	60	78	72	31	31	38	40	53
Lt	31	11	18	31	33	31	11	36

	PW8	PW9	PW10	PW11	PW12	PW13	PW14	PW15	PW16	PW17
Q	65	67	69	68	68	68	58	74	76	79
L	10	2	10	12	9	15	21	6	5	4
F	25	31	21	20	23	17	21	20	19	17
Qm	42	59	59	65	63	63	56	69	66	65
Lt	33	10	20	15	14	20	23	11	15	18

	PW18	PW19	PW20	PW21	PW22	PW23	TM1	TM2	TM3	TM4
Q	78	80	74	79	76	79	80	71	76	43
L	6	5	9	6	8	10	12	7	10	33
F	16	15	17	15	16	11	8	22	14	24
Qm	72	70	61	68	70	62	66	53	57	22
Lt	12	15	22	17	14	27	26	25	29	54

	TM5	TM6	TM7	TM8	TM9	TM10	TM11	TM12	TM13	TM14
Q	70	62	62	70	73	64	67	73	74	68
L	7	18	27	13	8	12	14	6	9	16
F	23	20	11	17	19	24	19	21	17	16
Qm	42	46	41	22	62	46	52	61	60	38
Lt	35	34	48	61	19	30	29	18	23	46

	AF1	AF2	AF3	AF4	AF5	AF6	AF7	AF8	AF9	AF10
Q	37	43	29	62	30	32	59	51	35	32
L	11	14	14	17	47	33	18	23	33	15
F	52	43	57	21	23	35	23	26	32	53
Qm	30	35	27	49	15	24	43	30	23	28
Lt	18	22	16	30	62	41	34	44	45	19

								lower sequence
	AF11	AF12	AF13	AF14	AF15	AF16	AF17	KP1
Q	51	36	61	39	29	36	51	43
L	15	30	27	25	36	50	38	43
F	34	34	12	36	35	14	11	14
Qm	44	29	46	28	27	28	38	27
Lt	22	37	42	36	38	58	51	59

	KP2	KP3	KP4	KP5	KP6	AD1	AD2	AD3	KC1	KC2
Q	45	60	48	50	37	55	32	43	50	65
L	42	21	30	25	42	20	34	21	18	15
F	13	19	22	25	21	25	34	36	32	20
Qm	26	34	38	31	21	44	20	36	38	49
Lt	61	47	40	44	58	24	46	28	30	31

	KC3	BC1	BC2	TB1	TB2	TB3	TR1	TR2	TR3	TR4
Q	58	39	33	51	53	50	42	44	45	51
L	11	45	33	15	14	12	21	18	22	26
F	31	16	34	34	33	38	37	38	33	23
Qm	44	20	20	34	36	45	38	41	37	36
Lt	25	64	46	32	31	17	25	21	30	41

	TR5	TR6	TR7	TR8	TR9	TR10	TR11	TR12	TR13	TR14
Q	32	33	44	32	61	62	52	49	55	52
L	32	34	20	26	12	10	11	16	12	10
F	36	33	36	42	27	28	37	35	33	38
Qm	27	26	37	23	48	56	45	43	42	48
Lt	37	41	27	35	25	16	18	22	25	14

	TR15	TR16	TR17	TR18	TR19	TR20	TR21	TR22	TA1	TA2
Q	44	33	63	42	63	50	60	62	56	45
L	39	38	21	35	16	24	14	18	11	8
F	17	29	16	23	21	26	26	20	33	47
Qm	20	17	27	22	50	26	48	36	51	40
Lt	63	54	57	55	29	48	26	44	16	13

	TA3	TA4	TA5	TA6	TA7	TA8	TA9	TA10	TA11	AL1
Q	52	49	53	43	54	39	46	42	50	32
L	20	13	10	17	21	18	14	27	20	29
F	28	38	37	40	25	43	40	31	30	39
Qm	40	42	48	34	43	33	38	20	28	32
Lt	32	20	15	26	32	24	22	49	42	29

	AL2	AL3	AL4	AL5	AL6	KK1	KK2	KK3	KK4	KK5
Q	38	32	28	17	37	47	55	42	34	43
L	42	49	24	44	15	16	17	31	20	20
F	20	19	48	39	48	37	28	27	46	37
Qm	15	25	27	16	21	23	39	40	27	39
Lt	65	56	25	45	31	40	33	33	27	41

Appendix one : Continued

Silurian

	SW1	SW2	SW3	SW4	SW5	SW6	SW7	HC1	HC2	HC3
Qp	77	68	73	72	72	76	75	90	88	84
Lv	16	20	17	10	12	15	20	7	6	5
Ls	7	12	10	18	16	9	5	3	6	11
Qm	82	90	87	84	88	84	94	88	96	91
P	10	6	9	10	7	9	4	9	2	3
K	8	4	4	6	5	7	2	3	2	6

					upper sequence			
	HQ1	HQ2	HQ3	HQ4	AL*1	AL*2	AL*3	AL*4
Qp	82	79	72	54	44	37	39	49
Lv	14	15	20	45	39	41	45	34
Ls	4	6	8	1	17	22	16	17
Qm	74	83	80	52	63	59	72	77
P	23	14	18	46	34	40	28	20
K	3	3	2	2	3	1	0	3

	AL*5	AL*6	AL*7	WG1	WG2	WG3	WG4	WG5	WG6	WG7
Qp	36	63	84	36	31	53	18	30	55	33
Lv	38	25	16	49	49	40	64	67	45	34
Ls	26	12	0	15	20	7	18	3	0	33
Qm	56	68	50	68	65	60	89	87	82	88
P	42	24	45	28	32	24	8	9	9	12
K	2	8	5	4	3	16	3	4	9	0

	WG8	WG9	WG10	WG11	WG12	WG13	WG14	WP1	WP2	WP3
Qp	20	50	25	86	56	62	85	73	75	48
Lv	40	50	75	14	29	19	10	22	20	34
Ls	40	0	0	0	15	19	5	5	5	18
Qm	85	75	50	80	82	48	61	79	81	55
P	10	23	43	11	10	33	25	15	16	35
K	5	2	7	9	8	19	14	6	3	10

	SC1	SC2	SC3	SC4	middle sequence			
	25	26	27	28	AF1	AF2	AF3	AF4
Qp	58	52	50	25	38	15	34	28
Lv	40	44	47	70	40	80	62	55
Ls	2	4	3	5	22	5	4	17
Qm	67	80	73	62	45	32	70	38
P	29	15	19	30	52	67	8	52
K	4	5	8	8	3	1	22	10

	AF5	AF6	AF7	AF8	AF9	AF10	AF11	AF12	AF13	AF14
Qp	31	46	45	30	27	38	28	27	36	31
Lv	58	54	55	48	66	62	72	73	64	69
Ls	11	0	0	22	7	0	0	0	0	0
Qm	41	65	54	42	34	56	32	46	80	43
P	55	22	24	51	64	27	61	46	20	32
K	4	13	22	7	2	17	7	8	0	25

	AF15	TM1	TM2	TM3	TM4	TM5	TM6	TM7	TM8	TM9
Qp	33	72	67	74	67	70	75	50	55	47
Lv	55	16	22	16	25	21	17	34	27	31
Ls	12	12	11	10	8	9	8	16	18	22
Qm	44	63	60	70	81	80	87	73	65	79
P	49	27	26	16	10	12	8	17	26	14
K	7	10	14	14	9	8	5	10	9	7

	TM10	TM11	TM12	TM13	TM14	TM15	PW1	PW2	PW3	PW4
Qp	60	40	60	59	63	67	78	83	78	58
Lv	25	50	30	32	27	15	16	12	19	33
Ls	15	10	10	9	10	18	6	5	3	9
Qm	67	78	66	73	77	71	44	47	55	45
P	25	14	44	15	17	19	46	38	32	43
K	8	8	0	12	6	10	10	15	13	12

	PW5	PW6	PW7	PW8	PW9	PW10	PW11	PW12	PW13	PW14
Qp	72	40	68	67	65	69	75	65	76	67
Lv	20	55	29	27	31	28	19	26	16	30
Ls	8	5	3	6	4	3	6	9	8	3
Qm	41	78	86	90	89	86	80	81	82	79
P	45	18	8	6	8	12	12	12	12	13
K	14	4	6	4	3	2	8	7	6	8

				lower sequence				
	PW15	PW16	PW17	KP1	KP2	KP3	KP4	KP5
Qp	64	70	63	42	27	34	56	50
Lv	30	25	31	56	71	58	38	48
Ls	6	5	6	2	2	8	6	2
Qm	82	86	85	55	66	60	63	60
P	12	8	10	40	26	33	30	35
K	6	6	5	5	8	7	7	5

	KP6	KP7	AD1	AD2	AD3	KC1	KC2	KC3	KC4	KC5
Qp	45	28	50	52	47	43	23	38	40	62
Lv	47	66	41	43	50	55	77	60	58	35
Ls	8	6	9	5	3	2	0	2	2	3
Qm	55	49	64	37	50	19	21	20	43	61
P	37	41	36	63	50	81	79	80	40	30
K	8	10	0	0	0	0	0	0	17	9

	KC6	BC1	BC2	BC3	BC4	BC5	TB1	TB2	TB3	TB4
Qp	52	52	65	32	33	28	35	18	35	33
Lv	46	48	30	57	54	57	56	82	65	67
Ls	2	0	5	11	13	15	9	0	0	0
Qm	54	72	59	55	46	37	12	20	54	42
P	40	24	38	40	48	60	84	73	43	58
K	6	4	3	5	6	3	4	7	3	0

	TB5	TR1	TR2	TR3	TR4	TR5	TR6	TR7	TR8	TR9
Qp	50	22	35	18	24	31	50	43	32	53
Lv	50	76	59	75	68	65	50	57	68	41
Ls	0	2	6	7	8	4	0	0	0	6
Qm	48	50	53	44	44	35	64	55	55	53
P	52	49	47	56	54	61	18	45	45	14
K	0	1	0	0	2	4	18	0	0	6

	TR10	TR11	TR12	TR13	TR14	TR15	TR16	TR17	TR18	TR19
Qp	83	55	60	39	40	73	46	48	56	43
Lv	17	45	40	61	58	27	50	52	41	57
Ls	0	0	0	0	2	0	4	0	3	0
Qm	68	56	56	55	50	63	50	70	49	64
P	19	24	23	27	30	25	40	25	51	20
K	13	20	21	18	20	12	10	5	0	16

	TR20	TA1	TA2	TA3	TA4	TA5	TA6	TA7	TA8	TA9
Qp	68	49	68	42	38	45	38	59	45	51
Lv	28	51	32	53	60	51	58	35	55	47
Ls	4	0	0	5	2	4	4	6	0	2
Qm	62	52	54	47	56	46	53	48	45	52
P	36	48	46	43	25	45	35	40	43	41
K	2	0	0	10	19	9	12	12	12	7

	AL1	AL2	AL3	AL4	AL5	AL6	KK1	KK2	KK3	KK4	kk5
Qp	5	12	6	10	28	40	25	6	13	23	23
Lv	92	88	94	84	61	55	71	94	87	75	70
Ls	3	0	0	6	11	5	4	0	0	2	2
Qm	44	56	36	11	59	59	41	70	58	50	50
P	43	26	60	82	37	22	47	18	27	42	0
K	13	18	4	7	4	19	12	12	15	8	8

Appendix one (Continued): Results of plagioclase and K-feldspar analyses

	lower sequence (rock fragments)						
	TB1	TB2	TB3	TB4	TB5	TB6	TB7
$SiO2$	63.92	66.47	66.37	65.08	62.34	65.82	63.90
$Al2O3$	20.85	20.57	19.57	20.40	18.89	19.42	18.49
CaO	0.12	0.41	0.82	0.67	0.36	0.48	0
$Na2O$	10.20	10.64	11.07	10.26	10.59	11.33	5.07
$K2O$	1.38	0.47	0.30	0.63	0.25	0.21	8.90
Total	96.47	98.56	98.13	97.04	92.43	97.26	96.36

Number of ions per unit formula (on the basis of 32 oxygens)

Si	11.62	11.79	11.84	11.73	11.56	11.83	11.95
Al	4.47	4.30	4.11	4.33	4.13	4.11	4.07
Na	3.59	3.65	3.83	3.58	3.81	3.95	1.84
K	0.32	0.10	0.06	0.14	0.06	0.05	2.12

End member proportions

An	2	4	7	6	3	4	0
Ab	86	92	91	89	95	94	36
Or	12	6	2	5	2	2	64

	TB8	TB9	TB10	TB11	TB12	TB13	TB14
SiO2	66.93	64.64	64.06	60.23	62.47	62.23	63.68
Al2O3	19.37	18.56	18.20	23.21	17.84	17.53	20.22
CaO	0	0	0.29	0	0	0	0.11
Na2O	9.79	7.16	2.68	7.77	1.14	0.54	10.47
K2O	2.59	5.27	12.58	3.14	15.08	16.52	1.37
Total	98.68	95.63	97.52	64.60	96.53	96.82	95.85

Number of ions per unit formula (on the basis of 32 oxygens)

Si	11.94	11.96	11.99	11.22	11.92	11.95	11.59
Al	4.07	4.05	4.01	5.10	4.01	3.97	4.34
Ca	0	0	0	0.05	0	0	0.02
Na	3.38	2.57	0.97	2.79	0.42	0.20	3.69
K	0.59	1.24	3.00	0.74	3.67	4.05	0.32

End member proportions

An	0	0	0	3	0	0	1
Ab	79	58	18	69	7	3	88
Or	21	42	82	28	93	97	11

	KP1	KP2	KP3	KP4	KP5	KP6	KP7
SiO2	62.73	65.05	64.43	61.98	63.92	65.87	66.72
Al2O3	22.77	16.36	20.61	22.26	18.30	12.29	19.15
CaO	2.45	0	1.36	1.55	0.24	0.35	0.18
Na2O	9.24	4.37	10.91	9.48	0.54	10.61	9.40
K2O	0.67	4.77	0.08	1.27	16.39	1.11	2.45
Total	97.86	92.55	97.39	96.54	99.39	97.23	98.20

Number of ions per unit formula (on the basis of 32 oxygens)

Si	11.32	11.95	11.62	11.31	8.18	11.89	11.98
Al	4.74	3.97	4.38	4.79	2.76	4.10	4.05
Ca	0.47	0	0.26	0.30	0.03	0.06	0.03
Na	3.23	1.55	3.81	3.35	0.13	3.71	3.27
K	0.15	2.29	0.02	0.29	2.67	0.25	0.56

End member proportions

An	20	0	11	13	1	3	2
Ab	75	31	88	77	3	88	78
Or	5	69	1	10	96	9	20

	TR1	TR2	TR3	TR4	TR5	TR6	TR7
SiO2	63.87	63.07	63.10	64.47	65.57	65.19	65.41
Al2O3	18.13	17.49	18.31	17.87	20.29	20.42	19.08
CaO	0	0.13	0	0	1.14	1.34	0.67
Na2O	2.14	0.42	0.92	0.85	10.80	11.0	10.58
K2O	12.96	16.02	15.47	15.77	0.12	0	0.92
Total	97.10	97.13	97.80	98.96	97.92	97.95	96.06

Number of ions per unit formula (on the basis of 32 oxygens)

Si	8.24	12.02	11.87	12.01	11.73	11.67	11.83
Al	2.75	3.93	4.06	3.92	4.28	4.31	4.07
Ca	0	0.02	0	0	0.22	0.25	0.13
Na	0.53	0.15	0.33	0.30	3.74	3.82	3.71
K	2.13	3.89	3.71	3.65	0.02	0	0.21

End member proportions

An	0	1	0	0	9	11	5
Ab	14	2	6	5	90	89	87
Or	86	97	94	95	1	0	8

lower sequence (matrix).

	TB1	TB2	TB3	TB4	TB5	KP1	KP2
SiO2	63.98	67.58	66.68	66.75	65.93	67.80	64.85
Al2O3	19.21	19.47	19.91	19.38	18.63	19.72	20.43
CaO	0.56	0.10	0.54	0	0.16	0	0.93
Na2O	12.98	11.52	11.63	11.33	11.34	11.95	10.47
K2O	0.32	0	0.19	0	0.13	0	0
Total	97.05	98.67	98.95	97.46	96.19	99.47	96.68

Number of ions per unit formula (on the basis of 32 oxygens)

Si	11.66	11.95	11.81	11.94	11.98	11.88	11.59
Al	4.13	4.06	4.16	4.08	3.99	4.12	4.30
Ca	0.02	0.10	0.10	0	0.03	0	0.17
Na	4.59	3.95	3.99	3.93	3.99	4.06	3.72
K	0.07	00	0.04	0	0.03	0	0

End member proportions

An	4	1	4	0	1	0	8
Ab	94	99	96	100	98	100	92
Or	2	0	0	0	1	0	0

	KP3	KP4	KP5	TR1	TR2	TR3	TR4
SiO2	66.02	66.63	66.79	66.48	65.94	65.32	66.75
Al2O3	19.73	19.46	19.13	19.67	19.99	18.92	19.49
CaO	0.56	0.16	0.24	0.45	0.81	0.32	0.30
Na2O	11.23	11.10	11.26	11.41	11.67	10.96	11.87
K2O	0.09	0.10	0.16	0	0.10	0.09	0
Total	97.63	97.45	97.58	98.01	98.51	95.61	98.41

Number of ions per unit formula (on the basis of 32 oxygens)

Si	11.82	11.93	11.94	11.86	11.74	11.91	11.88
Al	4.16	4.10	4.03	4.14	4.19	4.06	4.09
Ca	0.10	0.03	0.04	0.08	0.15	0.06	0.05
Na	3.90	3.85	3.90	3.94	4.03	3.87	4.07
K	0.02	0.02	0.03	0	0.02	0.02	0

End member proportions

An	5	1	2	4	6	3	2
Ab	94	98	97	96	93	96	98
Or	1	1	1	0	1	1	0

upper sequence (rock fragments)

	WG1	WG2	WG3	WG4	WG5	WG6	WG7
SiO2	68.70	64.78	65.71	66.10	64.90	64.18	64.30
Al2O3	19.50	21.29	21.14	20.29	21.89	21.91	21.29
CaO	1.33	1.57	1.84	0.90	3.31	2.40	2.57
Na2O	10.08	9.92	10.11	10.55	10.09	9.65	10.14
K2O	0.22	0.12	0.22	0.23	0.12	0	0
Total	99.83	97.68	99.02	98.07	100.31	98.14	98.30

Number of ions per unit formula (on the basis of 32 oxygens)

Si	11.79	11.58	11.63	11.77	11.4	11.46	11.48
Al	4.01	4.48	4.41	4.26	4.53	4.61	4.48
Ca	0.25	0.30	0.35	0.17	0.62	0.46	0.49
Na	3.41	3.44	3.47	3.64	3.43	3.34	3.51
K	0.04	0.02	0.05	0.05	0.02	0	0

End member proportions

An	11	14	15	8	15	13	12
Ab	87	85	83	90	84	87	88
Or	2	1	2	2	1	0	0

	WG8	AL*1	AL*2	AL*3	AL*4	SC1	SC2
SiO2	63.0	63.33	64.01	65.83	64.99	64.76	63.18
Al2O3	22.29	21.76	22.33	21.79	22.18	22.29	22.82
CaO	3.41	3	3.35	2.76	3.20	3.19	3.82
Na2O	9.71	9.40	9.47	10.27	9.68	9.89	9.58
K2O	0.12	0.24	0.31	0	0	0.27	0.26
Total	98.62	97.73	99.37	100.65	100.05	100.4	99.66
Number of ions per unit formula (on the basis of 32 oxygens)							
Si	11.26	11.39	11.33	11.48	11.40	11.36	11.20
Al	4.70	4.61	4.66	4.48	4.58	4.61	4.77
Ca	0.65	0.57	0.63	0.51	0.60	0.60	0.72
Na	3.36	3.27	3.25	3.47	3.92	3.36	3.29
K	0.02	0.05	0.07	0	0	0.06	0.06
End member proportions							
An	16	15	16	13	15	24	28
Ab	83	84	82	87	85	74	70
Or	1	1	2	0	0	2	2

		upper sequence (matrix)				
	SC3	WG1	WG2	WG3	WG4	WG5
SiO2	63.33	66.6	67.3	67.79	67.47	68.63
Al2O3	21.76	19.21	19.49	19.47	14.29	19.61
CaO	3.14	0	0	0	0.24	0
Na2O	9.36	8.94	11.79	11.66	11.62	11.52
K2O	0.27	0	0	0.08	0	0
Total	97.86	94.75	98.58	99.0	98.62	99.76
Number of ions per unit formula (on the basis of 32 oxygens)						
Si	11.39	11.89	11.93	11.96	11.95	11.97
Al	4.61	4.04	4.07	4.05	4.03	4.03
Ca	0.60	0	0	0	0.04	0
Na	3.26	4.16	4.05	3.99	3.99	3.89
K	0.06	0	0	0.01	0	0
End member proportions						
An	25	0	0	0	1	0
Ab	73	100	100	99	99	100
Or	2	0	0	1	0	0

	WG6	AL1	AL2	AL3	AL4	SC1	SC2
SiO2	66.46	65.77	65.94	66.88	66.61	67.88	67.75
Al2O3	19.27	20.14	20.24	19.19	20.26	19.56	19.37
CaO	0	1.30	1.21	1.20	0.50	0.13	0.13
Na2O	11.47	10.26	10.91	11.12	11.41	11.09	11.71
K2O	0	0.09	0	0	0	98.66	98.96
Total	97.20						

Number of ions per unit formula (on the basis of 32 oxygens)

Si	11.94	11.78	11.75	11.90	11.77	11.95	11.95
Al	4.08	4.25	4.25	4.02	4.22	4.08	4.02
Ca	0	0.25	0.23	0.23	0.09	0.02	0.02
Na	3.99	3.56	3.77	3.83	3.91	3.78	4.0
K	0	0.02	0	0	0	0	0

End member proportions

An	0	6	6	6	2	1	1
Ab	100	93	94	94	98	99	99
Or	0	1	0	0	0	0	0

	SC3	SC4	WP1	WP2	WP3	WP4	WP5
SiO2	66.14	64.05	65.95	65.55	67.09	66.4	66.63
Al2O3	19.06	21.43	19.05	19.08	19.80	19.77	19.59
CaO	0.12	2.33	0	0.10	0.25	0.40	0.22
Na2O	11.15	10.59	11.75	12.01	11.40	11.29	11.38
K2O	0.12	0.18	0	0.11	0	0	0
Total	96.59	98.58	96.75	96.85	98.54	97.86	97.82

Number of ions per unit formula (on the basis of 32 oxygens)

Si	11.95	11.45	11.92	11.87	11.89	11.86	11.89
Al	4.06	4.52	4.06	4.07	4.13	4.16	4.12
Ca	0.02	0.44	0	0.0	0.05	0.07	0.04
Na	3.90	3.67	4.11	4.22	3.91	3.91	3.98
K	0.02	0.04					

End member proportions

An	1	18	0	0	1	2	1
Ab	99	81	100	99	99	98	99
Or	0	1	0	1	0	0	0

key to appendix one

Silurian

S=Scart Grit
HQ=Quartz Conglomerate
Conglomerate
HC=Craigshley

upper sequence

Formation

WG=Whitehouse Group
SC=Shalloch Formation
AL*=Shalloch Formation
Conglomerate
WP=Shalloch Formation

lower sequenc

TA=Changue Formation
KK=Kilrany

TR=Changue Formation(1-16)
TR=Darley Formation(17-22)
TB=Changue Formation
AL=Craigmulock

BC=Craigmulock Formation
KP=InfraKilrany Greywackes
AD=Benan Conglomerate
KC=Kirkland

middle sequence

AF=Ardwell Flag
TM=Ardwell Group and Cascade Grits
PW= Cascade Grits (1-9) and Whitehouse Group (10-23)

Note that the framework modes are presented as follows:

$Q + F + L = 100$
$Qm + F + L = 100$
$Qp + Lv + Ls = 100$
$Qm + P + K = 100$

Definition of these terms and others is given in table 4.1

Appendix two: Results of chemical analyses.

lower sequence

	TA1	TA2	TA3	TA4	TA5	TA6	TA7
Major elements (wt%)							
SiO_2	67.63	67.74	68.24	67.57	55.15	62.85	60.80
TiO_2	0.83	0.80	0.83	0.79	0.94	0.82	1.06
Al_2O_3	12.05	11.78	12.18	12.35	15.74	12.56	12.61
Fetot	6.20	5.94	6.06	5.43	8.51	6.06	7.23
MnO	0.07	0.08	0.08	0.08	0.19	0.90	0.95
MgO	3.92	4.08	3.85	3.54	4.11	4.19	4.93
CaO	0.78	0.80	0.45	1.06	0.56	2.14	2.22
Na_2O	3.47	3.14	3.37	3.37	3.21	3.12	3.08
K_2O	1.37	1.49	1.61	1.45	1.78	1.49	1.51
P_2O_5	0.10	0.11	0.10	0.11	0.16	0.12	0.12
H_2O	3.07	3.01	3.02	2.91	2.91	3.2	3.1
CO_2	0.72	2.53	1.2	2.52	2.52	2.67	2.62
Total	100.2	101.68	100.99	101.18	101.1	100.07	101.23

Trace elements(ppm)							
Zr	169	163	180	163	166	151	209
Y	26	26	28	28	34	28	31
Sr	90	91	93	103	50	114	117
Rb	37	35	39	37	98	42	44
Th	5	6	2	6	8	5	4
Ga	12	12	12	13	18	12	14
Ni	122	150	107	134	110	132	172
Co	13	15	11	13	22	17	20
Cr	374	477	379	317	179	302	640
Ce	35	34	35	32	48	34	37
Ba	257	296	324	190	170	190	212
La	17	22	22	19	27	17	22

	TA8	TA9	TA10	TA11	TA12	TA13	TA14
Major elements (wt%)							
SiO2	66.44	72.57	61.73	66.82	67.13	66.92	68.15
TiO2	0.84	0.58	1.03	0.85	0.80	0.83	0.81
Al2O3	12.18	10.93	14.77	11.61	11.86	12.36	12.20
Fetot	6.26	4.79	7.11	6.24	5.96	6.17	6.58
MnO	0.08	0.07	0.07	0.11	0.95	0.09	0.07
MgO	4.22	2.93	4.57	4.00	4.01	3.92	3.88
CaO	0.81	0.38	0.39	1.32	1.06	1.00	0.29
Na2O	3.32	3.09	3.51	3.08	3.25	3.41	3.29
K2O	1.63	1.50	2.11	1.38	1.56	1.33	1.54
P2O5	0.11	0.08	0.14	0.11	0.10	0.12	0.11
H2O	2.9	2.01	2.75	2.55	2.01	2.1	2.3
CO2	2.6	0.91	0.97	0.99	0.92	0.85	0.96
Total	101.39	99.84	99.15	99.06	99.61	99.1	100.18

Trace elements(ppm)							
Zr	172	122	189	171	165	170	158
Y	29	24	33	27	27	26	25
Sr	93	83	111	87	96	99	88
Rb	40	32	56	31	37	31	39
Th	3	4	9	4	5	4	5
Ga	12	10	15	12	11	13	13
Ni	139	102	154	118	141	129	129
Co	17	11	19	16	16	15	12
Cr	407	325	281	412	390	290	407
Ce	35	26	46	34	30	32	34
Ba	324	387	338	254	300	243	286
La	19	16	26	21	22	18	24

	TA15	TA16	TA17	KK1	KK2	KK3	KK4
Major elements (wt%)							
SiO_2	62.29	64.79	65.65	58.39	54.18	58.47	55.34
TiO_2	0.93	0.95	0.85	1.59	1.39	1.58	1.45
Al_2O_3	13.24	12.00	13.11	13.13	14.89	13.22	13.74
Fetot	7.53	7.02	6.51	10.22	13.03	10.82	13.16
MnO	0.09	0.08	0.08	0.13	0.12	0.12	0.10
MgO	5.40	6.33	4.40	5.36	5.20	5.61	5.63
CaO	0.99	4.07	0.46	4.04	3.06	4.01	3.39
Na_2O	2.83	3.12	3.25	3.36	3.33	3.31	2.93
K_2O	1.91	1.51	1.56	0.84	1.01	0.97	0.95
P_2O_5	0.15	1.51	0.12	0.14	0.13	0.14	0.14
H_2O	2.35	2.65	2.5	3.28	2.3	3.2	3.25
CO_2	2.2	1.15	2.54	0.39	0.41	0.6	0.36
Total	99.91	100.61	101	100.88	100.96	102.01	100.44

Trace elements(ppm)							
Zr	156	193	168	119	134	133	112
Y	28	32	26	33	35	31	31
Sr	104	93	92	165	146	164	156
Rb	50	42	41	18	19	22	11
Th	3	2	2	3	1	4	0
Ga	14	14	13	14	19	15	15
Ni	140	135	121	70	66	74	59
Co	21	16	19	21	30	30	27
Cr	266	474	279	200	213	219	208
Ce	34	41	38	15	23	26	20
Ba	306	186	320	138	148	163	161
La	16	25	23	11	10	16	16

	KK5	TR1	TR2	TR3	TR4	TR5	TR6
Major elements (wt%)							
SiO2	57.17	65.70	63.57	65.47	63.68	62.48	64.29
TiO2	1.51	0.85	0.90	0.82	0.89	0.85	0.76
Al2O3	13.48	11.37	11.68	10.66	13.27	11.68	11.27
Fetot	10.50	6.63	6.48	6.60	7.11	7.06	5.90
MnO	0.14	0.08	0.07	0.10	0.09	0.12	0.09
MgO	5.38	5.39	4.22	5.51	5.00	6.15	3.46
CaO	3.83	1.20	2.97	1.56	0.36	1.65	4.11
Na2O	3.01	2.82	3.20	2.48	3.19	2.93	2.13
K2O	0.96	1.70	1.51	1.40	1.84	1.76	1.54
P2O5	0.13	0.12	0.13	0.08	0.13	0.11	0.10
H2O	3.15	2.87	3.01	3.07	2.7	3.11	4.22
CO2	0.45	0.59	2.70	2.83	0.71	2.97	1.45
Total	99.71	99.32	100.44	100.58	98.97	100.87	99.32
Trace elements(ppm)							
Zr	133	163	148	143	166	155	153
Y	31	25	25	23	24	27	27
Sr	164	87	106	72	100	91	77
Rb	22	36	44	29	46	40	38
Th	4	5	5	3	4	3	3
Ga	15	11	12	9	12	10	8
Ni	74	181	132	157	123	225	151
Co	30	14	14	23	21	24	18
Cr	219	756	311	648	291	591	504
Ce	26	31	29	15	22	24	31
Ba	163	284	338	261	304	281	141
La	16	21	18	8	13	15	21

	TR7	TR8	TR9	TR10	TR11	TR12	TR13
Major elements (wt%)							
SiO_2	66.29	59.45	68.50	68.45	64.80	66.45	66.42
TiO_2	0.72	0.77	0.69	0.85	0.85	0.86	0.96
Al_2O_3	11.21	11.62	11.68	11.60	11.12	12.04	12.06
Fetot	6.29	6.61	5.32	5.90	6.34	6.59	6.68
MnO	0.10	0.09	0.08	0.07	0.11	0.07	0.10
MgO	5.19	5.86	4.13	3.85	5.67	4.45	4.47
CaO	1.05	3.96	1.46	1.09	1.71	1.10	0.65
Na_2O	2.99	2.79	3.40	3.25	3.05	2.98	3.07
K_2O	1.76	1.74	1.87	1.50	1.52	1.80	1.65
P_2O_5	0.10	0.12	0.09	0.11	0.11	0.13	0.11
H_2O	2.89	3.40	2.11	2.8	2.70	2.74	2.63
CO_2	0.58	3.03	0.87	0.73	0.88	0.68	0.74
Total	99.17	99.44	100.2	100.2	98.86	99.89	99.54
Trace elements(ppm)							
Zr	135	128	140	164	160	169	184
Y	22	26	26	23	23	23	23
Sr	85	103	97	95	83	97	97
Rb	37	40	39	38	32	44	39
Th	1	0	5	4	4	6	6
Ga	11	10	9	11	9	10	13
Ni	213	264	115	97	182	86	118
Co	21	23	12	12	19	16	12
Cr	492	446	253	291	630	202	433
Ce	36	31	33	29	18	32	33
Ba	322	309	380	261	268	319	314
La	15	16	15	16	15	18	19

	TR14	TR15	TR16	TR17	TR18	TR19	TR20
Major elements (wt%)							
SiO2	64.26	67.80	65.09	65.11	64.89	67.33	65.25
TiO2	0.75	0.77	0.82	0.81	0.79	0.69	0.78
Al2O3	11.50	11.47	11.91	12.15	12.67	11.33	12.06
Fetot	5.70	5.77	6.80	6.56	6.66	5.43	6.09
MnO	0.09	0.08	0.09	0.08	0.07	0.06	0.07
MgO	4.18	4.98	5.23	5.16	5.55	4.47	4.73
CaO	3.75	0.71	0.93	1.05	0.42	1.82	1.69
Na2O	2.41	3.12	2.96	2.85	3.21	3.30	3.34
K2O	1.38	1.84	1.74	1.77	1.80	1.68	1.88
P2O5	0.10	0.10	0.12	0.12	0.12	0.09	0.10
H2O	3.12	2.10	2.8	2.93	2.74	2.78	2.98
CO2	2.7	0.6	0.63	0.69	0.68	0.74	0.73
Total	99.94	99.34	99.29	99.28	99.60	99.69	99.7

Trace elements(ppm)							
Zr	139	149	148	156	135	150	178
Y	24	24	23	24	25	24	22
Sr	76	89	84	97	89	103	117
Rb	34	40	42	38	42	34	37
Th	2	1	2	5	3	5	4
Ga	11	9	13	10	12	11	10
Ni	158	161	174	149	146	154	96
Co	19	13	17	15	18	16	13
Cr	429	502	435	412	235	386	254
Ce	23	27	23	26	25	15	27
Ba	157	337	285	337	302	339	296
La	19	12	8	19	13	12	18

	TR21	TR22	TR23	TR24	TR25	TR26	TR27
Major elements (wt%)							
SiO2	65.84	67.85	67.58	66.62	67.17	58.34	63.41
TiO2	0.79	0.77	0.80	0.79	0.84	0.81	1.07
Al2O3	11.80	11.18	11.40	11.68	11.07	11.29	11.62
Fetot	6.09	6.44	6.22	6.37	6.39	6.72	6.76
MnO	0.10	0.07	0.08	0.08	0.09	0.09	0.11
MgO	4.17	5.21	4.99	5.07	5.28	5.63	4.50
CaO	2.14	0.66	0.88	0.99	0.97	5.25	2.16
Na2O	3.06	2.83	2.79	2.99	2.90	2.70	2.51
K2O	1.42	1.60	1.69	1.77	1.48	1.66	1.49
P2O5	0.10	0.10	0.1	0.11	0.111	0.11	0.12
H2O	2.86	2.02	2.13	2.01	2.82	3.1	3.5
CO2	0.98	0.64	0.88	0.95	0.61	1.88	2.6
Total	99.35	99.37	99.55	99.43	99.73	97.58	99.83

Trace elements(ppm)							
Zr	145	146	147	141	153	149	240
Y	24	24	23	21	21	24	30
Sr	97	84	94	81	79	107	103
Rb	36	41	41	34	36	39	42
Th	4	3	3	4	3	3	4
Ga	10	9	10	10	12	12	10
Ni	147	195	140	192	139	276	112
Co	18	13	16	20	17	23	20
Cr	422	476	381	702	422	680	363
Ce	32	26	31	24	21	27	42
Ba	222	295	331	291	248	280	215
La	20	12	21	19	17	20	25

	TR28	TB1	TB2	TB3	TB4	TB5	TB6
Major elements (wt%)							
SiO2	70.24	65.58	66.14	67.76	62.71	63.26	62.39
TiO2	0.60	0.73	0.76	0.75	0.95	0.80	0.85
Al2O3	10.92	11.54	11.15	11.77	13.93	11.55	13.43
Fetot	4.82	5.99	5.37	5.67	7.11	6.21	7.14
MnO	0.08	0.10	0.11	0.10	0.08	0.09	0.11
MgO	3.94	4.07	4.39	4.45	4.51	4.92	4.95
CaO	1.26	2.19	2.14	0.86	0.82	3.18	1.19
Na2O	3.23	2.95	3.23	2.87	2.68	3.17	3.28
K2O	1.45	1.32	1.05	1.45	1.91	1.30	1.67
P2O5	0.09	0.10	0.15	0.11	0.14	0.11	0.13
H2O	2.13	2.65	2.37	2.45	2.75	2.63	2.56
CO2	0.55	2.14	2.34	2.25	1.90	2.13	2.35
Total	99.31	99.63	99.20	100.49	99.49	99.37	100.05
Trace elements(ppm)							
Zr	118	143	134	143	169	145	151
Y	27	28	27	23	27	22	26
Sr	99	94	81	75	68	97	86
Rb	29	32	28	31	55	32	47
Th	3	3	0	3	3	3	3
Ga	12	13	9	11	14	11	13
Ni	101	193	97	118	158	223	155
Co	9	20	12	15	16	15	22
Cr	274	598	192	284	279	577	244
Ce	25	25	22	31	34	20	31
Ba	305	277	158	258	188	255	207
La	16	21	13	14	23	22	18

	TB7	TB8	TB9	TB10	TB11	TB12	TB13
Major elements (wt%)							
SiO2	63.83	67.28	65.32	50.00	66.99	65.88	46.86
TiO2	0.80	0.72	0.84	1.57	0.82	0.81	1.64
Al2O3	11.52	11.16	11.67	14.14	12.01	12.01	12.96
Fetot	5.52	6.12	6.67	10.83	6.14	5.93	10.46
MnO	0.08	0.21	0.10	0.15	0.08	0.09	0.14
MgO	2.87	3.20	4.45	6.12	4.62	4.52	8.95
CaO	2.81	1.71	1.55	5.89	0.94	1.70	6.43
Na2O	2.42	2.77	3.13	4.39	3.45	3.02	2.54
K2O	1.66	1.32	1.11	1.15	1.09	1.49	1.12
P2O5	0.10	0.10	0.11	0.22	0.11	0.11	0.17
H2O	5.8	2.50	2.30	2.45	2.40	2.47	5.63
CO2	2.76	2.88	2.47	2.70	2.15	2.60	2.87
Total	100.17	99.97	99.72	99.60	100.8	100.77	99.77

Trace elements(ppm)							
Zr	145	137	162	141	160	155	120
Y	25	27	26	26	25	26	24
Sr	78	81	88	247	76	93	168
Rb	42	35	32	23	29	23	24
Th	4	2	3	0	3	1	0
Ga	11	10	11	15	12	12	13
Ni	156	244	121	189	153	117	231
Co	13	23	18	36	18	13	34
Cr	624	842	304	255	408	280	489
Ce	29	14	29	19	26	37	19
Ba	96	252	179	227	167	316	155
La	18	18	15	12	12	25	15

	TB14	TB15	TB16	TB17	TB18	TB19	TB20
Major elements (wt%)							
SiO2	47.38	66.35	52.66	63.62	65.89	65.38	68.35
TiO2	1.75	0.58	1.39	0.68	0.79	0.84	0.65
Al2O3	13.49	11.21	12.84	11.41	11.52	11.69	10.98
Fetot	10.58	4.90	9.59	6.29	6.22	6.72	5.41
MnO	0.16	0.07	0.12	0.12	0.11	0.11	0.10
MgO	9.26	3.55	7.26	4.57	4.42	4.66	3.71
CaO	6.62	2.58	4.36	2.58	1.44	1.54	1.87
Na2O	3.77	3.29	3.84	2.62	3.10	3.23	2.84
K2O	0.76	1.14	0.98	1.30	1.48	1.14	1.42
P2O5	0.17	0.09	0.14	0.11	0.11	0.12	0.09
H2O	4.5	4.71	4.12	3.98	2.69	2.65	2.55
CO2	1.97	1.85	1.94	2.08	2.51	2.40	2.28
Total	100.41	100.32	99.24	99.36	100.28	100.41	100.25
Trace elements(ppm)							
Zr	121	143	116	97	145	162	141
Y	24	23	24	28	20	26	23
Sr	136	75	133	129	92	88	91
Rb	16	31	22	24	36	32	13
Th	0	3	0	3	4	3	0
Ga	15	11	13	11	11	11	9
Ni	295	118	277	230	106	121	112
Co	28	15	29	32	17	18	11
Cr	600	284	695	653	262	304	324
Ce	12	31	16	11	31	29	18
Ba	157	258	192	189	308	179	304
La	6	14	11	5	18	15	9

	TB21	AL1	AL2	AL3	AL4	AL5	AL6
Major elements (wt%)							
SiO2	46.95	47.41	49.47	52.97	51.14	55.77	54.24
TiO2	1.17	1.30	1.79	1.32	1.14	1.43	1.30
Al2O3	10.11	10.34	12.62	11.12	10.89	11.63	11.71
Fetot	8.65	7.95	9.81	9.36	8.30	9.15	9.28
MnO	0.17	0.15	0.18	0.14	0.14	0.15	0.14
MgO	10.65	6.44	8.02	11.74	8.43	6.83	10.30
CaO	10.72	11.67	9.03	4.50	7.87	6.72	4.47
Na2O	2.24	2.97	2.44	2.58	2.64	3.30	2.74
K2O	2.29	0.80	0.69	0.77	0.80	0.97	0.89
P2O5	1.10	0.13	0.13	0.15	0.14	0.14	0.14
H2O	2.57	4.5	1.99	2.0	3.88	2.1	2.83
CO2	2.51	6.25	2.28	2.5	4.26	2.9	3.26
Total	99.13	99.91	98.45	99.15	99.63	101	101.3
Trace elements(ppm)							
Zr	183	112	116	120	110	125	120
Y	31	25	27	28	26	26	26
Sr	138	123	137	135	130	156	145
Rb	75	13	13	15	15	15	17
Th	12	0	1	2	1	0	0
Ga	16	10	12	12	11	13	14
Ni	364	291	293	364	339	268	328
Co	57	27	36	31	34	34	30
Cr	389	819	1070	672	657	567	478
Ce	264	18	10	13	16	14	11
Ba	965	136	144	135	134	138	143
La	103	17	5	10	6	10	13

	BC1	BC2	BC3	BC4	BC5	BC6	BC7
Major elements (wt%)							
SiO2	48.23	66.75	54.38	52.78	52.40	52.23	39.15
TiO2	1.04	0.79	1.29	1.22	1.10	1.43	1.03
Al2O3	9.89	11.69	11.79	11.31	9.42	11.26	8.66
Fetot	9.09	6.22	9.43	9.07	7.05	9.48	7.01
MnO	0.13	0.08	0.15	0.14	0.13	0.15	0.23
MgO	10.27	4.94	10.08	9.47	5.82	8.18	5.75
CaO	7.83	0.99	4.74	6.22	10.99	6.65	19.47
Na2O	1.25	3.16	2.94	2.70	2.36	2.79	2.12
K2O	0.56	1.79	0.72	0.84	1.05	0.74	0.59
P2O5	0.11	0.10	0.14	0.15	0.09	0.14	0.12
H2O	2.15	2.05	3.15	4.05	2.7	3.95	2.65
CO2	9.15	1.93	1.80	1.99	7.08	2.10	13.03
Total	99.7	100.49	100.61	100.39	100.19	99.46	99.81

Trace elements(ppm)							
Zr	94	106	120	119	140	130	96
Y	20	26	30	26	23	29	20
Sr	72	31	144	139	136	167	123
Rb	16	11	14	18	25	14	13
Th	5	0	0	0	3	0	1
Ga	11	10	11	11	10	15	8
Ni	570	272	384	402	224	360	209
Co	43	25	29	34	23	31	21
Cr	760	957	616	874	746	736	473
Ce	9	13	13	12	15	19	12
Ba	110	119	156	153	201	122	135
La	2	11	9	9	11	10	13

	KP1	KP2	KP3	KP4	KP5	KP6	KP7
Major elements (wt%)							
SiO2	55.06	56.47	57.44	62.48	60.02	60.13	57.83
TiO2	1.12	1.05	1.14	0.99	1.37	1.38	1.15
Al2O3	11.98	11.67	12.68	11.55	12.29	12.93	13.15
Fetot	8.88	8.44	9.60	8.57	9.62	10.82	9.90
MnO	0.13	0.12	0.10	0.11	0.09	0.11	0.09
MgO	5.36	5.36	5.85	5.23	6.02	6.07	6.00
CaO	5.70	5.47	2.87	2.51	3.08	2.90	2.74
Na2O	2.32	2.28	2.44	2.56	2.42	2.29	2.72
K2O	1.15	1.26	1.19	1.04	0.99	1.23	1.01
P2O5	1.21	0.16	0.13	0.12	0.14	0.14	0.14
H2O	3.21	2.90	4.02	2.45	2.15	1.05	2.18
CO2	3.30	3.85	2.10	3.26	2.80	1.7	3.6
Total	99.43	99.04	99.57	100.87	100.99	100.75	100.51

Trace elements(ppm)							
Zr	117	245	121	110	127	120	120
Y	40	23	28	27	33	27	31
Sr	108	94	91	109	145	136	141
Rb	24	37	25	22	21	28	25
Th	4	4	5	2	2	0	4
Ga	15	10	16	14	16	15	16
Ni	62	26	62	58	69	71	70
Co	28	11	24	24	26	25	23
Cr	178	87	175	141	196	216	172
Ce	27	34	18	21	30	17	24
Ba	170	329	258	187	166	186	149
La	12	15	9	9	13	13	10

	KP8	KP9	AD1	AD2	AD3	KC1	KC2
Major elements (wt%)							
SiO2	59.58	56.41	60.87	55.60	60.63	42.09	38.66
TiO2	1.10	1.35	1.08	1.18	1.05	1.30	1.32
Al2O3	12.16	12.06	11.37	11.45	10.52	11.36	9.78
Fetot	8.96	9.96	7.96	8.99	8.71	10.75	8.89
MnO	0.10	0.09	0.10	0.11	0.11	0.16	0.21
MgO	5.88	5.50	6.87	4.97	6.74	8.93	8.10
CaO	2.96	3.92	2.69	6.85	4.17	10.33	15.39
Na2O	2.45	2.53	3.01	3.45	3.06	2.59	2.31
K2O	0.92	0.72	0.65	0.84	0.90	0.85	0.58
P2O5	0.14	0.13	0.09	0.13	0.11	0.13	0.12
H2O	2.27	2.8	3.6	3.8	3.15	3.75	3.35
CO2	3.05	3.95	0.75	1.65	0.95	7.35	9.15
Total	99.57	99.42	99.04	99.02	100.1	99.59	97.86
Trace elements(ppm)							
Zr	113	119	110	114	113	150	172
Y	28	28	26	31	26	21	23
Sr	108	104	31	158	124	170	184
Rb	16	15	17	20	22	23	14
Th	0	2	2	1	4	1	2
Ga	13	15	13	12	11	15	10
Ni	54	60	117	130	218	382	297
Co	24	23	20	21	23	48	32
Cr	159	168	254	413	438	913	1093
Ce	16	21	20	24	20	10	11
Ba	144	150	135	160	186	135	119
La	10	13	10	12	12	5	13

Middle

sequence

	KC3	KC4	KC5	KC6	AF1	AF2
Major elements (wt%)						
SiO_2	37.65	61.27	59.83	62.79	55.60	46.85
TiO_2	1.36	0.87	0.77	0.70	1.12	1.20
Al_2O_3	9.89	10.06	9.47	9.80	15.56	10.86
Fetot	8.98	7.23	6.50	6.30	9.44	7.12
MnO	0.28	0.08	0.11	0.12	0.13	0.13
MgO	9.05	6.47	6.26	5.69	5.92	4.29
CaO	16.37	4.10	5.81	3.37	2.93	14.12
Na_2O	1.98	2.22	2.20	2.18	3.53	3.25
K_2O	0.61	1.25	1.12	1.61	1.45	0.60
P_2O_5	0.14	0.11	0.09	0.10	0.11	0.15
H_2O	3.15	3.78	3.95	3.70	2.26	2.2
CO_2	9.75	2.05	2.95	2.85	2.95	10.2
Total	99.21	99.49	99.00	99.21	101.55	100.97
Trace elements(ppm)						
Zr	171	134	117	120	120	108
Y	25	22	23	26	29	29
Sr	169	105	89	90	180	140
Rb	13	32	27	41	33	12
Th	0	0	2	1	0.0	2.0
Ga	12	10	7	8	16	10
Ni	272	247	222	261	58	47
Co	34	21	11	10	24	21
Cr	866	583	459	558	162	166
Ce	23	22	16	19	21	17
Ba	129	244	216	263	242	137
La	15	19	18	27	14	14

	AF3	AF4	AF5	AF6	AF7	AF8	AF9
Major elements (wt%)							
SiO2	51.03	62.40	60.06	61.62	43.55	53.72	58.27
TiO2	0.75	1.07	1.17	1.07	0.73	1.75	1.33
Al2O3	11.81	13.76	12.96	12.42	9.47	14.02	12.83
Fetot	5.14	6.94	8.57	7.52	4.84	9.31	7.91
MnO	0.11	0.95	0.09	0.07	0.12	0.09	0.08
MgO	2.65	3.52	5.32	4.26	2.49	5.40	4.45
CaO	12.57	3.49	3.54	5.00	19.60	5.30	4.55
Na2O	3.30	3.73	3.39	3.10	3.19	2.98	3.37
K2O	1.05	1.22	1.01	0.94	0.51	1.58	1.29
P2O5	0.16	0.09	0.11	0.11	0.26	0.14	0.13
H2O	2.35	0.31	1.9	1.77	2.31	2.3	2.12
CO2	10.1	3.08	2.48	3.05	12.3	3.01	3.17
Total	101	100.56	100.6	101.1	99.17	99.6	99.58
Trace elements(ppm)							
Zr	99	92	115	87	87	155	120
Y	31	30	30	24	28	38	31
Sr	157	142	155	131	279	192	153
Rb	23	21	18	16	14	17	16
Th	1.0	0.0	4.0	0.0	0.0	0.0	0.0
Ga	8	15	14	15	9	16	13
Ni	29	34	51	37	27	54	43
Co	11	10	19	16	9	18	22
Cr	96	122	143	113	93	205	172
Ce	32	34	19	14	28	25	27
Ba	164	224	212	136	112	216	212
La	25	18	13	17	5	14	16

	AF10	AF11	AF12	AF13	AF14	AF15	AF16
Major elements (wt%)							
SiO_2	53.88	55.63	58.11	59.03	58.85	41.64	51.21
TiO_2	1.62	1.67	1.13	1.13	1.35	1.30	1.16
Al_2O_3	12.74	13.78	15.02	13.26	12.00	9.97	11.84
Fetot	7.91	10.36	8.37	7.92	7.89	7.01	8.40
MnO	0.16	0.13	0.12	0.09	0.10	0.18	0.11
MgO	5.15	5.87	4.77	4.90	4.33	4.20	5.07
CaO	7.85	3.99	3.42	5.01	6.53	18.58	9.48
Na_2O	3.23	3.52	4.07	3.57	2.72	2.64	3.39
K_2O	0.63	0.97	1.26	1.27	1.11	0.64	0.81
P_2O_5	.0.13	0.14	0.12	0.12	0.11	0.12	0.13
H_2O	2.11	1.27	1.99	1.75	2.18	2.39	2.3
CO_2	4.4	2.3	2.05	3.0	3.77	10.66	5.55
Total	100.56	99.63	100.43	100.99	100.94	99.33	99.45
Trace elements(ppm)							
Zr	126	127	117	108	113	95	95
Y	31	36	29	30	29	30	29
Sr	159	189	212	173	145	140	141
Rb	20	13	24	16	15	11	13
Th	2.0	0.0	2.0	0.0	2.0	0.0	0.0
Ga	15	19	16	14	12	11	13
Ni	97	56	49	51	48	37	55
Co	28	26	21	22	23	17	26
Cr	210	226	154	153	159	159	191
Ce	29	28	19	21	22	24	16
Ba	149	137	282	254	145	163	168
La	13	28	17	16	22	23	12

	AF17	AF18	AF19	AF20	AF21	AF22	AF23
Major elements (wt%)							
SiO2	60.02	60.39	59.00	56.92	67.50	55.65	59.74
TiO2	1.43	0.89	1.57	1.18	0.80	1.68	1.29
Al2O3	13.85	15.44	13.95	14.54	12.23	13.77	13.84
Fetot	7.82	7.43	8.43	8.70	6.16	9.23	8.15
MnO	0.10	0.09	0.11	0.12	0.08	0.13	0.11
MgO	4.51	5.12	4.84	4.84	2.84	5.17	5.26
CaO	3.60	2.10	3.04	4.12	2.98	5.57	2.92
Na2O	3.68	3.47	3.78	3.72	3.20	3.37	3.36
K2O	0.66	1.99	1.06	1.08	1.43	0.95	1.39
P2O5	0.13	0.11	0.13	0.12	0.08	0.15	0.12
H2O	2.34	2.05	2.32	2.01	2.18	2.2	1.85
CO2	1.29	0.25	0.88	2.21	0.25	3.0	3.05
Total	99.43	99.33	99.11	99.56	99.73	100.87	101.08

Trace elements(ppm)							
Zr	111	105	136	120	83	135	123
Y	30	23	31	31	26	33	33
Sr	155	224	180	192	129	204	170
Rb	13	20	16	24	21	16	17
Th	1.0	0.0	2.0	1.0	3.0	0.0	0.0
Ga	15	16	15	15	13	15	14
Ni	48	38	50	60	32	53	52
Co	15	14	30	23	11	24	19
Cr	169	111	197	169	96	202	159
Ce	31	16	23	23	27	32	27
Ba	159	388	180	256	222	262	280
La	18	10	16	14	11	18	18

	AF24	AF25	AF26	AF27	TM1	TM2	TM3
Major elements (wt%)							
SiO2	62.31	54.32	58.31	54.90	57.93	57.62	57.74
TiO2	0.98	1.77	1.23	1.17	1.43	1.32	1.15
Al2O3	12.31	12.50	14.38	16.43	10.90	10.63	10.57
Fetot	9.88	8.72	10.32	8.74	7.33	7.47	9.27
MnO	0.12	0.13	0.10	0.12	0.12	0.13	0.11
MgO	3.38	5.76	5.23	5.86	4.66	3.89	4.74
CaO	5.93	7.15	3.44	2.43	5.13	6.42	6.06
Na2O	3.11	2.83	3.60	4.10	2.26	2.26	2.47
K2O	0.86	0.96	1.70	1.44	0.47	0.47	0.46
P2O5	0.12	0.16	0.13	0.16	0.07	0.07	0.08
H2O	1.7	2.1	1.83	2.0	1.95	2.37	2.47
CO2	3.0	2.98	3.02	2.20	6.23	7.12	7.46
Total	100.99	100.5	101.6	101.1	99.9	99.6	100.4
Trace elements(ppm)							
Zr	92	135	116	117	91	89	89
Y	29	34	31	33	24	24	22
Sr	157	175	193	188	154	158	157
Rb	13	14	18	17	7	11	11
Th	0.0	0.0	11	1.0	0.0	0.0	0.0
Ga	12	14	81	16	15	13	13
Ni	42	59	32	56	105	109	98
Co	18	22	153	34	36	20	18
Cr	120	204	22	168	322	360	302
Ce	23	20	263	32	14	6	17
Ba	160	198	13	250	104	82	79
La	17	13	116	17	8	11	3

	TM4	TM5	TM6	TM7	TM8	TM9	TM10
Major elements (wt%)							
SiO2	57.42	55.25	51.43	57.81	61.09	56.28	59.69
TiO2	1.58	1.50	1.65	1.17	1.21	1.55	1.08
Al2O3	10.96	10.20	10.99	11.09	11.86	11.91	12.40
Fetot	9.27	7.27	8.25	7.61	7.90	9.00	7.59
MnO	0.11	0.14	0.14	0.12	0.08	0.12	0.09
MgO	6.28	4.02	5.44	4.46	6.13	6.32	4.95
CaO	4.06	7.80	8.35	6.11	2.47	3.36	3.49
Na2O	2.07	2.07	2.08	2.34	3.15	2.68	2.98
K2O	0.47	0.43	0.57	0.50	0.44	0.46	0.55
P2O5	0.08	0.07	0.12	0.08	0.07	0.08	0.07
H2O	1.97	2.19	2.15	2.05	1.9	1.95	1.75
CO2	6.23	8.39	8.25	7.25	6.21	6.22	6.07
Total	100.5	99.3	99.42	100.5	102.5	99.9	100.9
Trace elements(ppm)							
Zr	88	91	99	90	92	118	94
Y	21	24	27	22	23	22	20
Sr	134	181	256	274	120	113	136
Rb	11	10	15	11	6	6	13
Th	3.0	3.0	1.0	0.0	1.0	1.0	0.0
Ga	15	12	13	13	15	15	13
Ni	232	99	192	97	74	175	137
Co	29	19	23	23	28	35	19
Cr	641	361	277	308	209	551	345
Ce	5	15	9	11	10	12	9
Ba	107	84	127	93	117	119	100
La	6	9	11	9	5	4	10

	TM11	TM12	TM13	TM14	TM15	TM16	PW1
Major elements (wt%)							
SiO_2	58.14	48.97	57.46	56.91	42.53	57.57	60.64
TiO_2	1.09	0.91	1.53	1.41	1.37	1.19	1.12
Al_2O_3	11.76	10.94	11.13	11.40	8.77	10.32	12.43
Fetot	7.84	7.63	8.87	8.26	6.39	5.62	8.55
MnO	0.10	0.10	0.11	0.11	0.16	0.13	0.09
MgO	5.04	3.81	5.57	5.04	3.82	2.38	4.43
CaO	4.33	10.41	4.29	5.39	17.35	7.31	2.66
Na_2O	2.81	2.51	2.41	2.49	2.01	2.08	3.40
K_2O	0.55	0.59	0.51	0.50	0.43	0.51	1.25
P_2O_5	0.08	0.08	0.08	0.10	0.10	0.09	0.10
H_2O	2.7	2.2	2.37	1.89	2.2	1.85	2.79
CO_2	6.54	8.2	7.23	6.17	7.98	7.10	1.68
Total	100.9	96.3	101.5	99.6	93.1	96.1	99.14
Trace elements(ppm)							
Zr	92	81	88	87	109	83	102
Y	22	23	23	20	25	20	23
Sr	186	175	120	150	184	152	114
Rb	15	11	9	8	10	8	14
Th	3	1	3	1	1	4	1
Ga	14	13	15	14	14	13	16
Ni	151	137	117	180	183	92	37
Co	21	26	29	35	29	22	21
Cr	389	263	326	454	415	263	126
Ce	9	16	15	12	11	17	26
Ba	100	97	103	106	123	70	192
La	3	6	5	8	7	12	20

	PW2	PW3	PW4	PW5	PW6	PW7	PW8
Major elements (wt%)							
SiO2	59.78	58.03	60.41	60.42	66.05	66.82	75.47
TiO2	1.33	1.30	1.27	1.03	0.63	1.18	0.49
Al2O3	12.12	13.72	12.91	13.67	12.76	11.16	8.43
Fetot	10.32	8.27	7.93	7.28	5.41	7.16	4.53
MnO	0.10	0.07	0.08	0.06	0.07	0.05	0.06
MgO	4.59	6.04	5.30	4.87	3.74	4.13	2.10
CaO	2.13	2.28	2.48	2.82	2.17	1.16	1.56
Na2O	3.24	3.31	3.36	3.65	3.66	2.55	2.16
K2O	0.92	1.17	0.95	1.31	1.44	0.96	0.58
P2O5	0.09	0.13	0.10	0.11	0.08	0.07	0.04
H2O	2.6	2.24	1.89	2.3	1.8	1.9	1.75
CO2	1.88	2.1	3.6	1.92	2.75	3.8	3.79
Total	99.1	98.6	100.28	99.44	100.56	100.94	100.9

	PW2	PW3	PW4	PW5	PW6	PW7	PW8
Trace elements(ppm)							
Zr	108	125	113	112	96	102	100
Y	27	31	28	25	28	22	19
Sr	117	121	119	98	98	84	140
Rb	12	17	15	17	20	11	14
Th	2	2	3	0	1	2	2
Ga	18	18	18	18	15	14	9
Ni	44	57	44	59	47	77	21
Co	21	27	30	24	25	13	22
Cr	126	160	175	147	145	91	149
Ce	38	20	31	28	23	21	17
Ba	170	227	211	243	250	165	162
La	20	22	18	19	13	10	5

	PW9	PW10	PW11	PW12	PW13	PW14	PW15
Major elements (wt%)							
SiO2	74.67	56.68	49.18	43.45	67.58	68.90	69.75
TiO2	051	1.11	0.42	0.38	0.74	0.82	0.93
Al2O3	7.60	11.24	7.06	6.04	9.61	9.59	9.78
Fetot	3.99	7.37	3.36	2.92	4.66	5.22	5.94
MnO	0.07	0.12	0.79	0.59	0.26	0.19	0.14
MgO	1.69	2.84	1.51	1.17	1.87	1.77	1.90
CaO	4.37	8.38	18.62	23.26	5.54	4.41	2.87
Na2O	1.72	1.98	1.60	1.39	1.77	1.99	1.99
K2O	0.48	1.04	0.62	0.49	1.12	1.08	1.00
P2O5	0.05	0.07	0.12	0.09	0.12	0.13	0.15
H2O	1.85	1.79	2.37	2.47	2.85	2.01	1.95
CO2	3.6	3.56	1.36	16.6	3.4	3.35	3.5
Total	100.6	96.2	99.18	98.85	99.52	99.46	99.9
Trace elements(ppm)							
Zr	91	193	66	68	239	278	340
Y	18	37	28	26	19	27	29
Sr	94	226	157	206	99	102	79
Rb	13	26	18	12	3	40	36
Th	3	5	1	1	3	7	5
Ga	9	14	10	8	8	11	12
Ni	22	41	18	21	20	47	50
Co	11	20	5	12	41	16	16
Cr	65	138	62	42	14	96	106
Ce	18	44	32	26	97	49	52
Ba	130	318	132	111	237	256	218
La	8	22	11	10	47	24	20

	PW16	PW17	PW18	PW19	PW20	PW21	PW22
Major elements (wt%)							
SiO2	72.50	67.65	64.54	68.15	72.40	73.27	70.15
TiO2	0.76	0.82	0.89	0.79	0.94	0.84	1.05
Al2O3	9.31	10.80	10.59	10.50	10.30	9.32	10.57
Fetot	5.29	5.97	5.83	5.78	5.61	5.38	5.96
MnO	0.12	0.16	0.26	0.14	0.08	0.10	0.13
MgO	2.07	2.15	2.06	2.16	1.95	1.82	1.95
CaO	3.24	3.34	4.74	3.27	1.34	2.14	2.49
Na2O	1.74	2.25	2.08	2.04	2.15	2.00	1.93
K2O	0.98	1.17	1.21	1.11	1.04	1.01	1.12
P2O5	0.11	0.16	0.18	0.14	0.16	0.13	0.24
H2O	1.05	1.93	2.8	2.01	1.15	1.27	1.15
CO2	2.95	3.4	3.85	3.2	3.05	2.89	3.95
Total	100.12	99.8	99.03	99.29	100.22	100.17	100.69
Trace elements(ppm)							
Zr	219	249	268	225	339	286	374
Y	26	30	32	29	31	26	44
Sr	81	95	107	92	79	75	91
Rb	36	44	44	40	37	37	40
Th	5	6	9	7	7	7	8
Ga	13	13	14	13	14	12	14
Ni	45	44	43	46	43	41	42
Co	18	12	18	19	17	16	20
Cr	105	86	91	83	100	94	103
Ce	45	53	58	55	66	46	72
Ba	234	263	266	257	232	230	264
La	21	27	29	27	32	24	33

	PW23	PW24	PW25	PW26	PW27	PW28	PW29
Major elements (wt%)							
SiO2	68.59	68.47	73.80	71.06	71.43	75.88	71.23
TiO2	0.84	0.72	0.84	0.90	0.91	0.76	0.84
Al2O3	10.05	8.75	9.66	10.11	9.12	8.18	10.62
Fetot	5.57	4.42	5.74	6.74	4.86	4.82	5.66
MnO	0.16	0.23	0.08	0.10	0.14	0.09	0.11
MgO	1.95	1.67	2.04	2.11	1.88	1.80	2.00
CaO	4.08	6.33	1.54	1.47	3.53	1.60	1.91
Na2O	1.96	1.88	1.87	1.91	1.88	1.60	1.91
K2O	1.11	0.96	1.01	1.08	1.04	0.90	1.29
P2O5	0.12	0.12	0.12	0.14	0.12	0.10	0.13
H2O	1.99	2.05	1.35	1.8	1.89	1.85	2.95
CO2	3.10	3.65	2.75	2.25	3.97	3.6	1.8
Total	99.52	99.3	100.8	99.67	100.77	101.18	99.46
Trace elements(ppm)							
Zr	248	238	263	286	268	207	248
Y	27	25	26	26	24	21	24
Sr	97	104	72	77	85	73	89
Rb	41	34	36	38	35	31	46
Th	5	7	7	6	4	3	5
Ga	13	11	13	13	12	10	15
Ni	44	33	46	52	37	37	48
Co	18	13	17	20	15	15	15
Cr	91	87	108	107	117	109	101
Ce	47	44	46	47	36	42	56
Ba	314	228	231	246	237	205	254
La	23	21	22	19	20	23	28

upper sequence

	WG1	WG2	WG3	WG4	WG5	WG6	WG7
Major elements (wt%)							
SiO_2	40.37	66.06	64.57	48.71	62.84	49.08	46.25
TiO_2	0.73	0.83	0.85	0.44	0.52	0.44	0.71
Al_2O_3	8.59	10.79	11.45	9.66	10.43	9.53	11.97
Fetot	4.58	5.72	5.76	3.34	3.56	4.08	6.66
MnO	0.57	0.16	0.19	0.19	0.07	0.11	0.57
MgO	1.78	2.23	2.30	1.44	1.47	1.47	2.48
CaO	21.67	4.42	4.33	16.98	8.75	16.67	13.52
Na_2O	1.89	2.03	2.05	2.51	2.79	2.27	3.37
K_2O	0.57	1.13	1.27	0.90	0.62	1.01	0.60
P_2O_5	0.07	0.13	0.15	0.03	0.04	0.04	0.06
H_2O	1.35	1.45	1.43	1.32	1.45	1.12	1.37
CO_2	13.36	6.48	6.45	13.57	6.5	13.69	12.4
Total	95.53	100.63	100.8	99.09	99.04	99.5	99.96

Trace elements(ppm)							
Zr	116	277	251	144	174	141	91
Y	34	27	32	26	23	22	29
Sr	329	140	141	600	646	595	280
Rb	16	43	46	23	18	25	20
Th	2	5	6	1	1	2	0
Ga	11	11	12	9	10	10	13
Ni	18	42	48	21	13	13	31
Co	15	13	11	14	7	4	12
Cr	56	94	92	61	103	54	88
Ce	43	44	64	33	25	52	23
Ba	94	231	253	341	146	505	105
La	12	21	25	12	9	18	16

	WG8	WG9	WG10	SC1	SC2	SC3	SC4
Major elements (wt%)							
SiO2	72.30	61.14	72.30	62.64	63.38	61.81	68.71
TiO2	0.85	0.21	0.85	0.82	0.53	0.52	0.69
Al2O3	10.09	5.75	10.09	11.50	7.46	9.40	8.81
Fetot	5.92	1.44	5.92	6.63	3.54	5.77	6.16
MnO	0.08	0.20	0.08	0.13	0.21	0.11	0.11
MgO	2.70	0.75	2.70	3.27	1.82	2.80	2.62
CaO	2.06	15.38	2.06	5.13	10.99	8.33	4.49
Na2O	2.40	1.47	2.41	2.41	1.38	1.92	1.29
K2O	0.22	0.32	0.22	0.97	0.98	0.81	1.08
P2O5	0.04	0.03	0.04	0.06	0.04	0.09	0.06
H2O	0.98	1.57	0.98	1.88	1.59	1.62	1.8
CO2	3.75	11.5	3.75	3.66	7.93	7.05	3.26
Total	101.39	99.76	101.39	99.1	99.85	100.23	99.08
Trace elements(ppm)							
Zr	129	68	129	220	93	91	143
Y	21	14	121	28	24	32	26
Sr	101	336	101	341	236	169	176
Rb	9	9	9	22	19	19	23
Th	3	0	3	4	0	2	5
Ga	11	5	11	13	7	8	12
Ni	13	3	13	39	15	31	27
Co	11	0	11	19	4	16	12
Cr	68	43	68	152	92	109	94
Ce	18	16	18	36	24	16	23
Ba	40	166	40	287	283	165	318
La	16	10	16	18	14	11	10

	AL*1	AL*2	AL*3	AL*4	AL*5	AL*6	AL*7
Major elements (wt%)							
SiO2	59.60	62.20	69.01	56.18	73.24	67.90	68.54
TiO2	0.95	1.27	0.62	0.73	0.48	0.64	0.89
Al2O3	12.25	10.75	9.16	7.81	8.11	10.90	11.47
Fetot	6.87	7.38	4.85	4.38	4.21	6.34	6.31
MnO	0.11	0.14	0.08	0.21	0.08	0.09	0.06
MgO	4.28	3.74	2.54	2.01	2.50	3.25	4.52
CaO	4.46	5.33	4.54	13.59	3.67	2.60	0.53
Na2O	2.98	1.90	2.33	1.52	3.67	2.54	3.02
K2O	1.65	0.70	0.46	0.70	1.89	0.45	1.58
P2O5	0.13	0.07	0.05	0.05	0.35	0.05	0.10
H2O	2.5	2.99	2.8	3.8	0.9	1.8	0.85
CO2	2.55	3.26	3.4	8.15	1.2	2.7	1.25
Total	98.33	99.73	99.84	99.13	100.3	99.26	99.12

Trace elements(ppm)							
Zr	177	259	114	93	80	109	93
Y	32	33	22	24	19	21	26
Sr	117	217	247	200	161	219	217
Rb	43	19	14	16	11	14	12
Th	4	4	2	2	1	0	2
Ga	11	11	8	7	7	13	8
Ni	98	39	27	22	16	27	20
Co	20	19	14	14	9	12	14
Cr	247	169	109	107	74	97	87
Ce	36	39	17	24	13	17	6
Ba	311	143	104	171	55	126	81
La	26	20	12	16	9	8	6

		Silurian				
	WP1	S1	S2	S3	S4	S5
Major elements (wt%)						
SiO2	56.58	73.22	76.69	70.66	67.96	68.34
TiO2	0.85	0.95	0.73	0.79	0.81	0.86
Al2O3	8.01	9.84	7.39	9.09	10.87	10.66
Fetot	3.67	5.30	4.24	4.57	5.48	5.40
MnO	0.50	0.08	0.07	0.07	0.08	0.07
MgO	1.65	2.50	1.50	1.42	1.59	1.61
CaO	13.59	1.21	2.05	1.96	1.44	1.53
Na2O	1.47	2.28	2.24	1.80	2.08	2.46
K2O	0.96	1.00	0.66	1.01	1.38	1.40
P2O5	0.13	0.14	0.09	0.12	0.13	0.13
H2O	2.15	1.15	1.6	1.85	1.45	1.65
CO2	9.15	3.07	3.8	4.05	4.2	5.14
Total	99.7	100.74	101.06	97.39	97.47	99.25

Trace elements(ppm)						
Zr	350	377	214	274	243	260
Y	48	25	16	25	25	25
Sr	111	70	60	195	279	131
Rb	33	38	25	34	51	50
Th	4	7	5	5	8	2
Ga	9	12	8	10	14	12
Ni	27	27	20	24	22	24
Co	3	8	14	12	10	10
Cr	127	99	85	76	77	88
Ce	34	55	41	50	62	54
Ba	215	227	155	189	289	426
La	20	31	21	25	29	21

	S6	S7	S8	S9	HQ1	HQ2	HQ3
Major elements (wt%)							
SiO2	67.39	71.18	61.47	58.99	83.12	83.42	79.12
TiO2	0.97	0.88	1.20	1.35	0.71	0.47	0.64
Al2O3	11.57	10.09	11.88	10.42	4.38	3.75	7.31
Fetot	5.52	5.00	8.01	6.12	1.50	2.00	3.61
MnO	0.08	0.07	0.07	0.08	0.07	0.07	0.06
MgO	1.54	1.65	4.52	3.10	1.03	1.28	0.95
CaO	1.25	1.32	3.55	8.69	2.22	2.37	1.21
Na2O	2.85	2.37	2.66	2.50	0.07	0.09	0.41
K2O	1.37	1.18	0.83	0.80	0.63	0.46	1.01
P2O5	0.18	0.12	0.09	0.09	0.08	0.08	0.12
H2O	2.1	1.24	1.59	1.95	2.65	2.50	2.44
CO2	4.25	4.38	4.64	4.93	4.15	4.70	3.68
Total	99.07	99.48	100.52	99.02	100.61	99.17	100.56
Trace elements(ppm)							
Zr	395	330	215	275	2882	255	312
Y	31	25	30	57	13	22	20
Sr	139	98	115	185	290	164	168
Rb	50	44	27	37	25	13	38
Th	9	3	5	4	7	0	6
Ga	14	12	15	20	5	9	8
Ni	26	22	28	22	0	9	6
Co	13	9	11	1	0	30	7
Cr	107	85	140	135	18	38	53
Ce	67	57	36	40	35	9	51
Ba	274	372	220	220	158	120	202
La	33	31	16	9	18	16	24

	HQ4	HC1	HC2	HC3
Major elements (wt%)				
SiO2	71.78	70.71	64.24	68.36
TiO2	0.74	0.71	0.89	0.79
Al2O3	7.11	8.15	10.99	11.56
Fetot	4.26	4.59	6.80	6.21
MnO	0.10	0.14	0.10	0.05
MgO	1.43	2.68	5.15	4.02
CaO	4.53	3.93	2.72	1.56
Na2O	0.07	1.59	2.76	2.74
K2O	1.02	1.09	1.09	1.32
P2O5	0.13	0.10	0.10	0.14
H2O	2.94	3.6	3.15	2.35
CO2	4.92	1.35	1.65	0.95
Total	99.03	98.64	99.64	100.05
Trace elements(ppm)				
Zr	365	110	243	239
Y	24	41	18	27
Sr	165	99	59	114
Rb	39	26	31	42
Th	9	4	5	6
Ga	10	14	9	14
Ni	12	57	25	36
Co	0	31	15	18
Cr	44	161	102	95
Ce	55	27	21	41
Ba	240	173	289	323
La	25	11	11	19

Appendix two: continued (Niggli numbers)

	TA1	TA2	TA3	TA4	TA5	TA6	TA7
si	298.15	303.15	306.66	307.57	206.91	256.79	229.02
ti	2.75	2.69	2.81	2.70	2.65	2.52	3.00
al	31.31	31.07	32.26	33.13	34.80	30.24	27.99
fm	46.32	47.22	46.28	42.62	47.01	44.15	48.17
mg	0.56	0.58	0.56	0.56	0.49	0.58	0.57
c	3.68	3.84	2.17	5.17	2.25	9.37	8.96
k	0.21	0.24	0.24	0.22	0.27	0.24	0.24
alk	18.68	17.88	19.30	19.08	15.94	16.24	14.88

	TA8	TA9	TA10	TA12	TA13	TA14	TA15
si	285.09	386.57	237.12	293.32	295.30	291.01	304.14
ti	2.71	2.32	2.98	2.81	2.65	2.71	2.72
al	30.80	34.31	33.44	30.04	30.75	31.68	32.09
fm	47.20	42.46	46.72	46.78	46.02	45.60	47.91
mg	0.57	0.55	0.56	0.56	0.57	0.56	0.54
c	3.72	2.17	1.61	6.21	5.00	4.66	1.39
k	0.24	0.24	0.28	0.23	0.24	0.20	0.24
alk	18.27	21.06	18.24	16.97	18.24	18.07	18.62

	TA15	TA16	TA17	KK1	KK2	KK3	KK4
si	234.70	311.14	275.59	185.13	161.82	240.85	165.34
ti	2.64	3.43	2.68	3.79	3.12	4.89	3.26
al	29.40	33.96	32.43	24.53	26.21	32.09	24.19
fm	51.67	25.94	48.09	49.71	52.43	34.44	54.66
mg	0.59	0.02	0.57	0.51	0.44	1.00	0.46
c	4.0	20.94	2.07	13.73	9.79	17.70	10.85
k	0.31	0.24	0.24	0.14	0.17	0.16	0.18
alk	14.93	19.15	17.40	12.03	11.57	15.77	10.30

	KK5	TR1	TR2	TR3	TR4	TR5	TR6
si	181.50	264.63	251.29	267.99	251.95	230.61	271.38
ti	3.61	2.57	2.68	2.52	2.65	2.36	2.41
al	25.22	26.99	27.21	25.72	30.94	25.41	28.04
fm	50.54	52.45	44.14	53.94	50.65	53.44	40.51
mg	0.50	0.62	0.56	0.62	0.58	0.63	0.54
c	13.03	5.18	12.58	6.84	1.53	6.53	18.59
k	0.17	0.28	0.24	0.27	0.28	0.28	0.32
alk	11.21	15.38	16.07	13.50	16.88	14.63	12.86

	TR7	TR8	TR9	TR10	TR11	TR12	TR13
si	273.68	207.77	296.59	307.09	253.78	278.0	282.38
ti	2.24	2.02	2.25	2.87	2.50	2.71	3.07
al	27.28	23.93	29.80	30.67	25.67	29.69	30.22
fm	51.48	47.91	43.98	45.66	51.78	48.49	49.69
mg	0.62	0.64	0.61	0.56	0.64	0.57	0.57
c	4.64	14.83	6.77	5.24	7.18	4.93	2.96
k	0.28	0.29	0.27	0.23	0.25	0.28	0.26
alk	16.60	13.33	19.44	18.43	15.38	16.89	17.13

	TR14	TR15	TR16	TR17	TR18	TR19	TR20
si	261.95	288.72	261.33	262.49	254.86	284.73	261.12
ti	2.30	2.47	2.48	2.46	2.33	2.19	2.35
al	27.63	28.79	28.18	28.87	29.33	28.24	28.44
fm	42.88	50.10	51.84	50.91	52.17	45.45	46.55
mg	0.59	0.63	0.60	0.61	0.62	0.62	0.61
c	16.38	3.24	4.00	4.54	1.77	8.25	7.25
k	0.27	0.28	0.28	0.29	0.27	0.25	0.27
alk	13.11	17.88	15.98	15.69	16.73	18.06	17.76

	TR21	TR22	TR23	TR24	TR25	TR26	TR27
si	275.28	286.63	286.82	273.91	279.91	198.41	260.51
ti	2.48	2.45	2.55	2.44	2.63	2.07	3.31
al	29.08	27.83	28.51	28.30	27.19	22.63	28.14
fm	45.15	53.28	51.43	50.78	52.83	45.74	48.45
mg	0.58	0.62	0.61	0.61	0.62	0.62	0.57
c	9.59	2.99	4.00	4.36	4.33	19.13	9.51
k	0.23	0.27	0.28	0.28	0.25	0.29	0.28
alk	16.19	15.90	16.06	16.56	15.65	12.50	13.90

	TR28	TB1	TB2	TB3	TB4	TB5	TB6
si	329.12	279.98	284.48	301.63	251.07	242.16	238.26
ti	2.11	2.34	2.46	2.51	2.86	2.30	2.44
al	30.16	29.04	28.26	30.88	32.87	26.06	30.23
fm	44.51	45.14	45.52	48.52	48.33	45.96	48.69
mg	0.62	0.57	0.62	0.61	0.56	0.61	0.58
c	6.33	10.02	9.86	4.10	3.52	13.04	4.87
k	0.23	0.23	0.18	0.25	0.32	0.21	0.25
alk	19.01	15.81	16.35	16.50	15.28	14.94	16.21

	TB7	TB8	TB9	TB10	TB11	TB12	TB13
si	295.01	315.69	272.93	135.50	283.48	274.22	120.42
ti	2.78	2.54	2.64	3.20	2.61	2.54	3.17
al	31.38	30.86	28.74	22.57	29.95	29.66	19.66
fm	38.97	43.99	48.68	46.81	48.69	46.62	54.50
mg	0.51	0.51	0.57	0.53	0.60	0.60	0.63
c	13.92	8.60	6.94	17.10	4.26	7.58	17.70
k	0.25	0.24	0.19	0.25	0.40	0.15	0.16
alk	15.74	16.55	15.64	13.52	17.10	16.14	8.16

	TB14	TB15	TB16	TB17	TB18	TB19	TB20
si	115.71	297.99	152.09	260.71	279.79	267.95	314.48
ti	3.21	1.96	3.02	2.10	2.52	2.59	2.25
al	19.42	29.67	21.86	27.56	28.83	28.24	29.77
fm	53.15	40.32	52.09	47.31	47.85	49.19	44.17
mg	0.63	0.59	0.60	0.59	0.58	0.58	0.58
c	17.32	12.42	13.49	11.33	6.55	6.76	9.22
k	0.12	0.19	0.14	0.25	0.24	0.19	0.25
alk	10.11	17.59	12.56	13.81	16.77	15.81	16.84

	TB21	AL1	AL2	AL3	AL4	AL5	AL6
si	108.03	150.10	126.03	166.24	139.23	159.63	145.61
ti	2.02	3.10	3.43	3.12	2.33	3.08	2.62
al	13.71	19.29	18.95	20.57	17.47	19.62	18.53
fm	51.50	30.39	49.26	54.91	51.21	48.84	59.86
mg	0.71	1.00	0.62	1.00	0.67	0.60	0.69
c	26.43	39.59	24.65	15.13	22.96	20.61	12.86
k	0.40	0.15	0.16	0.16	0.17	0.16	0.18
alk	8.36	10.73	7.15	9.39	8.36	10.93	8.66

	BC1	BC2	BC3	BC4	BC5	BC6	BC7
si	127.14	275.84	145.18	141.04	152.93	144.03	92.68
ti	2.06	2.46	2.59	2.45	2.41	2.97	1.83
al	15.37	28.47	18.55	17.81	16.20	18.30	12.08
fm	58.38	49.77	59.05	55.95	40.80	53.29	32.77
mg	0.69	0.61	0.68	0.67	0.62	0.63	0.62
c	22.12	4.38	13.56	17.81	34.37	19.65	49.39
k	0.23	0.27	0.14	0.17	0.23	0.15	0.15
alk	4.14	17.38	8.84	8.43	8.63	8.76	5.76

	KP1	KP2	KP3	KP4	KP5	KP6	KP7
si	228.10	187.65	193.95	232.39	201.87	194.46	190.48
ti	3.49	2.62	2.89	2.77	3.47	3.36	2.85
al	29.25	22.85	25.23	25.32	24.36	24.64	25.53
fm	33.09	47.65	53.83	52.98	54.52	55.59	53.99
mg	1.00	0.56	0.55	0.55	0.55	0.53	0.55
c	25.30	19.48	10.38	10.00	11.10	10.05	9.67
k	0.25	0.27	0.24	0.21	0.21	0.26	0.20
alk	12.36	10.02	10.55	11.70	10.02	9.72	10.81

	KP8	KP9	AD1	AD2	AD3	KC1	KC2
si	206.83	188.58	208.85	172.99	196.80	99.70	88.62
ti	2.87	3.39	2.79	2.76	2.56	2.32	2.28
al	24.88	23.76	22.99	21.00	20.12	15.86	13.21
fm	53.83	52.46	55.68	44.09	53.88	50.69	43.01
mg	0.57	0.52	0.63	0.52	0.61	0.62	0.64
c	11.01	14.04	9.89	22.84	14.50	26.22	37.80
k	0.20	0.16	0.12	0.14	0.16	0.18	0.14
alk	10.28	9.74	11.44	12.07	11.49	7.23	5.98

					middle sequence	
	KC3	KC4	KC5	KC6	AF1	AF2
si	81.98	216.08	207.20	243.86	170.64	127.26
ti	2.23	2.31	2.01	2.04	2.59	2.45
al	12.69	20.91	19.33	22.43	28.14	17.38
fm	44.09	53.19	49.25	51.35	48.88	31.92
mg	0.67	0.64	0.66	0.64	0.55	0.54
c	38.20	15.49	21.56	14.02	9.64	41.10
k	0.17	0.27	0.25	0.33	0.21	0.11
alk	5.03	10.40	9.86	12.20	13.34	9.60

	AF3	AF4	AF5	AF6	AF7	AF8	AF9
si	158.89	233.60	201.95	217.81	116.59	163.32	200.16
ti	1.76	3.01	2.96	2.84	1.47	4.00	3.44
al	21.67	30.36	25.68	25.87	14.94	25.12	25.97
fm	24.34	39.19	48.35	42.45	19.69	45.77	43.23
mg	0.51	0.50	0.55	0.53	0.50	0.53	0.53
c	41.94	14.00	12.75	18.94	56.22	17.27	16.75
k	0.17	0.18	0.16	0.17	0.10	0.26	0.20
alk	12.05	16.45	13.22	12.74	9.15	11.85	14.05

	AF10	AF11	AF12	AF13	AF14	AF15	AF16
si	160.14	168.72	189.44	192.17	197.45	103.36	147.09
ti	3.62	3.81	2.77	2.77	3.41	2.43	2.51
al	22.32	24.63	28.86	25.44	23.73	14.58	20.04
fm	42.18	50.18	43.71	43.18	41.57	28.63	39.86
mg	0.54	0.53	0.53	0.55	0.52	0.54	0.54
c	25.0	12.97	11.95	17.48	23.48	49.42	29.18
k	0.11	0.15	0.17	0.19	0.21	0.14	0.14
alk	10.50	12.23	15.48	13.91	11.22	7.37	10.92

	AF17	AF18	AF19	AF20	AF21	AF22	AF23
si	209.75	206.78	200.84	183.38	289.90	170.66	203.18
ti	3.76	2.29	4.02	2.86	2.58	3.87	3.30
al	28.53	31.16	27.99	27.61	30.96	24.89	27.74
fm	44.06	45.27	46.15	44.33	38.09	44.93	47.52
mg	0.53	0.58	0.53	0.52	0.48	0.53	0.56
c	13.48	7.70	11.09	14.22	13.71	18.30	10.64
k	0.11	0.27	0.16	0.16	0.23	0.16	0.21
alk	13.94	15.87	14.78	13.84	17.24	11.88	14.09

	AF24	AF25	AF26	AF27	TM1	TM2	TM3
si	225.71	157.89	187.54	163.0	271.25	268.85	256.91
ti	2.67	3.87	2.98	2.61	5.04	4.63	3.85
al	26.28	21.41	27.26	28.75	30.08	29.23	27.72
fm	37.79	46.56	46.17	48.99	32.52	27.05	31.43
mg	0.48	0.54	0.54	0.53	1.0	1.0	1.0
c	23.02	22.27	11.85	7.73	25.74	32.10	28.89
k	0.15	0.18	0.24	0.19	0.12	0.12	0.11
alk	12.91	9.75	14.71	14.53	11.66	11.62	11.96

	TM4	TM5	TM6	TM7	TM8	TM9	TM10
si	194.96	196.53	160.12	206.14	217.78	189.48	218.48
ti	4.03	4.01	3.86	3.14	3.24	3.92	2.97
al	21.93	21.38	20.16	23.31	24.92	23.63	26.69
fm	55.47	40.77	44.57	44.12	53.76	54.51	47.81
mg	0.57	0.52	0.57	0.54	0.61	0.58	0.56
c	14.77	29.73	27.85	23.34	9.43	12.12	13.66
k	0.13	0.12	0.15	0.12	0.08	0.10	0.11
alk	7.83	8.11	7.41	9.23	11.89	9.74	11.83

	TM11	TM12	TM13	TM14	TM15	TM16	PW1
si	207.22	153.84	199.55	196.55	116.57	239.54	222.08
ti	2.92	2.15	4.0	3.66	2.82	3.72	3.08
al	24.70	20.25	22.78	23.20	14.17	25.31	26.83
fm	47.80	35.88	52.01	47.41	28.78	32.36	47.74
mg	0.56	0.50	0.55	0.55	0.54	0.46	0.51
c	16.54	35.04	15.96	19.95	50.96	32.59	10.44
k	0.11	0.13	0.12	0.12	0.12	0.14	0.19
alk	10.96	8.83	9.24	9.44	6.09	9.74	14.99

	PW2	PW3	PW4	PW5	PW6	PW7	PW8
si	215.34	195.32	215.78	214.34	275.70	297.66	482.46
ti	3.60	3.29	3.41	2.75	1.98	3.95	2.36
al	25.73	27.22	27.18	28.58	31.39	29.30	31.76
fm	52.62	51.25	49.53	45.18	40.26	51.42	41.80
mg	0.47	0.59	0.57	0.57	0.58	0.53	0.48
c	8.22	8.22	9.49	10.72	9.71	5.54	10.69
k	0.16	0.19	0.16	0.19	0.21	0.20	0.15
alk	13.43	13.31	13.80	15.52	18.65	13.74	15.75

	PW9	PW10	PW11	PW12	PW13	PW14	PW15
si	448.29	202.68	159.48	127.48	332.51	352.22	372.83
ti	2.30	2.99	1.02	0.84	2.74	3.15	3.74
al	26.89	23.69	13.49	10.44	27.87	28.89	30.81
fm	33.15	34.97	15.50	11.56	30.97	33.57	39.03
mg	0.46	0.43	0.47	0.44	0.44	0.40	0.39
c	28.11	32.11	64.70	73.12	29.21	24.16	16.44
k	0.16	0.26	0.20	0.19	0.29	0.26	0.25
alk	11.85	9.24	6.31	4.87	11.96	13.38	13.72

	PW16	PW17	PW18	PW19	PW20	PW21	PW22
si	395.38	328.90	299.27	341.66	416.52	427.72	371.67
ti	3.12	3.0	3.10	2.98	4.07	3.69	4.18
al	29.92	30.95	28.94	31.02	34.92	32.06	33.00
fm	38.54	37.42	34.58	37.95	41.01	39.47	39.16
mg	0.44	0.42	0.41	0.43	0.41	0.40	0.39
c	18.93	17.40	23.55	17.57	8.26	13.39	14.14
k	0.27	0.25	0.28	0.26	0.24	0.25	0.28
alk	12.61	14.23	12.93	13.47	15.81	15.08	13.70

	PW23	PW24	PW25	PW26	PW27	PW28	PW29
si	342.93	339.13	430.06	388.50	394.58	506.86	415.11
ti	3.16	2.68	3.68	3.70	3.78	3.82	3.68
al	29.61	25.54	33.18	32.58	29.69	32.20	36.47
fm	35.49	28.80	42.89	44.92	35.68	42.15	42.19
mg	0.41	0.43	0.41	0.38	0.43	0.43	0.41
c	21.86	33.59	9.62	8.61	20.89	11.45	5.74
k	0.27	0.25	0.26	0.27	0.27	0.27	0.31
alk	13.04	12.06	14.32	13.89	13.73	14.20	15.59

upper sequence

	WG1	WG2	WG3	WG4	WG5	WG6	WG7
si	110.37	308.52	294.20	154.37	267.48	155.39	136.43
ti	1.50	2.92	2.91	1.05	1.66	1.05	1.58
al	13.84	29.70	30.75	18.04	26.16	17.78	20.81
fm	16.68	35.63	35.37	14.77	20.73	16.66	25.69
mg	0.43	0.44	0.44	0.46	0.45	0.42	0.42
c	63.48	22.12	21.14	57.66	39.91	56.55	42.73
k	0.17	0.27	0.29	0.19	0.13	0.23	0.10
alk	6.0	12.56	12.75	9.53	13.20	9.01	10.77

	WG8	WG9	WG10	SC1	SC2	SC3	SC4
si	378.53	257.98	378.34	249.64	269.57	243.74	335.44
ti	3.35	0.67	3.35	2.46	1.70	1.54	2.53
al	31.13	14.30	31.12	27.01	18.70	21.85	25.35
fm	44.39	9.29	44.37	39.31	22.87	33.58	41.69
mg	0.47	0.51	0.47	0.49	0.50	0.49	0.46
c	11.56	69.54	11.55	21.91	50.08	35.20	23.49
k	0.06	0.13	0.06	0.21	0.32	0.22	0.36
alk	12.92	6.87	12.96	11.78	8.35	9.38	9.47

	AL1	AL2	AL3	AL4	AL5	AL6	AL7
si	216.82	244.28	340.78	205.21	359.55	314.73	301.29
ti	2.60	3.75	2.30	2.01	1.77	2.23	2.94
al	26.26	24.88	26.66	16.81	23.46	29.78	29.72
fm	42.01	43.70	36.72	22.98	33.84	44.57	50.49
mg	0.55	0.50	0.51	0.48	0.54	0.50	0.59
c	17.38	22.43	24.02	53.19	19.31	12.91	2.50
k	0.27	0.20	0.11	0.23	0.25	0.10	0.26
alk	14.34	8.99	12.60	7.01	23.39	12.74	17.30

			Silurian				
	WP1		S1	S2	S3	S4	S5
si	213		414.64	526.32	458.77	391.93	386.91
ti	2.41		4.05	3.77	3.86	3.51	3.66
al	17.79		32.84	29.89	34.78	36.95	35.57
fm	19.67		43.69	37.24	36.07	37.45	36.59
mg	0.47		0.48	0.41	0.38	0.36	0.37
c	54.87		7.34	15.08	13.64	8.90	9.28
k	0.30		0.22	0.16	0.27	0.30	0.27
alk	7.68		16.13	17.79	15.51	16.71	18.56

	S6	S7	S8	S9	HQ1	HQ2	HQ3
si	369.37	427.94	230.41	213.64	1026.97	9.76.48	734.02
ti	4	3.98	3.38	3.68	6.60	4.14	4.47
al	37.37	35.75	26.24	22.24	31.89	25.87	39.97
fm	35.35	37.41	47.85	33.41	32.91	39.95	38.34
mg	0.36	0.40	0.53	0.50	0.58	0.56	0.34
c	7.34	8.50	14.26	33.72	29.39	29.73	12.03
k	0.24	0.25	0.17	0.17	0.86	0.77	0.62
alk	7.34	8.50	14.26	33.72	29.39	29.73	9.66

	HQ4	HC1	HC2	HC3
si	475.37	378.14	251.38	301.84
ti	3.69	2.86	2.62	2.62
al	27.75	25.69	25.34	30.08
fm	35.35	39.83	50.06	47.09
mg	0.40	0.54	0.60	0.56
c	32.15	22.52	11.40	7.38
k	0.91	0.31	0.21	0.24
alk	4.76	11.96	13.19	15.45

key to appendix two

Silurian
_S=Scart Grit
HQ=Quartz Conglomerate

HC=Craigskelly

Ordovician
upper sequence

WG=Whitehouse Group
SC=Shalloch Formation
AL*=Shalloch Formation
WP=Shalloch Formation

Ordovician
middle sequence
AF=Ardwell Flags
TM=Ardwell Group and Cascade Grits
PW=Cascade Grits (1-9) and Whitehouse Group (10-27)

Ordovician
lower sequence
TA=Changue Formation
KK=Kilrany conglomerate

TR=Changue Formation(1-16)
TR=Darley Formation(17-28)
TB=Changue Formation
AL=Craigmulock Formation
BC=Craigmulock Formation
KP=InfraKilrany .Greywackes
AD=Benan Conglomerate
KC=Kirkland Conglomerate

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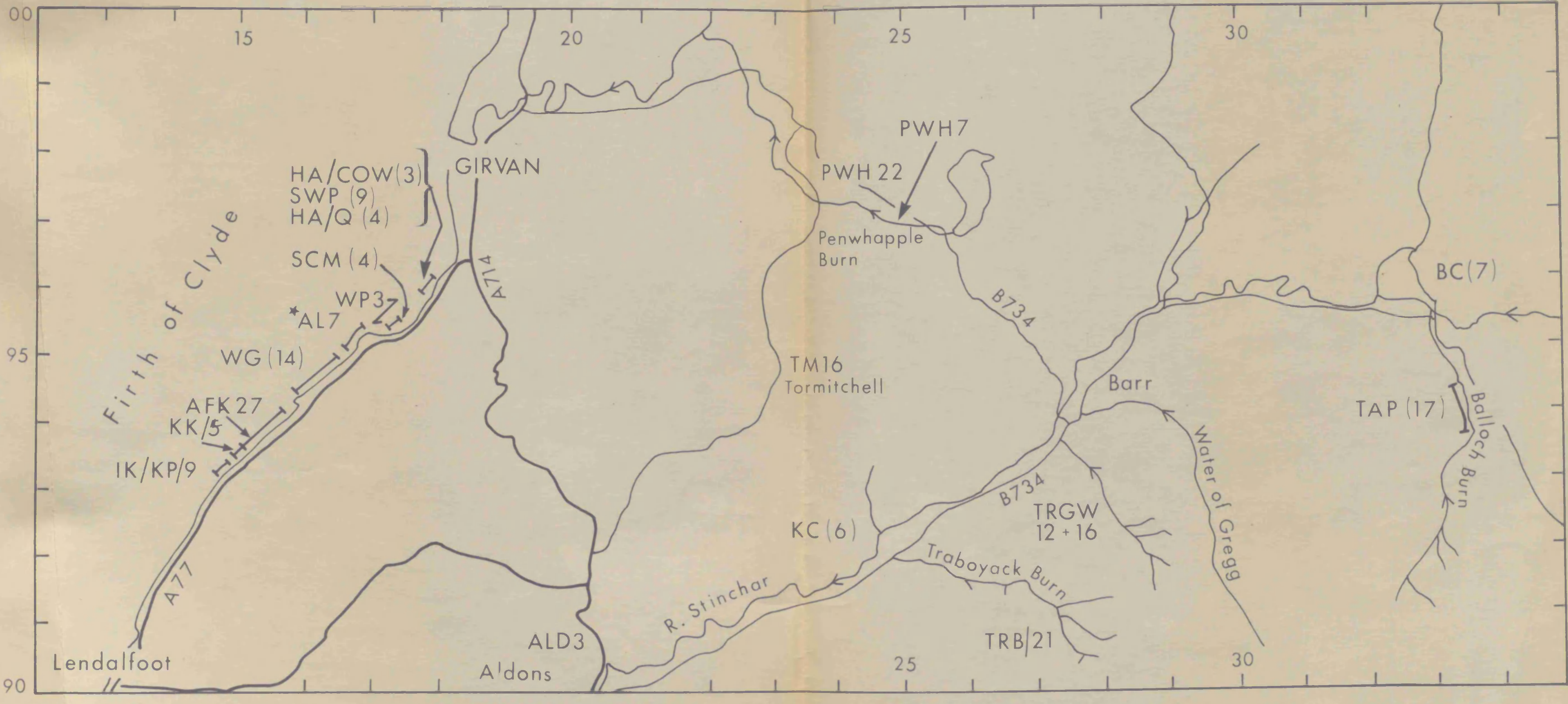
Fig 2.1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GIRVAN
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WG (14)
AFK27
KK/5
IK/KP/9
Firth of Clyde
A714
A77
Lendalfoot
ALD3
Aldons
PWH7
PWH 22
Penwhapple Burn
B734
TM16
Tormitchell
Barr
KC (6)
B734
TRGW
12 + 16
R. Stinchar
Traboyack Burn
TRB/21
Water of Gregg
BC(7)
TAP (17)
Balloch Burn
25
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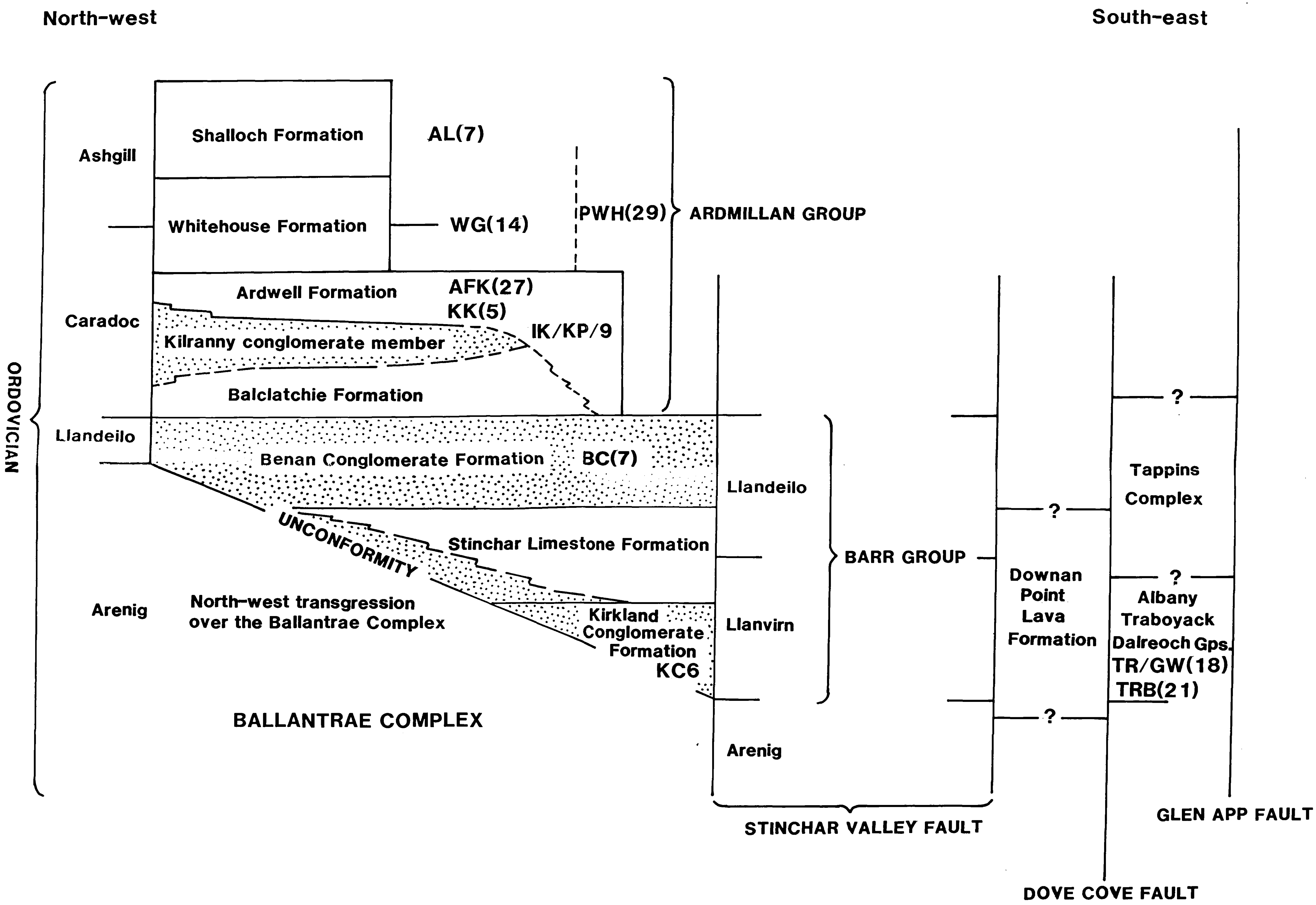
LOCATION OF ORDOVICIAN SAMPLES FIG 2.3



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