

DECLARATION

I hereby declare that this thesis has been composed by myself, and that the work described herein is my own unless specifically acknowledged.

(M.F. Thirlwall)

THE PETROCHEMISTRY OF
THE BRITISH OLD RED SANDSTONE
VOLCANIC PROVINCE

MATTHEW FRANCIS THIRLWALL B.A.

A Thesis submitted for the Degree of Doctor of
Philosophy

University of Edinburgh

October 1979



This thesis is dedicated to

"Pippin"

ABSTRACT

The lavas and minor intrusions associated with the sediments of the Old Red Sandstone were extensively sampled over a broad area of Scotland, northern England and the north of Ireland. The main areas of outcrop are Lorne, Glencoe and Ben Nevis (the SW Highlands); the Sidlaw, Ochil and North Fife Hills (the North Midland Valley); Ayrshire and the Pentland Hills (the South Midland Valley); the Cheviot Hills; St. Abb's Head and Shetland. Most of the samples collected have been examined petrographically, and 597 have been analysed for 10 major and 17 trace elements. The phenocryst compositions of many of the lavas has also been investigated by microprobe. The large number of samples to be analysed required the development of a rapid and accurate system of analysis by X-ray fluorescence spectrometry, and a wide range of data processing and data handling computer programs, described in the Appendices.

In general, the rocks have strong affinities with modern calc-alkaline volcanic suites, although those from Shetland and from Straiton, Ayrshire, show some characteristics transitional to tholeiitic types. Although the rocks of each outcrop area are petrographically and chemically diverse, the variation is generally inexplicable by fractional crystallisation processes, except for Shetland and (possibly) the Cheviot Hills. Chemical variation in most areas can only be explained by complex contamination models.

Rocks with >100 ppm Ni are unusually abundant for calc-alkaline suites, and may be found in most outcrop areas. These rocks show pronounced geographical variation in their concentrations of Sr, P, light rare earth elements, Ba, K, Y and, to a lesser extent, Nb and Sc. All except Y and Sc show a marked increase in a traverse from the South Midland Valley to the SW Grampian Highlands, and a similar relationship also exists for rocks poorer in Ni. This geographical variation is similar to that seen in modern subduction-related calc-alkaline suites, and constitutes strong evidence that the rocks of the province were genetically related to a subduction zone. Little satisfactory evidence is available for the age of the Scottish Lower Old Red Sandstone, and it is believed that the rocks were deposited during the Silurian, rather than the Lower Devonian as has been

generally accepted, prior to final closure of the Iapetus Ocean. The rocks of the Cheviot Hills are thought to have been erupted a little later, after final closure. The bulk of the volcanic rocks were however probably directly related to the subduction responsible for closure.

In order to explain the geographical variation in concentrations of the above elements in terms of a single subduction zone, it is necessary to postulate a major change in strike of the zone from ENE in southern Scotland to nearly N in the North Sea. This strike change, in conjunction with almost east-west relative plate motion, can explain the contrast in end-Silurian deformation styles between Britain and Scandinavia. It is believed that motion was largely transcurrent on the British-Irish sector of the subduction zone.

The possible origins of the geographic variation in incompatible element concentrations are constrained by the failure of Rb and Zr to correlate with other incompatible elements, and by the decrease in Y with increasing depth to the inferred Benioff zone. These variations are best explained by a model involving

- (i) generation of melts in the vicinity of the subducted lithosphere
- (ii) their ascent through the mantle and the zone-refining of dispersed incompatible elements (but not those located in minor crystalline mantle phases such as phlogopite, ilmenite or apatite).

The concentration of an incompatible element in a particular magma is then mainly a function of the path length to the surface and the distribution of minor phases along that path.

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CHAPTER 1 : INTRODUCTION

The prolonged crustal instability of the British region during the Lower Palaeozoic, terminating in the Caledonian Orogeny, has provided a fertile source of material for research in all branches of geology. Most recent models for the tectonic development of the region are in accord in postulating an ocean, Iapetus, separating an Anglo-European continent from one comprising Scotland and America north of the Appalachians. Strong evidence, from faunal provincialism (e.g. Williams, 1972) and from palaeomagnetism (e.g. Briden et al., 1973), supports the existence of this ocean for much of Cambrian and Ordovician time, with final closure and continental suturing during the Silurian. The subduction necessary to produce closure has formed the basis of several interpretations of Lower Palaeozoic tectonomagmatic events; for example, those of Dewey (1969), Mitchell and McKerrow (1975) and Phillips et al. (1976).

Recent work in the Southern Uplands (McKerrow et al., 1977) has provided convincing evidence that the Ordovician to Silurian sedimentary successions of this area represent material deposited on the northern floor of Iapetus, and accreted onto the northern continental margin during subduction of the ocean floor, as suggested by Mitchell and McKerrow (1975). In contrast, Church and Gayer (1973) suggest termination of northward subduction in the late Caradoc. Evidence for southeastward subduction has been

presented by Fitton and Hughes (1970) for the Lake District and Wales, and for southeast Ireland by Stillman and Williams (1979). These authors have demonstrated the existence of spatial changes in the chemistry of the volcanic rocks in these regions, from tholeiitic or transitional rocks with flat chondrite-normalized rare earth element (REE) patterns in the north, to light REE enriched calc-alkaline rocks in the south, comparable with changes with increasing distance from the trench in many modern magmatic arcs (e.g. Jakes and White, 1972). The Iapetus suture at present erosion level must therefore pass along the Solway Firth: Phillips et al. (1976) list evidence for its extrapolation into Ireland.

Evidence from volcanic rocks for northward subduction is far less satisfactory, for the major pre-Carboniferous volcanic episode in the north is generally thought to be of Devonian age, and thus significantly younger than the Silurian date of closure inferred from the ending of marine sedimentation and the unification of the palaeomagnetic and faunal records of both sides of the orogen. Mitchell and McKerrow (1975) suggest that the Wrae volcanics of Peebleshire, and the andesite clasts in Upper Ordovician greywackes at the Rhinns of Galloway, are representatives of calc-alkaline volcanism associated with the accretion of sediment at the Southern Uplands subduction zone. These volcanic episodes are trivial relative to the later outburst, and the rocks at Wrae have recently been shown to be peralkaline rhyolites (Thirlwall, in preparation), and

thus most probably quite unrelated to subduction. Furthermore, the nature of the rocks of the Siluro-Devonian volcanic episode is not clear from the literature. While generally believed to be calc-alkaline (e.g. Taylor, 1972; Groome, 1972), alkali basalts have been described from Orkney (Kellock, 1969), a mugearite from Shetland (Mykura, 1976), trachyandesites in the Sidlaw and Ochil Hills (Harry, 1956; Francis et al., 1970) and trachytes in the Pentland and Cheviot Hills (Mykura, 1960; Carruthers et al., 1932). Gandy (1973a) proposed a petrogenetic model for the volcanic rocks of the Sidlaw Hills involving two-stage fractional crystallisation of olivine-tholeiite. The volcanic rocks of the Cheviot Hills lie across the suture line of Phillips et al. (1976) and can therefore not be related to the subduction models proposed therein.

Despite these uncertainties, Phillips et al. (1976) use calc-alkaline rocks from both sides of the suture as evidence for oblique collision between a west-striking northern subduction zone and a southwest-striking southern zone, followed by 560 miles (900 km) of dextral strike-slip. In the south, they interpret the younger age of the Siluro-Ordovician volcanic episode to the southwest as a result of later closure in this direction, but do not clearly demonstrate a similar phenomenon in the north. Here they use the Devonian age of the magmatism as evidence for dextral translation of the Devonian closing position in the north to become opposite to the Caradocian closing position in the south, despite faunal and palaeomagnetic evidence

suggesting Silurian closure.

1.1 : OBJECTIVES OF RESEARCH

It is clear from the preceeding discussion that most models for the Lower Palaeozoic development of the British Isles suffer difficulties in their postulation of post-Llanvirn northward subduction because of the lack of consistent and comprehensive petrochemical data for the post-Llanvirn pre-Carboniferous volcanic rocks of Scotland, Northumberland and northern Ireland. The research described in this thesis was designed to remedy this deficiency, to determine the petrochemical affinities of the rocks of the Siluro-Devonian volcanic episode, and to place restrictions on models for their petrogenesis.

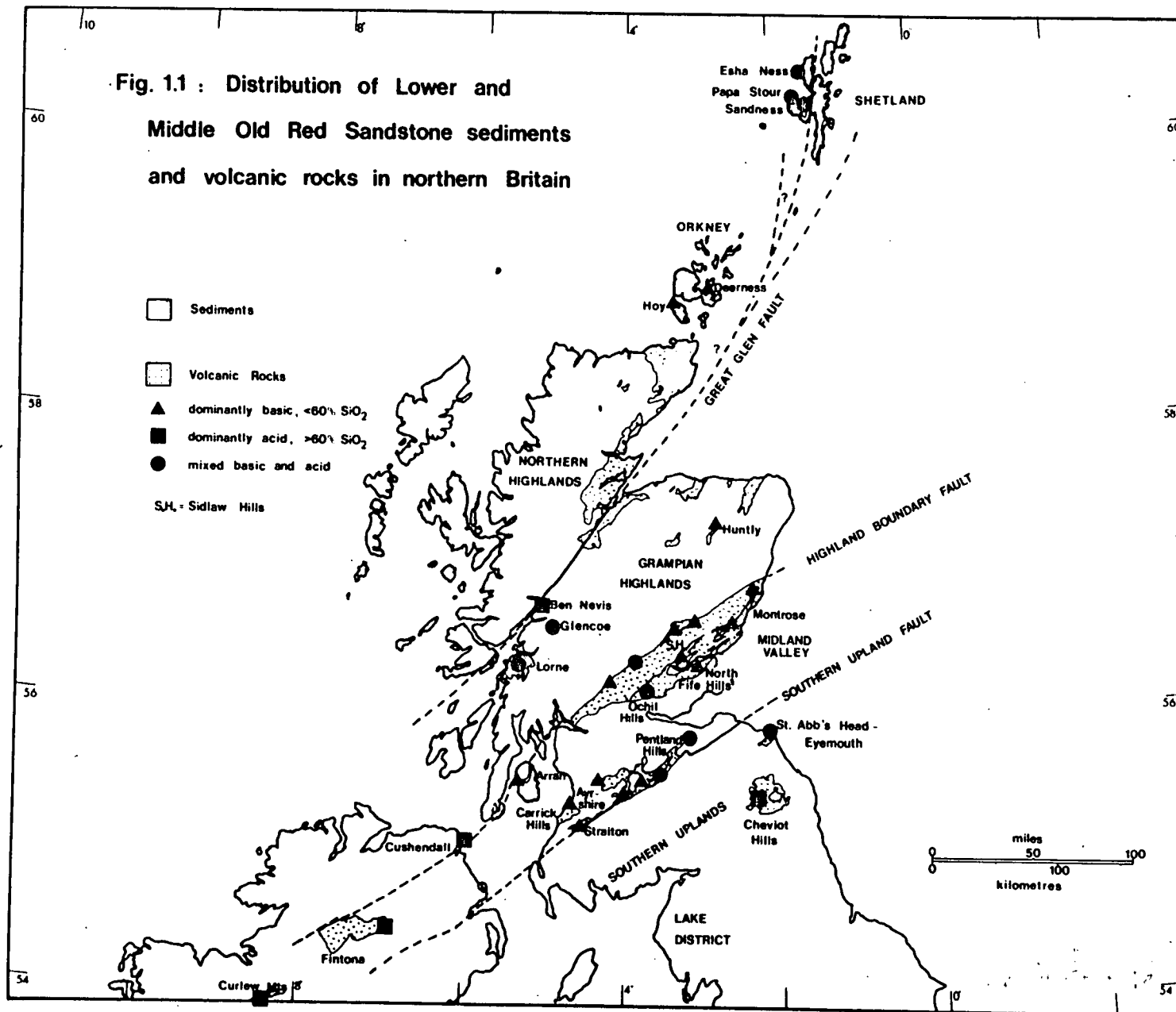
1.2 : THE OLD RED SANDSTONE

With the exceptions of the aforementioned Wrae volcanics, the Caradocian alkaline complex of Bail Hill (M. McMurtry, pers. comm., 1979), the clasts at the Rhinns of Galloway, and spilitic volcanics in the Southern Uplands and Mayo Trough Ordovician, all post-Llanvirn, pre-Carboniferous volcanic rocks north of the suture of Phillips *et al.* (1976) are associated with the essentially untectonized continental sediments known throughout Britain and Scandinavia as the Old Red Sandstone (O.R.S.). The conglomerates, sandstones and shales of this large lithostratigraphic grouping are thought to have been

deposited in a number of intermontane and lacustrine basins. Their present outcrop, together with the locations of contemporaneous volcanism, is shown in Fig. 1.1. Only small pockets of O.R.S. conglomerates exist between the southernmost depositional basin of the Scottish Old Red Sandstone (Berwickshire - Northumberland) and the large depositional basin of the Anglo-Welsh cuvette, and it is probable that these basins were not linked for much of the duration of O.R.S. deposition. No volcanic rocks are associated with the O.R.S. sediments south of the suture of Phillips et al. (1976), and the same relationship is true further northeast, where volcanic rocks are present in the Old Red Sandstone of east Greenland, but are absent from the Norwegian Old Red Sandstone.

The Midland Valley basin has by far the thickest development of O.R.S. sediments and volcanic rocks (19000 ft, 6000m; Armstrong and Paterson, 1970), and its sedimentary history has been described by Bluck (1978) and Morton (1979). These authors have suggested progressive subsidence along the bounding faults and infilling from the edges by a succession of alluvial and debris flow fans, derived from the surrounding mountains. In the southeast there may have been some link with the Berwickshire-Cheviot area, although thicknesses of sediment here are not great. In the southwest, Morton (1979) postulates a link through Kintyre to the SW Grampian basin, which he considers to have been filled in by the Lorne Plateau lavas. There is some evidence that the SW Grampian basin may have been a tidal

Fig. 1.1 : Distribution of Lower and Middle Old Red Sandstone sediments and volcanic rocks in northern Britain



cuvette (Tarlo and Gurr, 1964).

In the northeast, sedimentation was dominated by the Orcadian Lake, which at its maximum extent may have covered the area between the Moray Firth and western Shetland, with marginal alluvial deposition in Sutherland, Cromarty and northern Aberdeenshire. Further north, in Shetland, three distinct sedimentary successions have been juxtaposed by faulting, of which the western (Melby) has most similarities with the Orcadian sequence (Mykura, 1976). The central area (Sandness and Walls Formations) is most unusual in that the Old Red Sandstone has suffered polyphase deformation, and the sediments were thought by Mykura and Phemister (1976) to be probably of deeper water facies than normal, although not marine. Recent re-interpretation by Melvin (1977) has confirmed their fluvial nature. The southeastern succession was probably originally the most northerly, and in facies resembles the Orcadian sediments (Mykura, 1976, p.69).

It is difficult to judge how far the distribution shown in Fig. 1.1 is the product of the primary depositional pattern and the extent to which this has been modified by differential uplift and erosion. The high degree of rounding of quartzite clasts in fanglomerates on the northern margin of the Midland Valley suggests that they had been previously involved in alluvial processes, presumably in small Highland basins. Similarly, the abundance of volcanic clasts in these fanglomerates demonstrates that

volcanic rocks were more widespread in the Highlands than at present, and that the apparently close relation between location of volcanic rocks and major transcurrent faults is mainly the result of preservation of Old Red Sandstone near these faults.

Correlation of Old Red Sandstone strata between the several depositional basins is based on rare horizons with fish and arthropod faunas, together with some plants. Three divisions have been recognized using this palaeontological information, although unconformities provide the main mapping criteria. These are the Lower, Middle and Upper Old Red Sandstones. In many areas continental facies sedimentation began before deposition of the Lower, and continued after deposition of the Upper Old Red Sandstone: the terms have therefore acquired chronostratigraphic meanings.

In England, Wales and Scotland south of Aberdeen, rocks of the Middle division are absent, and the Upper division, resting unconformably on older rocks, is overlain conformably by the lowest Carboniferous strata. The Lower division appears to rest conformably on older rocks in Lanarkshire and Ayrshire, and in the Anglo-Welsh cuvette rests conformably on Ludlow strata with the intervening type Downtonian. In general, however, it rests unconformably on rocks ranging in age from Pre-Cambrian to Silurian. In northeast Scotland, rocks of the Lower division have only recently been recognized, and the succession is dominated by

strata belonging to the Middle division. Fossils are infrequent in the Irish Old Red Sandstone, and the stratigraphy is less well-established than in Britain.

1.3 : AGE OF THE SCOTTISH OLD RED SANDSTONE

It has been observed that the term Old Red Sandstone has acquired a chronostratigraphic meaning, so that it is often used as a synonym for the term Devonian. It is clear that the O.R.S. of the Anglo-Welsh cuvette is of Devonian age, and that Upper O.R.S. conformably overlain by Carboniferous strata is Devonian or younger, but neither of these have associated volcanic rocks. The only volcanic rocks assigned to the Upper Old Red Sandstone are the Hoy lavas (Fig. 1.1; Mykura, 1976, p.89), and some doubts are expressed about this assignation. The Devonian age of the remainder of the Scottish Old Red Sandstone rests on correlation of fish and arthropod faunas and on lithological similarities with the Welsh Border succession. Lithological correlation is clearly invalid, for Old Red Sandstone facies sediments are present in both Silurian and Carboniferous strata. Well preserved faunas have been collected from Shetland (Mykura and Phemister, 1976), Caithness and Orkney (Wilson *et al.*, 1935), Lorne (Kynaston and Hill, 1908) and in the Stonehaven, Arbuthnott and Garvock groups of the northern Midland Valley (Armstrong and Paterson, 1970). Those from Caithness, Orkney and Shetland are not directly comparable with faunas from the Welsh Borderland, but are assigned to the Middle Old Red Sandstone. The fauna from

the Stonehaven Group has been assigned to the Downtonian (Westoll, 1945), but Lamont (1952) considers it to be earlier. The fauna from Lorne is similar to the Arbuthnott Group fauna, which was assigned to the Dittonian by Westoll (1951). It should be noted that the use of fish as accurate time markers in continental facies sediments must be suspect, for the spreading of newly evolved species will be very slow in the absence of direct freshwater links. Plant spores may prove to be better for chronostratigraphic correlation, but at present there is a lack of stratigraphic control.

A few radiometric age determinations have been made on volcanic members of the Old Red Sandstone. An Rb-Sr isochron age of 365 ± 2 Ma (recalculated to $\lambda^{87}\text{Rb} = 1.42 \times 10^{-11} \text{ yr}^{-1}$) derived from three samples of the Grind of the Navir ignimbrite, Shetland, has been reported by Flinn et al. (1968). Samples SH5 and SH6 are representative of this formation, and it is unlikely that Rb and Sr were immobile under the alteration that these rocks have suffered. The possibility that the quoted age is an alteration age should be considered. A stepwise degassing $^{40}\text{Ar}/^{39}\text{Ar}$ age determination on two samples of the Hoy lavas has been reported by Halliday et al. (1977), giving 'plateau ages' of 368 ± 8 and 353 ± 7 Ma. This is a substantial difference between the two samples. Brown (1975) has reported results of Rb-Sr and K-Ar isotopic studies in the Lorne and Glencoe areas. The Lorne lavas, and rocks of the later Etive plutonic complex, fall on good isochrons giving ages between

410 and 420 Ma, the lava isochron giving an age of 415 ± 7 Ma. Samples from Glencoe were thought by Brown (1975) not to form an isochron within error, but Groome (1972) has interpreted the same data as an isochron of age 480 ± 20 Ma. The Lorne samples have recently been re-analysed with improved precision, but leading to only very minor change in the age (Brown, pers. comm., 1979).

With the exception of the age from Glencoe, these dates in general seem to confirm the vertebrate stratigraphy, although the most reliable isochron, that for the Lorne lavas, would be Upper Silurian on the timescale of Harland *et al.* (1964). However, a recent Rb-Sr isochron age of 421 ± 3 Ma on the Ashgillian Stockdale Rhyolite, Lake District, has led to an important revision of the Palaeozoic time-scale (Gale *et al.*, 1979), with a shortening of the Silurian to 24 Ma. On this basis, the Lorne lavas are early Silurian in age, and the possibility that the vertebrate ages are sufficiently imprecise to encompass the whole of the Silurian must be seriously considered. It is notable that the youngest reliable age for rocks overlain by Old Red Sandstone north of the Southern Uplands Fault is an Upper Llandovery graptolite fauna in the Pentland Hills, although Wenlock graptolites occur close to the O.R.S unconformity in the Cheviot Hills.

There appears therefore to be little evidence for a Devonian age for most of the O.R.S volcanic sequences, and some evidence in favour of a Silurian age. Accordingly, the

terms Lower, Middle and Upper Old Red Sandstone are not used with any chronostratigraphic meaning in this thesis.

1.4 : THE CIRCA 400 MA PLUTONIC EPISODE

The restriction of Old Red Sandstone volcanic rocks to the northern side of the Iapetus suture is not paralleled in the distribution of plutonic rocks. Granitic bodies of batholithic proportions are found intrusive into Lower Palaeozoic and older rocks throughout Scotland, Ireland and northern England, with a number of smaller plutons in Wales and Leicestershire. Many of these have recently been the subjects of precise lead and strontium isotope studies, which have resulted in the recognition of a number of magmatic episodes, closely spaced in time. In England many plutons previously thought to be end-Silurian have been shown to be Ordovician (e.g. Rundle, 1979), and thus possibly related to the southeast directed subduction zone of Fitton and Hughes (1970). The few remaining plutons are distinctly younger than 400 Ma (e.g. Shap, 394 ± 3 Ma; Wadge *et al.*, 1978). Distinkhorn, and the Southern Uplands plutons, show some similarities with the English plutons in their lack of inherited zircons (Pidgeon and Aftalion, 1978) but some appear to be slightly older (e.g. Loch Doon, 408 ± 2 Ma; Halliday and Stephens, in press). Initial Sr isotope ratios are generally close to 0.707 for all these rocks, but higher values are found further south (Wensleydale, 0.721; Dunham, 1974).

Granitic plutons in the Highlands form two groups broadly corresponding to the forceful and permitted granites of Read (1961), the former generally earlier with high initial $^{87}\text{Sr}/^{86}\text{Sr}$ and chemistries similar to their country rocks, and the latter with low initial $^{87}\text{Sr}/^{86}\text{Sr}$ and incompatible element enriched chemistries. Brown (1979) interprets the first of these as the product of crustal melting associated with major tectonism, but suggests that the latter were intruded in a period of post-suturing crustal relaxation. The Donegal plutons appear to be anomalous in their low initial $^{87}\text{Sr}/^{86}\text{Sr}$ (Brown, 1979).

In addition to the plutonic rocks, large numbers of minor intrusions of around 400 Ma age are present in Britain, particularly in the Scottish Highlands. The hornblende-pyroxene rocks of the Appinite suite have been interpreted as feeders to the Lorne lavas (Groome and Hall, 1974), but in general there has been little work on these minor intrusions. The large numbers of Caledonian dykes are generally later than the volcanic rocks, and have a more restricted compositional range in the SW Highlands area (Groome, 1972).

1.5 : THE OLD RED SANDSTONE VOLCANOES

The continental facies of the associated sediments clearly implies that the O.R.S volcanic rocks were erupted in a continental environment. Pillow lavas are never seen, but the widespread sand-veining of lavas was taken by Geikie

(1902) to suggest fracturing of lava on eruption into small bodies of water. The volcanic rocks have all suffered to some extent from hydrothermal alteration (Chapter 2), most probably in an immediately post-eruptive, deuteric interaction with meteoric water, although some show evidence for contact metamorphism by later plutons (e.g. Glencoe). Tops and bases of flows are frequently autobrecciated and vesicular, these features often extending through the whole flow. Frequent reddening of flow tops is additional evidence for subaerial eruption.

Unlike modern subaerial andesite volcanoes, the volcanic products are almost entirely lava flows. Substantial accumulations of pyroclastic rocks are only found at the base of the volcanic sequence in the Ochil Hills (Francis *et al.*, 1970) and at Lorne, where they have been interpreted as lahar deposits (Groome, 1972). The absence of pyroclastic material may imply that the magmas were less viscous or poorer in volatiles than modern andesitic magmas, but it is also possible that the high fluvial activity resulted in rapid erosion and transport of the pyroclastic rocks.

The lava flows have nowhere been shown to exhibit depositional dip as if on the flanks of major stratovolcanoes, and often have wide lateral extent. While this may again suggest low viscosity magmas, it is also possible that the preserved volcanics represent regions most remote from the central cones, and that eruption into a

rapidly subsiding intermontane basin destroys any
resemblance to volcanic cone structures.

CHAPTER 2 : ALTERATION

The products of the Old Red Sandstone volcanoes have all been subjected to some degree of post-eruptive alteration, frequently resulting in the replacement of all the primary igneous minerals by a chlorite-sericite-haematite-calcite-quartz assemblage. Such alteration may lead to difficulty in the interpretation of petrography and chemistry, and is therefore reviewed prior to discussion of these subjects.

2.1 : MACROSCOPIC EXTENT

Fortunately, total replacement of primary minerals is not ubiquitous in any of the volcanic outcrop areas, and careful search will reveal almost unaltered samples. These may usually be distinguished in the field by the lustre of fresh groundmass feldspar, and are typically free from veins, amygdales, closely spaced joints and other fractures. Pyroclastic rocks and autobrecciated parts of lava flows are generally severely altered. The restriction of altered rocks to more permeable parts of the volcanic sequence suggests that hydrothermal fluids were of much greater importance in effecting alteration than any regional temperature rise due to plutonism, and the latter is probably only important in close proximity to major intrusions (e.g. the Cruachan Granite, Glencoe). The greater frequency of fresh samples in the north Midland Valley may be the result of the lack of intrusive activity

in this area, or may be due to mineralogical differences, in particular the paucity of phenocryst plagioclase in SW Highland rocks.

2.2 : MINERALOGICAL EFFECTS

Alteration of primary minerals frequently hinders their identification in thin section, particularly in the case of groundmass minerals or small numbers of poorly shaped phenocrysts. Groundmasses usually contain one or more chloritic minerals, probably mainly replacing glass, but sometimes also replacing groundmass olivine or pyroxenes. Lavas with more than 60% silica often have a very fine granular groundmass of quartz, feldspar, haematite and a chloritic mineral, which may be very difficult to resolve. It is not certain whether this is a primary texture or the result of devitrification or recrystallisation.

Over 95% of the rocks collected are porphyritic, and therefore the difficulty in groundmass phase recognition caused by alteration is not too important. Pseudomorphed phenocryst minerals may be identified by a combination of criteria: shape, alteration product, internal structure, and the presence in the same rock of other more easily recognized pseudomorphs or fresh minerals. The frequent association of olivine, orthopyroxene, calcic clinopyroxene and plagioclase as phenocrysts in mafic lavas allows the determination of their relative susceptibility to

alteration, and partially altered phenocrysts allow the identification of characteristic alteration products.

(a) Olivine

Olivine pseudomorphs may usually be recognized by their characteristic bipyramidal shape and by their internal fracture pattern, which is often marked by haematite. The latter feature allows the recognition of anhedral phenocrysts. Olivine was the mineral most prone to alteration, and is seen as fresh relicts in only five samples. Alteration/replacement products are varied, and range from serpentine and iddingsite through chloritic minerals and haematite to quartz or calcite. Distinction from orthopyroxene or hornblende is difficult in a few samples (e.g. L61), and it is not impossible that these minerals are present in association with olivine in a few rocks from which olivine alone has been recorded. The large number of hornblende-olivine-phyric basic rocks reported from Lorne by Groome (1972) contrasted with the small number noted in this study may in part be the result of this difficulty.

(b) Pyroxene

Fresh pyroxene phenocrysts are either diopsidic augite or orthopyroxene, of which the latter is much the more susceptible to alteration. Orthopyroxene is characteristically pseudomorphed by a pleochroic pale green

or brown chlorite, while clinopyroxene may be pseudomorphed by carbonate and some chlorite. When euhedral, the octagonal shape allows distinction from other minerals, and they may usually be distinguished from each other by their alteration products. It is possible, however, that small patches of carbonate may represent pseudomorphed clinopyroxene in some rocks from which it has not been reported. The former existence of pigeonite, pseudomorphed by a chlorite similar to that pseudomorphing orthopyroxene, has been inferred from exsolution relationships in some Shetland and Straiton pyroxenes. At Ben Nevis, clinopyroxene is pseudomorphed by tremolitic amphibole (e.g. analyses 6,8, Table C2), probably indicating higher temperature alteration than is usual. At Esha Ness, haematite-rich pseudomorphs of general pyroxene shape in the more siliceous rocks (SH1-3, 12, 13) may be the result of the alteration of more iron-rich augites.

(c) Feldspar

Plagioclase feldspars are less susceptible to alteration than calcic clinopyroxene in most of the province, contrasting with the behaviour of these minerals in the Lower Palaeozoic volcanic rocks of England and Wales (Fitton et al., in press), where alteration may have occurred at higher temperatures. Most of the Shetland lavas, however, and a few samples from elsewhere (e.g. PE18), show fresh augite coexisting with highly altered plagioclase. Plagioclase shows a range in

alteration products from very minor development of sericite to heavily sericitized, albitized, carbonated or rarely epidotized varieties, but is always easily distinguished from other phenocryst minerals. Some samples have both heavily altered and fresh feldspar, where the alteration is usually restricted to more calcic cores (e.g. 0C88B).

Alkali feldspar is rare as a phenocryst, and is usually partly kaolinized, when it may be difficult to distinguish from plagioclase.

(d) Amphibole

Amphibole, usually pargasitic, is probably slightly more susceptible to alteration than calcic clinopyroxene, although in samples from Ben Nevis fresh pargasitic amphibole coexists with the pale green tremolite after clinopyroxene. It may be altered to a variety of chloritic minerals, carbonate and sometimes quartz, and is characteristically surrounded by a wide opaque resorption rim. The latter, in conjunction with the 120° cleavage angle in basal sections, usually allows recognition of amphibole unless resorption has proceeded too far (resorption pseudomorphs). In some rocks (e.g. 0C87A), the former cleavage planes of pseudomorphed amphibole may be picked out by haematite.

(e) Biotite

Biotite is not common in the rocks of the province,

but it is probably fairly resistant to alteration. Where alteration does occur, it usually takes the form of haematite grains along the cleavage planes, followed by replacement by a bright green chlorite (e.g. GC6, MT52). The hexagonal basal and rectangular prism sections usually allow recognition, but resorption may create difficulties in distinction from amphibole (e.g. L113).

(f) Oxide Minerals

Reflected light microscopy indicates that in altered rocks both magnetite and ilmenite show phase separation, either as lamellae or patches, probably leading eventually, with oxidation, to the formation of haematite and rutile respectively. The latter mineral has not been positively identified, but is suspected in some altered samples.

The only other phenocryst minerals, apatite, quartz and garnet, do not suffer alteration in any of the rocks collected.

In addition to the alteration of primary minerals, a number of new minerals have been introduced by precipitation from hydrothermal fluids in joints and vesicles. The requirement of a geographically widespread collection has made unavoidable the collection of a few samples showing such features; for example, the one in situ lava on Arran is almost net-veined by carbonate. Carbonate is the main mineral so introduced, but quartz, chalcedony, chlorite and

infrequent zeolites also occur.

Mineral alteration, while extensive, does not therefore present any major difficulty in interpretation of the phenocryst mineralogy of the samples collected, although groundmass mineralogy is frequently difficult to determine. The common association of olivine, 2 pyroxenes and plagioclase allows the placing of most rocks on a petrographic alteration scale (PAS) from 1 to 5, bounded in the first two grades by disappearance of fresh olivine and orthopyroxene respectively, in the third by one of augite or plagioclase, and in the fourth by the other. Table A1 lists the alteration state (PAS) of all rocks analysed in this study: it is not very satisfactory as a measure of alteration for it relies on the presence of these four minerals in each rock.

2.3 : CHEMICAL EFFECTS

(a) Volatiles

The mineral alteration previously described should in general lead to an increase in the H_2O^+ and CO_2 content of a rock with increasing intensity, the CO_2 content being particularly sensitive to the introduction of carbonate. It will also lead to an increase in the Fe_2O_3/FeO ratio. These three parameters are very sensitive to only slight alteration, and for this reason, and also because it is relatively time-consuming, measurement of these was not

undertaken. The quoted Loss on Ignition (LOI) is a composite function of these approximately equal to $H_2O^+ + CO_2 - 0.11 \times FeO$, the last term resulting from oxidation of FeO on ignition. Provided that $H_2O^+ + CO_2$ in the unaltered sample was relatively small, the LOI may be used as an independant measure of alteration. The relationship between PAS and LOI is given in Table 2.1: rocks with high PAS show a very diffuse LOI distribution, and lower PAS samples have lower modal LOI.

Table 2.1 : Relationship between LOI and PAS. The number of samples of each alteration state is given for a range in LOI.

	%LOI									
	<1	1-1.5	1.5-2	2-2.5	2.5-3	3-3.5	3.5-4	4-4.5	4.5-5	>5
PAS	1	2	2			1				
	2	19	12	7	2	2	1	1		
	3	51	97	47	17	14	5	5		2
	4	21	25	17	15	17	7	11	6	2
	5	19	26	24	25	20	16	16	11	7
	*	1	3	5	1	1	1	1		

*= samples with fresh glass in groundmass and PAS=2

The use of LOI as a measure of alteration has several advantages over the PAS numbers. It is an objective measurement for each sample, not greatly affected by original mineralogical variation between rocks. It is possibly a direct measure of the degree of interaction of a sample with the volatiles believed to have caused the alteration, and is very responsive to carbonate alteration.

A number of mineralogically altered samples have low LOI. Most of these are silica-rich, where silicification is

the main form of alteration, and there is a lack of mafic constituents suitable for the formation of secondary hydrous or carbonate minerals. The effect of alteration on rhyolitic rocks must therefore be treated slightly differently, and too few have been collected to allow detailed conclusions to be drawn. Other petrographically altered low LOI rocks are the few contact-metamorphosed samples in the collection: the low LOI merely indicates lack of major interaction with volatiles since metamorphism.

It is noteworthy that most samples with alteration state 2 and $\text{LOI} > 1.5\%$ have fresh glass in the groundmass. All of these have a fresh 2 pyroxene-plagioclase phenocryst assemblage, and therefore the water implied by the high LOI must be present in the glass. This suggests that, despite its fresh appearance, the glass has interacted with meteoric water and should be regarded as altered. Further evidence for this will be presented in section (e).

(b) Chemical alteration and primary chemistry : criteria

Investigation of the chemical effect of alteration is necessarily dependant on the identification of pre-alteration chemistry. In ancient volcanic provinces this may cause a severe problem, but in the O.R.S. province the frequent occurrence of relatively fresh samples (PAS 1-3, $\text{LOI} < 2.5\%$) in most areas of volcanic outcrop makes this less difficult. The mineral alteration described in section 2.2 suggests that no element has remained immobile during

alteration of even these samples, for all elements are present in the olivine, orthopyroxene and interstitial glass which may here be altered. This will have no effect on the concentration of an element if the sample analysed has remained a closed system to that element. This will occur if there is no transporting medium available, if the rock is not permeable to the medium, or if the element is not readily transported. Under more intense alteration than experienced in this province, there is known to be considerable variation in the ease with which different elements may be transported (e.g. Smith and Smith, 1976), and it is likely that fresher samples would have remained closed to transportation of Al, Fe, Ti, Mn, P, Sc, V, Y, Zr, Nb, Cr and rare earth elements (REE). The hydrothermal fluids were probably silica-saturated, for chalcedony deposition is frequent in vesicles and joints. It is possible that the fluids were therefore unable to transport much silica from the fresher samples, and, in the absence of secondary silica, it is probable that these samples were also closed systems for Si.

It is most unlikely that alteration could produce systematic variation between concentrations of any pair of these elements. If systematic variation is observed, it is probable that it also existed between these and the more mobile elements (alkalis, alkaline earths, and possibly Cu, Zn, Ni and Th) prior to alteration. The effect of alteration may then be judged by the degree of scatter of this variation, and is only important if the more altered

samples show more scatter. Whole-rock variation diagrams in this thesis use 3 sizes of symbols, for $\text{LOI} \leq 2\%$, $2 < \text{LOI} \leq 3\%$ and $\text{LOI} > 3\%$, with smallest symbols for the highest LOI, to facilitate the interpretation of alteration effects on each diagram. The effect of alteration on variation between two mobile elements is harder to interpret, unless their variation with less mobile elements is previously well-understood, and spurious correlation may result.

In samples containing relict fresh minerals, the pre-alteration chemistry may sometimes be inferred from whole rock - phenocryst distribution relationships for minor elements. Both this method and the use of variation diagrams only provide information when there is substantial alteration of primary chemistry, and minor alteration may not be detected.

Since the intensity of alteration is similar throughout the province, with perhaps the least in the north Midland Valley, it is possible to extrapolate from areas showing systematic variation in the less mobile elements to areas which do not, for it is reasonable to assume that the mobility of an element will remain fairly constant throughout the province. It is therefore possible to judge whether scatter on a variation diagram is primary or the result of alteration.

(c) The less mobile elements

The elements suggested to be less mobile in section (b) are, with the exception of Si, those which are not readily transported by hydrothermal fluids. Systematic variation between these and SiO_2 in the more altered outcrop areas is most unlikely to be produced by mobilization during alteration. Such variation may be demonstrated for Lorne (average LOI=2.85%, PAS=3.99), Glencoe (LOI=1.34, PAS=4.27), Cheviot (LOI=2.21, PAS=3.79) and St. Abbs (LOI=4.74, PAS=4.26) for Al, Fe, Ti, Mn, P, Sc and V (e.g. Figs. 4.2, 4.6, 7.1, 8.1). No correlation with LOI is observed, except in a few cases where the only samples of a particular rock type are highly altered (e.g. L87 and L91 for Sc and Fe). In these cases, it is thought that the unusual rock types had primary chemistries unrelated to the main variation, although this may not be conclusively demonstrated.

Variation diagrams of these elements for samples from the less altered areas e.g. the Sidlaw Hills (average LOI=1.28, PAS=3.08) and the North Fife Hills (LOI=1.45, PAS=3.11) show far more scatter (e.g. Figs. 5.3, 5.7) than diagrams for the more altered areas. Again, with the exception of some unusual rock types, no correlation exists between LOI and breadth of scatter, which, taken in conjunction with the lower average LOI and PAS, implies that the scatter is primary and not the result of alteration. In areas with more severe alteration e.g. the Pentland Hills (LOI=3.41, PAS=4.05), it is again true that the breadth of

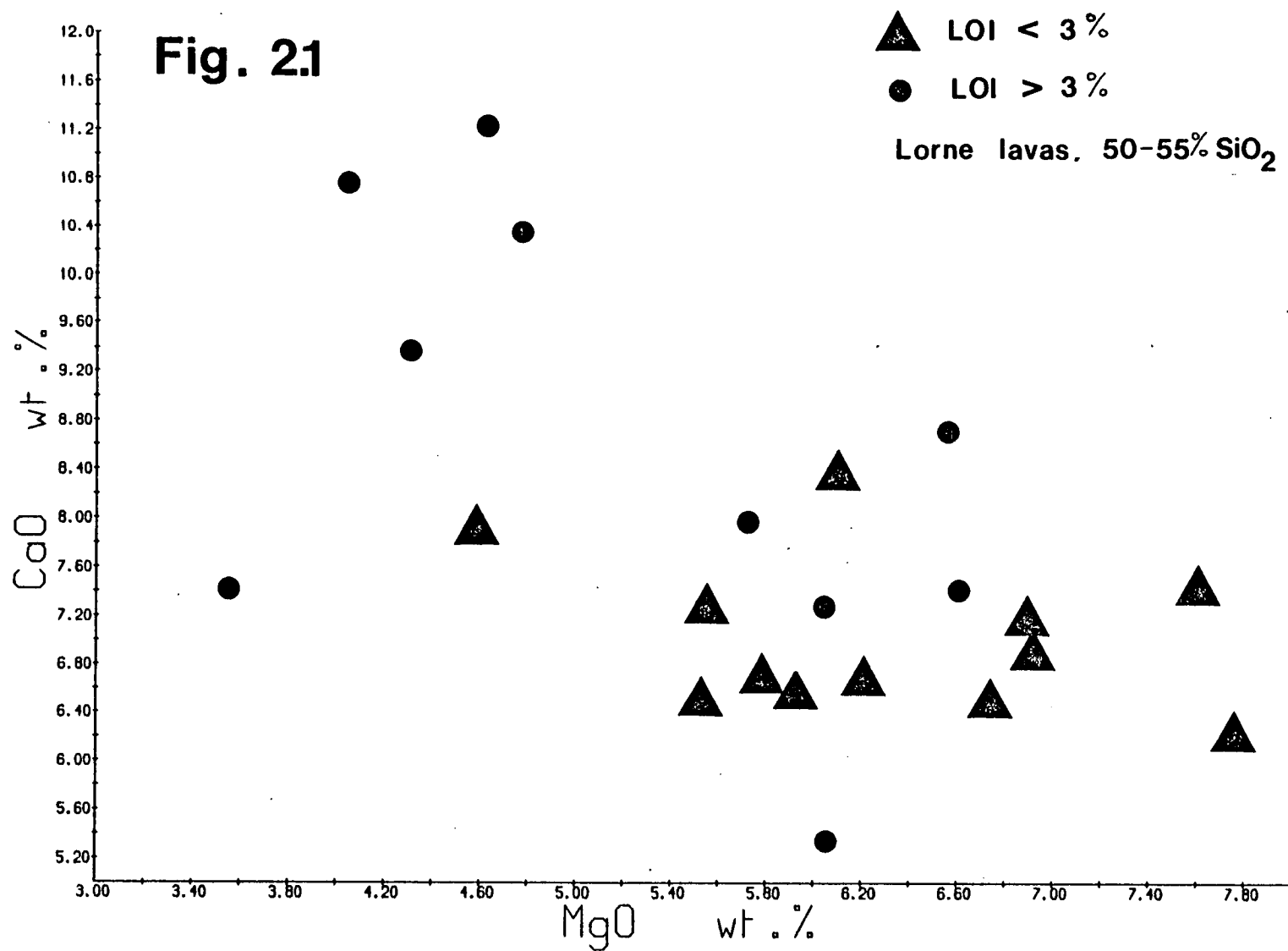
scatter does not correlate with LOI (e.g. Fig. 6.1), and sufficient low LOI, low PAS samples are present to suggest that the scatter is primary.

The elements Cr, Zr, Y and Nb, together with Ti and P considered above, are thought to be among the least mobile elements (e.g. Pearce and Cann, 1973; Smith and Smith, 1976), and their concentrations have been accepted as primary in rocks considerably more altered than those of the O.R.S. province. Mobility of REE has been demonstrated in rocks showing metasomatic alteration (e.g. Hellman et al., 1977), but such intensely altered rocks are very rare in the O.R.S. province and it is thought that REE may have been fairly immobile. Since elements more mobile than these appear not to have been redistributed by alteration in the samples under study, it is improbable that alteration could have affected the concentrations of Cr, Y, Zr, Nb and REE. It is difficult to use the same criteria to establish this, however, for there are few unscattered variation diagrams against silica for these elements. Despite this, breadth of scatter is not correlated with LOI, unusual samples excepted, and variation between pairs of these elements e.g. Zr and Ce, is often systematic. In particular, the constancy of Zr/Nb for some rock groups (e.g. the opx-cpx-phyric and opx-cpx-pl-phyric rocks of Lorne, Fig. 4.3) is strong evidence for the immobility of these elements.

(d) Ca, Mg, Ni

The systematic variation for relatively immobile elements demonstrated at Lorne, Glencoe, St. Abb's Head and the Cheviot Hills suggests that, prior to alteration, a similar variation may have existed for Ca, Mg and Ni. Mg and Ni are liable to be greatly affected by alteration of phenocryst olivine and pyroxene, and both Ca and Mg may be easily transported in solution. Ca is readily introduced in the form of carbonate, which at Lorne may often replace olivine. If alteration is not closed system for Ca and Mg, then such rocks should show Mg loss and Ca gain. Similarly, sericitization or albitization of plagioclase may lead to Ca loss and alkali gain.

Figs. 4.2 and 7.1 demonstrate that samples from Lorne and Cheviot with LOI<2 (larger symbols) show systematic variation with silica for MgO and CaO. The scatter in Ni variation with silica is not correlated with LOI, and Ni variation with Cr is more systematic (Fig. 7.2). It is concluded that Ni behaves as a relatively immobile element. A number of high LOI samples from Lorne and the Cheviot Hills show Ca and Mg concentrations considerably outside the scatter of the main variation. Mg has probably been lost by a number of samples, but Ca shows both losses and gains. The alteration of olivine to carbonate at Lorne produces an inverse Ca-Mg correlation for basic rocks (Fig. 2.1), despite the lack of such correlation for less altered samples. This is an example of a spurious systematic



relation between two more mobile elements resulting from alteration (section 2.3b). A number of low Ca, high LOI samples may be attributed to severe sericitization or albitization of feldspars (Fig. 7.1; C22, C34, C60).

The extension of these relationships to the Midland Valley samples is difficult because of the lack of systematic variation between immobile elements, but it is thought that the bulk of samples with low LOI retain primary Ca and Mg levels. An example of the effect of severe sericitization of plagioclase is provided by the three samples collected from the Dunnichen Member, MT6-8. These have very similar petrography except that MT6 and 7 are sericitized. Chemistries of the three samples are very similar, except that the sericitized samples show higher K and lower Ca and Sr.

(e) The alkali metals, Ba, Sr

These generally mobile elements (e.g. Smith and Smith, 1976) may be treated in the same fashion as Ca and Mg. Scatter on Na variation diagrams is in part produced by poor analytical precision, but more extreme values correlate with high LOI or petrographic alteration, and Na appears to be both lost and gained on alteration. K, Rb, Ba and Sr are probably more mobile, and while all four show systematic variation with silica for both Lorne and Cheviot samples (e.g. Figs. 9.1, 7.1), a large scatter is present which includes a number of low LOI samples. This could either be

due to mobilization of these elements in these low LOI samples, or to primary differences in concentrations of these elements unrelated to silica content.

At Lorne, the scattered low LOI samples are richer in these elements than the main variation trend with silica, and the bulk of the K-rich samples are also rich in Rb, Ba and Sr (Fig. 4.4). This is unlikely to be the result of alteration, for in low PAS rocks Sr is likely to be fixed in fresh groundmass plagioclase. Further, correlation with La/Y also exists (Fig. 4.4), and it may be concluded that much of the scatter of low LOI rocks at Lorne is primary.

In the Cheviot Hills, K and Rb are enriched and Sr is depleted in three high LOI, high PAS samples (C22, C34 and C35, Fig. 7.1), of which the first two have identical mineralogy to the 2 pyroxene-plagioclase-phyric andesites of the main trend. While it may not be proved that these compositions are the result of alteration, it is most unlikely that a K-rich mineral would not crystallise early from liquids with 7.5 and 5.8% K₂O (C22 and C34 respectively). Four low LOI samples (C9, 15, 33 and 54) show depletion of K, Rb and enrichment of Sr, Na, and, in three samples, Ba. These again have the same phenocryst mineralogy as the main trend samples, but are unusual in being vitrophyric with a fresh glass groundmass. They are petrographically very fresh (PAS=2), but have a slightly higher LOI than most samples with PAS=2 (Table 2.1). Analyses of phenocryst plagioclase from these and from main

trend rocks show no differences in K or Sr content (Plagioclase analyses 71 and 74, Tables C2 and C4), and the Sr content of plagioclase in C33 would imply an unreasonable phenocryst/host rock distribution coefficient of only slightly more than 1 (Chapter 3). It is concluded that the fresh glass has exchanged water, alkalis, Sr and Ba with hydrothermal solutions, and that devitrified glasses retain better their primary composition. Similar vitrophyric samples from the north Midland Valley (e.g. OC98, OC123, MT15) also display anomalously low K and Rb, again probably resulting from glass-volatile interaction.

It may be concluded from regions showing simple systematic variation between silica and immobile elements that K, Ba and Sr are not seriously modified by alteration in samples with LOI<3, PAS 1-3, unless the samples contain fresh groundmass glass. Rb appears to be slightly more mobile than K: there are several Cheviot samples anomalously low in Rb. Despite the scatter on variation diagrams for many less mobile elements, previously interpreted as primary, variation diagrams against silica for K, Rb, Ba and Sr for the least altered Midland Valley areas are relatively unscattered (e.g. Figs. 9.1, 9.3 for the Sidlaw Hills, North Fife Hills and coastal Ayrshire). This confirms that the scatter of the less mobile elements is not the result of alteration.

(f) Cu, Zn, Th

It is difficult to predict the behaviour of these elements under alteration. Systematic variation exists for all three in many areas, but in some cases a scatter exists which may neither be correlated with other elements nor with LOI. In the case of Cu and Zn this may have been caused by the mobility of sulphides, either in the magma or possibly during alteration. Zn removal during hydrothermal alteration has, however, been suggested for the Ordovician peralkaline rocks of Wrae (Thirlwall, in preparation). Th appears to be relatively immobile in the Cheviot lavas although there is some tendency towards lower Th in the samples with fresh glass. Scatter in areas such as Lorne may be partly caused by the low analytical precision, for there is no correlation with LOI.

(g) Conclusions

With the exception of the most acid lavas ($>68\% \text{SiO}_2$) and some thermally metamorphosed samples, loss on ignition (LOI) is a good objective measure of alteration. Because of the lack of LOI correlated scatter, it is inferred that almost all the non-acid rocks analysed have retained their original concentrations of Si, Al, Fe, Ti, Mn, P, Ni, Th, Y, Zr, Nb, Cr, Sc, V and REE. Insufficient samples prevent the determination of the effects of alteration on the more acid rocks, but it may be unimportant for these elements, with the exception of silica. Silicification may explain the

bend at about 73% SiO₂ on many Glencoe variation diagrams (e.g. Fig. 4.6), although it should be noted that this is not present for MnO and Zn.

Concentrations of the more mobile elements Ca, Mg, Na, K, Rb, Sr and Ba have probably not been affected by alteration in samples with low LOI (<2.5%) and relatively fresh mineralogies (PAS=1-3), except for K, Rb, Ba and Sr in certain samples with a fresh glassy groundmass. Many more altered samples have probably remained closed to transport of these elements, but in areas where there is little control from fresher samples (e.g. St. Abb's Head), it may be very difficult to determine the primary variation of these elements. It is again not possible to determine the effect of alteration on concentrations of these elements in the more acid rocks, but it is thought that the few mineralogically fresh samples may have retained primary magmatic concentrations.

Despite the lack of any major chemical alteration in the fresher samples, it is considered advisable to have a measure of alteration, the LOI, incorporated into each variation diagram, and to consider the possible effect of alteration on any major deduction made from the chemistry. It is useful in variation diagrams if alteration is only allowed to change the position of a point in a horizontal or vertical direction, and it is therefore inadvisable to plot variation diagrams between pairs of mobile elements. It follows that it is unwise to use a mobile element as an

index of differentiation, for it is convenient to be able to compare the behaviour of every element against the index of differentiation. Alteration in particular rules out the use of Larsen or Thornton-Tuttle differentiation indices, for these are complex functions of several elements whose behaviour under alteration may differ considerably. For similar reasons, the effect of alteration on the norm of a rock is difficult to predict.

Finally, it is important to note that the criteria used in recognizing the chemical effect of alteration only respond to moderately large chemical changes. It is highly probable that mobile elements have suffered small changes in most rocks, and this in particular restricts their use as indices of variation.

CHAPTER 3 : INTRODUCTION TO PETROCHEMISTRY

In the following chapters, the stratigraphy, petrography and chemistry of the Old Red Sandstone volcanic rocks will be discussed, separated into the outcrop areas of Fig 1.1.

3.1 : ROCK NOMENCLATURE

Rocks of calc-alkaline suites usually show a wide range in silica content, and most workers have used nomenclatural divisions separated by silica content, of basalt, basic andesite, andesite, dacite and rhyolite. The bounding silica concentrations used by such authors lie in the ranges 52-54, 56-58, 62-65 and 68-70% silica respectively, but there is no consensus on the precise divisions which should be used. Many recent classifications have subdivided these groups into shoshonitic, high-K and low-K, based on the belief that K content has special genetic significance (e.g. Ewart, in press). Comparable classifications have been used by Gandy (1973a) and Taylor (1972) for rocks of the O.R.S. province, but it is thought that major divisions based on K content are inadvisable because of the ease with which K may be mobilized during alteration. The use of silica as the major criterion for nomenclature can be very misleading, for it is commonly assumed that basalt is a 'primitive' rock type, and andesite an 'evolved' rock type. The occurrence in the province of rocks with <53% silica (i.e. basalts) and <10 ppm Cr and of

others with 57% silica (i.e. andesites) and 370 ppm Cr means that the semantic equation of 'basalt' and 'primitive' can not be assumed if a silica based nomenclature is used.

In general, silica content is not a particularly good indicator of rock chemistry in the Old Red Sandstone volcanic province, and therefore no attempt has been made to use a rigid nomenclatural system. Instead, the terms basalt, andesite etc. have been used merely as indicators of silica concentration, and should not be taken to imply 'primitive' or 'evolved' character. Where nomenclatural systems of previous authors have included well-defined groups (e.g. the "trachyandesites" of the Ochil Hills, Francis et al., 1970; the "mica-felsites" of the Cheviot Hills, Carruthers et al., 1932) their names have been retained for convenience, but most rocks have been classified by their petrography, in particular by their phenocryst mineral association. While this may often have little genetic significance, the phenocryst associations given in Appendix D are useful in that they provide a wholly non-chemical method of rock classification on variation diagrams. The phenocryst association is designated by a number following the '@' symbol in a rock number (Appendix D), and is written as a name using the following abbreviations: ol=olivine, opx=orthopyroxene, cpx=calcic clinopyroxene, pl=plagioclase, hb=amphibole and bi=biotite. For example, S33@11 is an ol-pl-phyric basalt. Rock analyses are given in Table B17.

3.2 : MINERAL ANALYSES

Mineral analyses referred to as numbers in the text are to be found in Tables C2-C4 of the Appendix. Table C2 quotes average core compositions for the phenocrysts of each rock; these are arranged by mineral type, and the numbers in the text refer to the analysis number for the particular mineral type. Table C3 lists selected core-rim pairs, and Table C4 lists the concentrations of some minor elements for some of the minerals in Table C2.

3.3 : VARIATION DIAGRAMS

About 1000 variation diagrams for rocks and minerals of the province have been produced using the computer program VARPLOT (Appendix D). A far larger number of diagrams than are presented here has therefore been considered in the course of this research, and it is believed that those not presented do not conflict with the petrogenetic hypotheses suggested in later chapters.

All variation diagrams for bulk rock compositions use smaller symbols for samples with higher Loss on Ignition (LOI), for the reasons given in Chapter 2. This is not the case on diagrams for mineral chemistry. Symbols usually refer to the phenocryst association or rock type as appropriate; the phenocryst associations may have quartz, apatite and opaque oxides additional to the phenocryst minerals quoted (see Appendix A for full list of phenocrysts

in each rock). Symbols on diagrams for mineral chemistry refer to the phenocryst association of the host rock. On variation diagrams involving mobile elements, more altered samples may on occasion be outside any relevant field boundaries given. This will occur if the anomalous composition of a rock is thought to be due to alteration.

3.4 : GEOCHEMISTRY

Much literature has accumulated concerning the geochemical behaviour of the elements analysed, and some items believed to be relevant to the petrochemistry of the O.R.S. province are summarized below.

(a) Silica is present in olivines, pyroxenes and feldspars in concentrations only slightly lower than that of an equilibrium basic liquid. Equilibration with these minerals can produce only minor silica enrichment in evolved liquids, and typical calc-alkaline trends of silica enrichment require equilibration with silica-poor phases such as garnet, amphibole, biotite or opaque oxides.

(b) Alumina is only likely to be reduced in evolved liquids by equilibration with assemblages rich in calcic plagioclase. Amphibole and some spinels may contain substantial alumina, but in general fractional crystallisation of plagioclase-free assemblages should lead to increase in alumina in evolved liquids.

(c) Iron. Lack of major iron enrichment relative to Mg in evolved rocks separates calc-alkaline from tholeiitic suites, and requires equilibration with a high Fe/Mg phase

such as garnet, amphibole or opaque oxides if a suite is thought to be genetically related.

(d) Magnesium will have lower concentrations in more evolved liquids unless plagioclase and opaque oxides constitute more than some 75% of the equilibrium crystal assemblage.

(e) Calcium will have lower concentrations in more evolved liquids unless these are in equilibrium with an assemblage rich in olivine, Ca-poor pyroxene, biotite or opaque oxide.

(f) Sodium will increase in more evolved liquids unless these are in equilibrium with an assemblage rich in sodic feldspar or amphibole.

(g) Potassium will increase in more evolved liquids unless these are in equilibrium with an assemblage rich in potassic feldspar or biotite.

(h) Titanium crystal-liquid distribution coefficients have been given by Pearce and Norry (1979); they are $\gg 1$ for amphibole, biotite and opaque oxides, and $\ll 1$ for olivine and plagioclase. See also Table C2.

(i) Manganese distribution is probably mainly controlled by variations in oxygen fugacity, for it may show much variation in oxidation state. Plagioclase is the only common Mn-poor igneous phase, and increase in Mn with evolution probably implies equilibration with plagioclase-rich assemblages.

(j) Phosphorus is only present in any quantity in phosphate minerals, and will therefore increase in evolved liquids unless these are in equilibrium with phosphate phases. Apatite is the most common phosphate mineral, although the presence of whitlockite in mantle mineral assemblages has

been suggested by Beswick and Carmichael (1978).

(k) Nickel and Chromium have high distribution coefficients for all mafic and oxide mineral phases (Gill, 1978), with Cr in particular strongly concentrated in clinopyroxene and spinel. Olivine-liquid distribution coefficients for Ni increase rapidly with decreasing magmatic MgO (Hart and Davis, 1978). Ni and Cr can not both increase in evolved liquids unless these are in equilibrium with assemblages very poor in mafic and oxide mineral phases. Ni concentrations may sometimes be affected by equilibration with sulphides.

(l) Vanadium has very high distribution coefficients for amphibole, biotite and oxide minerals (Gill, 1978), and equilibration with assemblages rich in these minerals will lead to strong depletion in V in evolved liquids, as noted by Taylor et al. (1969). V distribution coefficients for garnet and pyroxenes are also high, and increase in V with evolution implies equilibration with olivine-plagioclase rich assemblages.

(m) Scandium has high distribution coefficients for garnet and clinopyroxene, and low for olivine and plagioclase. Equilibration with garnet-rich assemblages, in particular, would lead to strong Sc depletion in evolved liquids.

(n) Copper and Zinc distribution may be mainly controlled by sulphide phases, although zinc concentrations in excess of 1% ZnO have been observed in some phenocryst titanomagnetites (Table C2).

(o) Rubidium substitutes for K in most igneous minerals, and has lower distribution coefficients than K for most phases

except biotite (Gill, 1978). Only equilibration with biotite- (or phlogopite-) rich assemblages can prevent decrease in K/Rb with evolution, but this could also lead to decrease in K and Rb concentrations.

(p) Strontium distribution coefficients are only >1 for plagioclase and apatite (Gill, 1978), although amphibole may contain substantial Sr (Table C4). Only equilibration with plagioclase-rich ($>c.40\%$) assemblages can prevent increase in Sr in evolved liquids.

(q) Barium distribution coefficients are high only for alkali feldspar and biotite, although plagioclase and amphibole may contain substantial Ba (Table C4). It has been suggested (Taylor, 1972) that equilibration with biotite/phlogopite could lead to K/Ba increase in residual liquids, but Ba content of micas is very variable (Table C4).

(r) Thorium distribution coefficients are not well-known, but they are probably $\ll 1$ for most igneous phases except zircon, thorite, allanite and phosphate minerals. There is a possibility of higher Th distribution coefficients for opaque oxide minerals.

(s) Zirconium and Niobium distribution coefficients have been given by Pearce and Norry (1979). High values are only quoted for amphibole, biotite+zircon and titanomagnetite in intermediate and acid liquids, but microprobe studies on phenocryst amphibole and titanomagnetite in intermediate rocks (e.g. GC29@16, Table C4, amphibole analysis 2 and spinel 9) suggest that, in both cases, the distribution coefficients for Zr are substantially less than 1. Only

phenocryst ilmenite has been found to contain significant Zr, but this is variable, giving phenocryst-whole rock distribution coefficients between 2 and 8, much greater than the value of 0.28 quoted by Pearce and Norry (1979). Coefficients given by Pearce and Norry (1979) for Nb are all greater than those for Zr, with the exception of zircon. This implies that Zr/Nb can not decrease with evolution. Analysis 5, Table C4, for Nb has confirmed that Zr/Nb is also lower in ilmenite than in host rock.

(t) Rare earth elements and Y distribution coefficients have been given by Schnetzler and Philpotts (1970) and many other workers for the REE, and by Pearce and Norry (1979) for Y. Y behaves geochemically as a heavy REE (Goldschmidt, 1954, p.310). Olivine, orthopyroxene and plagioclase have coefficients $\ll 1$ for all REE except Eu; heavier REE partition preferentially into clinopyroxene, amphibole and garnet, with coefficients just < 1 in basic liquids for clinopyroxene and amphibole, and high HREE coefficients (4-50) for garnet. LREE coefficients of these three phases are < 1 and therefore equilibration with assemblages rich in them will lead to LREE enrichment (higher La/Y) in evolved liquids. Garnet will be much the most effective at producing LREE enrichment. Apatite and zircon are the only common igneous minerals with high distribution coefficients for LREE (Nagasawa, 1970); apatite is slightly LREE enriched relative to the host rock (Table C2).

(u) Nomenclature

Throughout this thesis, the term 'large ion lithophile elements' (LILE) will be used for K, Rb, Ba, Sr, P and LREE;

and the term 'high field strength elements' (e.g. Pearce and Norry, 1979) will be used for Ti, Zr, Y and Nb. The term 'compatible trace element' will refer to Ni, Cr, Sc and V.

CHAPTER 4 : SOUTHWEST HIGHLANDS

The Old Red Sandstone successions of the southwest Grampian Highlands are dominated by volcanic rocks. There are three Lower O.R.S. outcrops, at Ben Nevis, Glencoe and the Lorne Plateau (Fig. 1.1). In this region the volcanic rocks are associated with a wide range of intrusive igneous rocks, including large granodioritic plutons, kentallenitic and appinitic stocks and a voluminous suite of NE-SW porphyritic microdiorite dykes.

4.1 : LORNE PLATEAU

The O.R.S. of the Lorne Plateau is a relatively thin (c. 2000 ft, 650 m; Kynaston and Hill, 1908) succession of lava flows, rare pyroclastic deposits and some sediments, disposed about a shallow SW-trending syncline and resting unconformably on Dalradian metasediments. The O.R.S. is cut by the NE-SW dyke swarm, and similar lavas (e.g. L82) form a highly altered screen in the plutonic Etive Complex. A few minor plugs and sills also cut the volcanics (Lee and Bailey, 1925), and are thought to be very closely related to the volcanism.

Detailed stratigraphic sequences have been given by Kynaston and Hill (1908) and Lee and Bailey (1925) for small areas near Oban, but the lack of marker horizons has prevented the erection of an accurate stratigraphy for the whole area. The lower part of the sequence appears to be

composed of andesites and basalts lacking phenocryst plagioclase, interbedded with sediments towards the base in the west. The sediments are rich in large lava clasts, and were considered by Groome (1972) to be the products of lahars. Central parts of the sequence are more varied and siliceous, with hornblende- and biotite-andesites and intermittent acid lavas and tuffs. The latter include several ignimbrites, correlated with those at Glencoe by Roberts (1966). The highest flows in the sequence have been described as hypersthene-andesites (Kynaston and Hill, 1908) and are rich in plagioclase phenocrysts.

The petrography of the volcanic rocks has been described by Kynaston and Hill (1908), Lee and Bailey (1925) and Groome (1972), who have all reported a wide variety of associations of the phenocryst minerals olivine, orthopyroxene ('hypersthene'), augite, hornblende, biotite, plagioclase, apatite, titanomagnetite and ilmenite. These occur in a variably textured feldspathic matrix, in which there is usually also augite and opaque material. Some of the groundmass feldspar is probably alkali feldspar (Bailey and Maufe, 1960, p.233) and biotite may also be a groundmass phase. Quartz crystals (up to 4mm) occur frequently in rocks without phenocryst plagioclase from western Lorne, and are usually rimmed by augite or its alteration products, or sometimes by biotite or hornblende (e.g. L21).

Groome (1972) has described the chemistry of some of the volcanic rocks from northern Lorne, and has shown that

the rocks are alkali-calcic (Peacock, 1931) and not high-alumina. He therefore described them as 'orogenic', on the basis of their relation to the Caledonian orogeny. He noted that the rocks are rich in Na, K, Cr, Ni and Sr and poor in Fe, Ca, Cu and Rb/K relative to rocks of most basalt-andesite-dacite-rhyolite associations.

The smooth variation between total iron and silica shown by the Lorne basalts and andesites led Groome and Hall (1974) to the conclusion that these rocks formed a closely related series, implying a common source. The acid lavas were thought to be derived from a different source, because of discontinuities on Harker diagrams for Fe, Sr, Ti and Li. Such discontinuities are not present when data from a wider area is considered (e.g. Fig. 4.2), although additional Li data is not available.

(a) General chemical characteristics

The chemical data reported here for samples from the Lorne Plateau confirm the general features of the Lorne rocks relative to most basalt-andesite associations. Additionally, the rocks have high concentrations of Zr, Nb, Th, P, LREE and relatively low concentrations of Y. The rocks therefore have a very highly fractionated REE pattern relative to chondrites.

The data presented here display the apparently smooth variation of element concentrations with silica described by

Groome and Hall (1974), and additionally, Sc and V decrease and Ba increases with increasing silica. Average analyses (Table 4.1) display the relative levels of each element with increasing silica.

Nb, Th, Y, Zr and LREE do not show the smooth variation with silica thought by Groome and Hall (1974) to be demonstrated by other elements in the basalts and andesites (Fig. 4.1). Scatter in the concentrations of these elements, with the possible exception of Th, is most unlikely to be the result of alteration (Chapter 2): at worst, this would result in translation of points parallel to the SiO_2 axis, and could therefore not produce the scatter, particularly in Zr concentrations. Further confirmation that alteration is not important is provided by the high degree of scatter on the Zr-Ce distribution (Fig. 4.1). Analytical precision and accuracy are good (Appendix B9), and the analytical errors are trivial relative to the magnitude of the scatter.

The use of phenocryst association as a means of classification in Fig. 4.1 instead of the silica-based divisions used by Groome and Hall (1974) demonstrates that the scatter is not random. For example, it is clear that opx-cpx-phyric samples have lower Th, Y and Zr than opx-cpx-pl-phyric samples, despite having roughly the same Nb, Ce and SiO_2 . Examination of other variation diagrams (e.g. Fig. 4.2) discloses that rocks of at least some phenocryst associations have distinctive chemistries for

TABLE 4.1 : Average analyses of SW Highlands volcanic rocks.

	1	2	3	4	5	6
SiO ₂	54.23	55.91	60.14	62.03	64.03	64.53
Al ₂ O ₃	16.68	16.30	16.58	16.67	16.54	16.53
Fe ₂ O ₃	8.14	7.40	6.09	5.36	4.56	4.42
MgO	5.41	5.39	3.82	3.08	2.29	2.37
CaO	7.19	6.68	4.72	4.13	3.69	3.78
Na ₂ O	3.96	3.88	4.50	4.23	4.30	4.38
K ₂ O	2.14	2.44	2.51	3.11	3.23	3.01
TiO ₂	1.40	1.18	0.94	0.88	0.71	0.61
MnO	0.11	0.09	0.08	0.07	0.07	0.07
P ₂ O ₅	<u>0.46</u>	<u>0.45</u>	<u>0.36</u>	<u>0.28</u>	<u>0.24</u>	<u>0.22</u>
Total	99.72	99.72	99.74	99.84	99.66	99.92
LOI	3.05	2.38	2.14	2.77	1.51	0.62
Ni	151	145	77	49	36	35
Cr	293	270	154	83	69	60
V	158	144	111	112	78	79
Sc	22	19	15	14	10	10
Cu	32	27	24	23	17	18
Zn	82	74	70	66	65	62
Sr	1151	1154	1108	993	963	1048
Rb	34	43	39	68	70	59
Th	4	4	4	7	5	4
Zr	207	191	166	200	222	139
Nb	15	13	10	10	10	8
Ba	952	1123	1225	1215	1368	1386
La	36	37	34	35	35	28
Ce	80	80	71	74	72	57
Nd	37	37	33	34	31	26
Sm	7	8	7	4	5	4
Y	21	19	16	18	17	13
No.	23	10	9	10	9	11

1 = ol-phyric samples, 2 = ol-cpx-phyric samples, Lorne.

3 = opx-cpx-phyric and related samples, 4 = opx-cpx-pl-phyric samples,
Lorne.

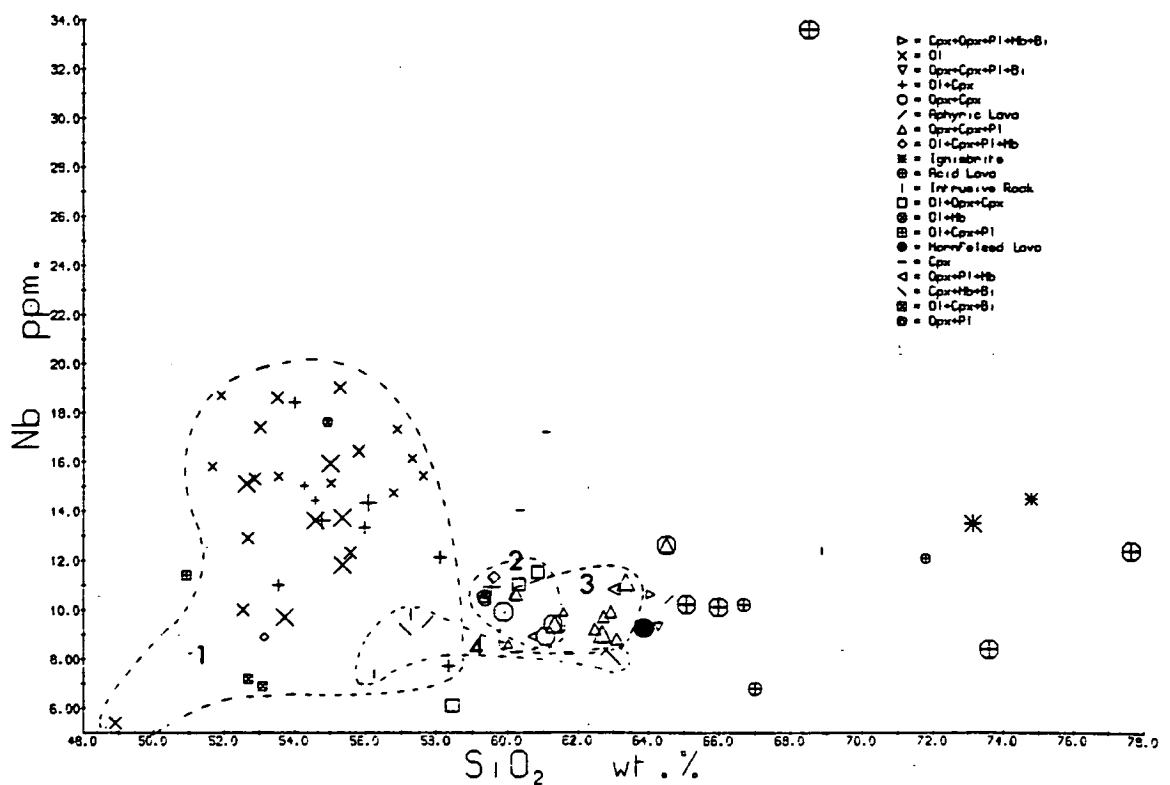
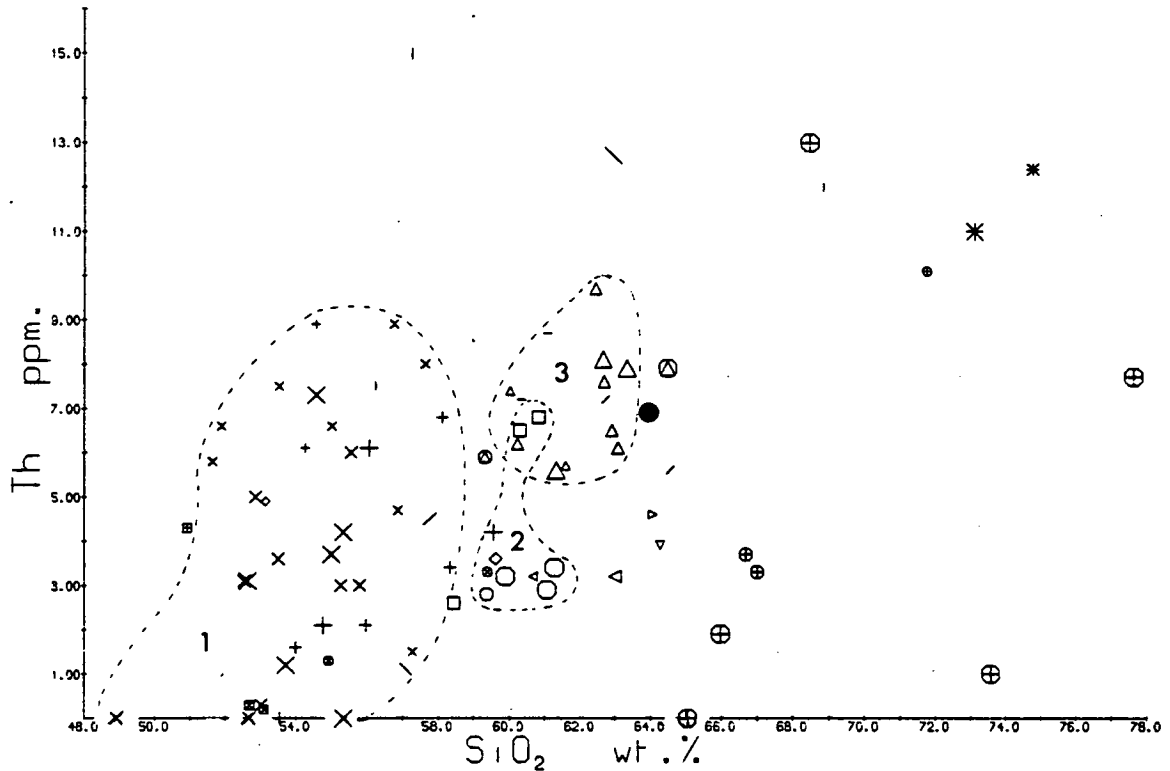
5 = Glencoe samples with $62 < \text{SiO}_2 < 67\%$.

6 = Ben Nevis samples.

Fig. 4.1 a & b : Bulk rock variation diagrams. Fields are:

- 1 = ol- and ol-cpx-phyric samples
 2 = opx-cpx-phyric and related samples
 3 = opx-cpx-pl-phyric samples
 4 = cpx-hb-bi-phyric samples and related intrusions

Conventions as section 3.3

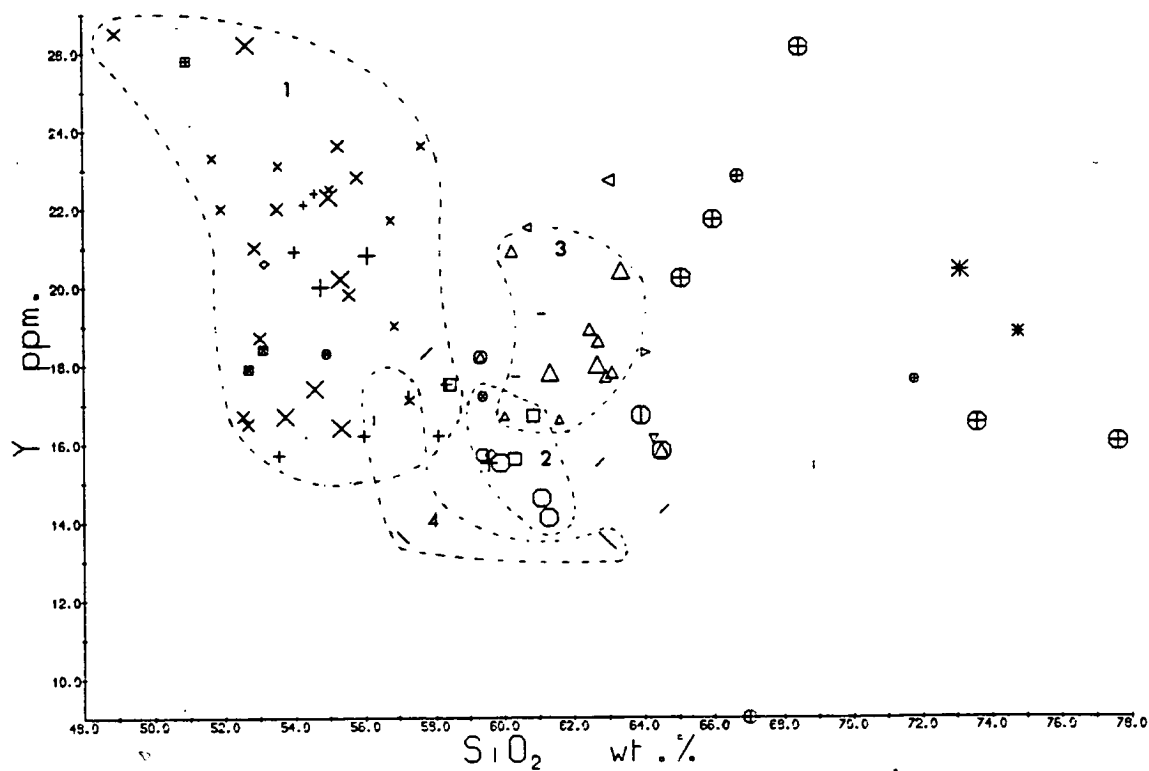
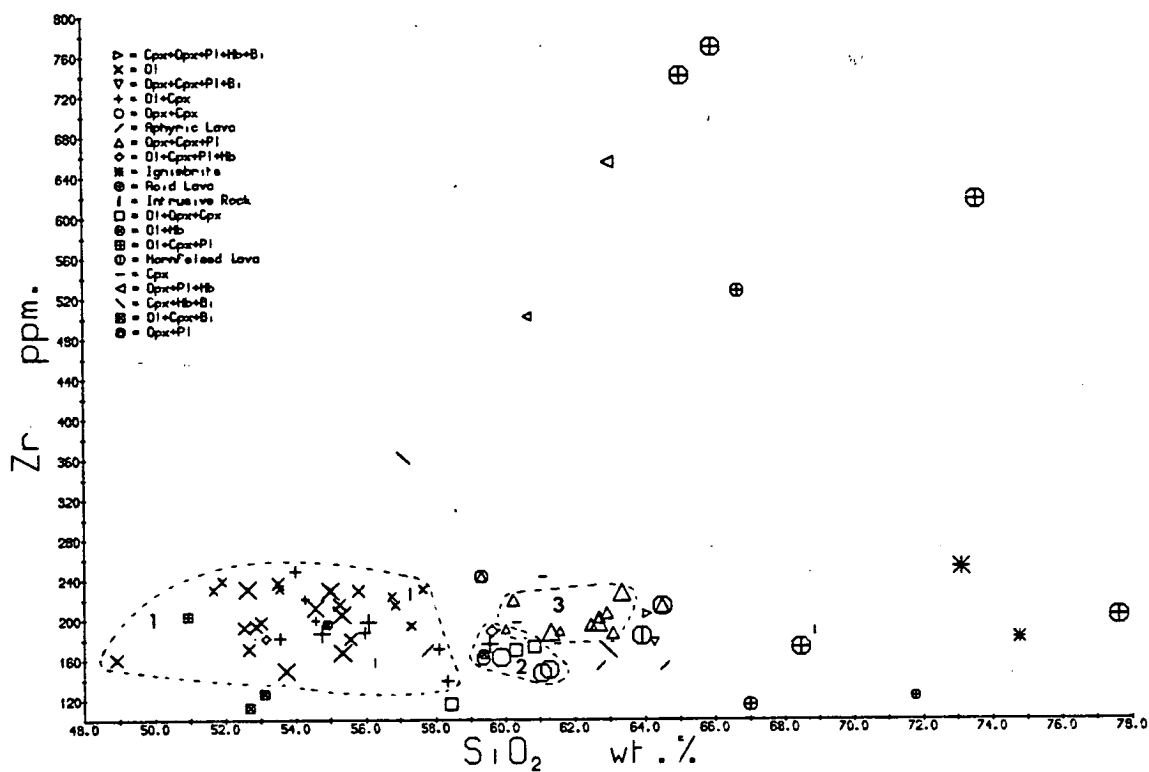


- ⊗ = Cpx+Opx+Pl+Hb+Bt
- X = Ol
- Δ = Opx+Cpx+Pl+Bt
- + = Ol+Cpx
- O = Opx+Cpx
- Δ = Aphyric Lava
- Δ = Opx+Cpx+Pl
- = Ol+Cpx+Pl+Hb
- ⊗ = Igneobrite
- = Acid Lava
- ⊗ = Intrusive Rock
- = Ol+Opx+Cpx
- ⊗ = Ol+Hb
- ⊗ = Ol+Cpx+Pl
- = Mafic Lava
- = Cpx
- Δ = Opx+Pl+Hb
- Δ = Cpx+Hb+Bt
- ⊗ = Ol+Cpx+Bt
- ⊗ = Opx+Pl



Fig. 4.1 c & d

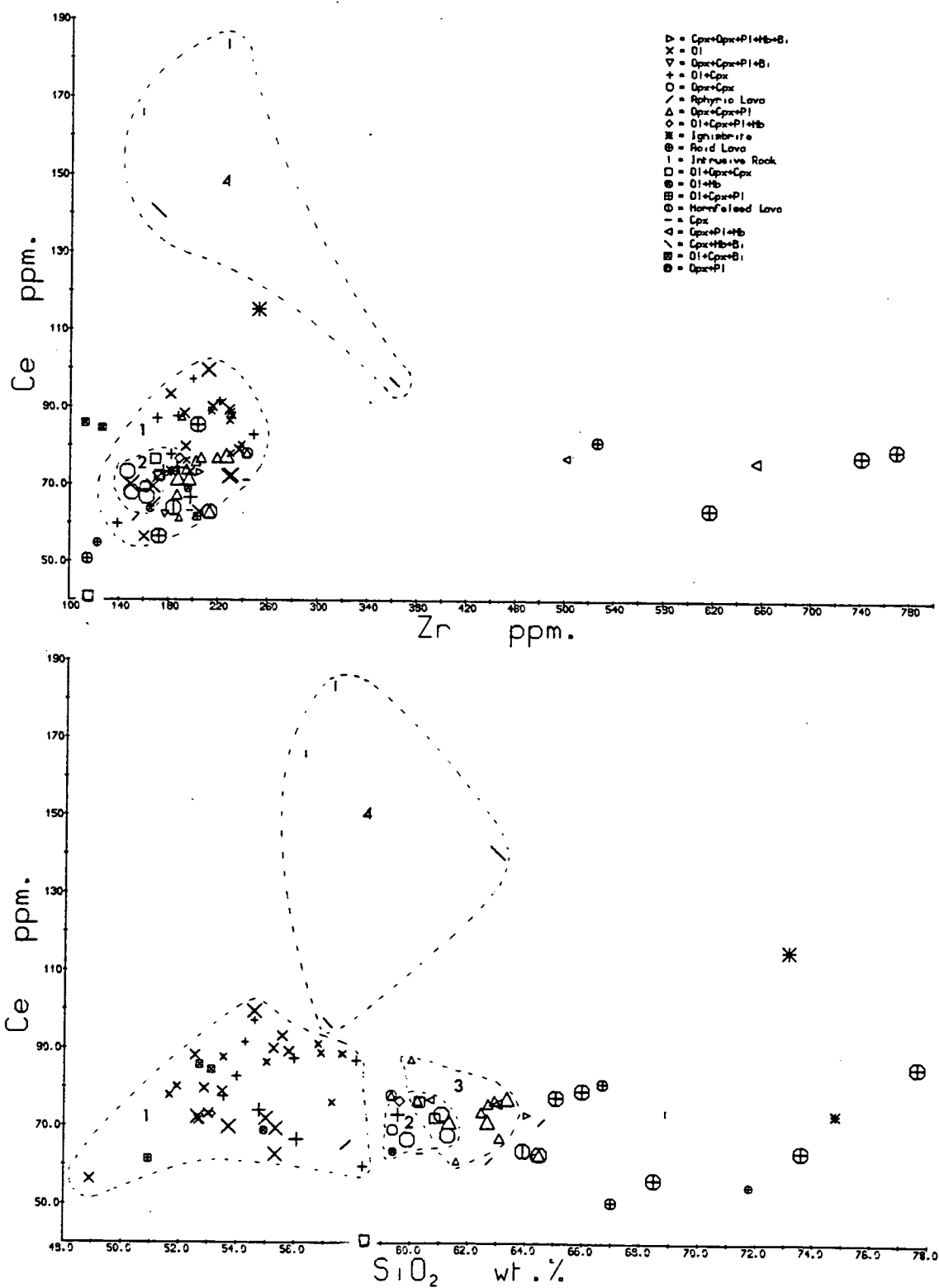
Field boundaries as Fig. 4.1 a & b



LORNE PLATEAU

Fig. 4.1 e & f

Fields as Fig. 4.1 a & b



LORNE PLATEAUFig. 4.2 a & b : Bulk rock variation diagrams

Fields as Fig. 4.1, conventions as section 3.3

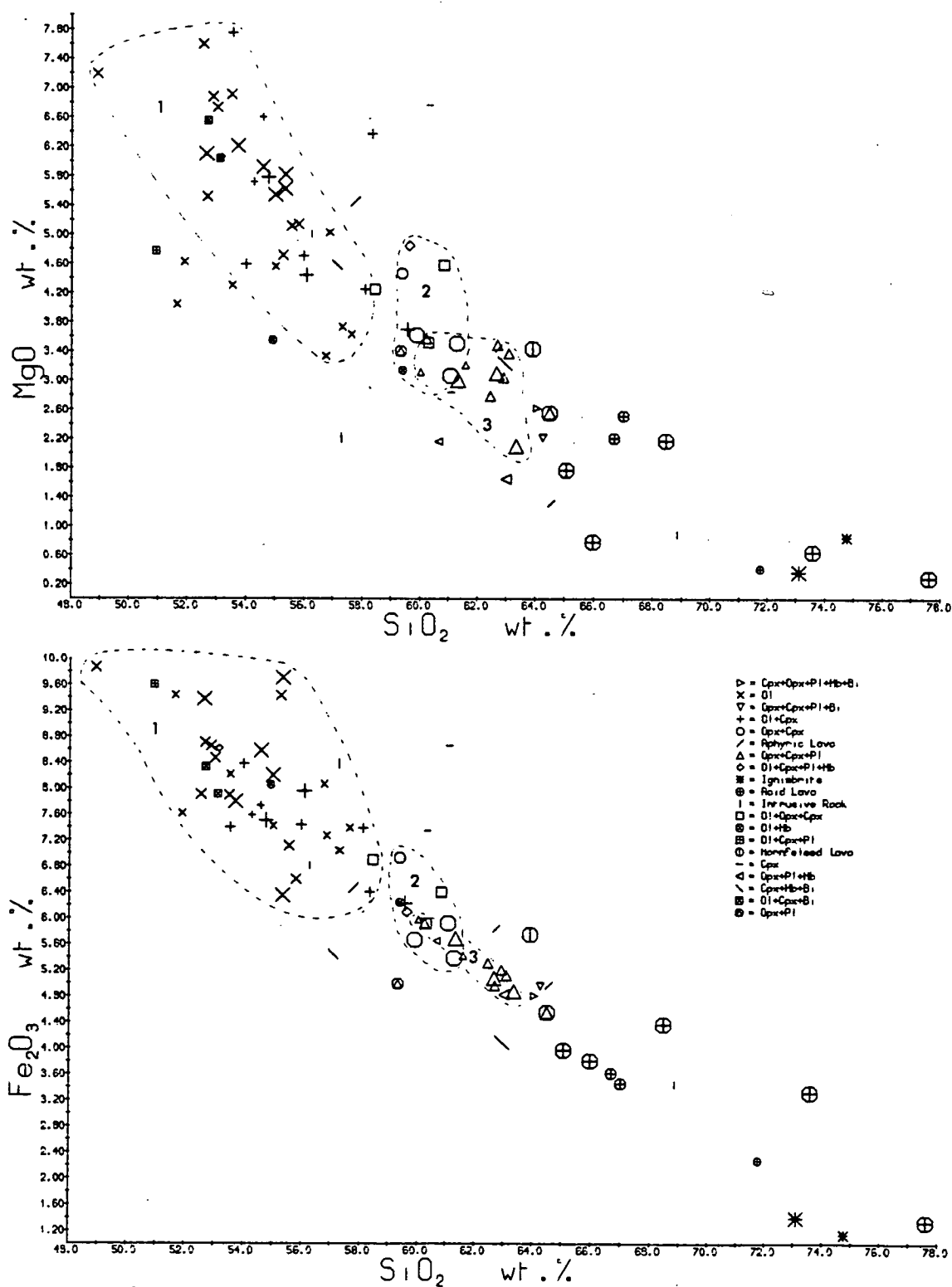
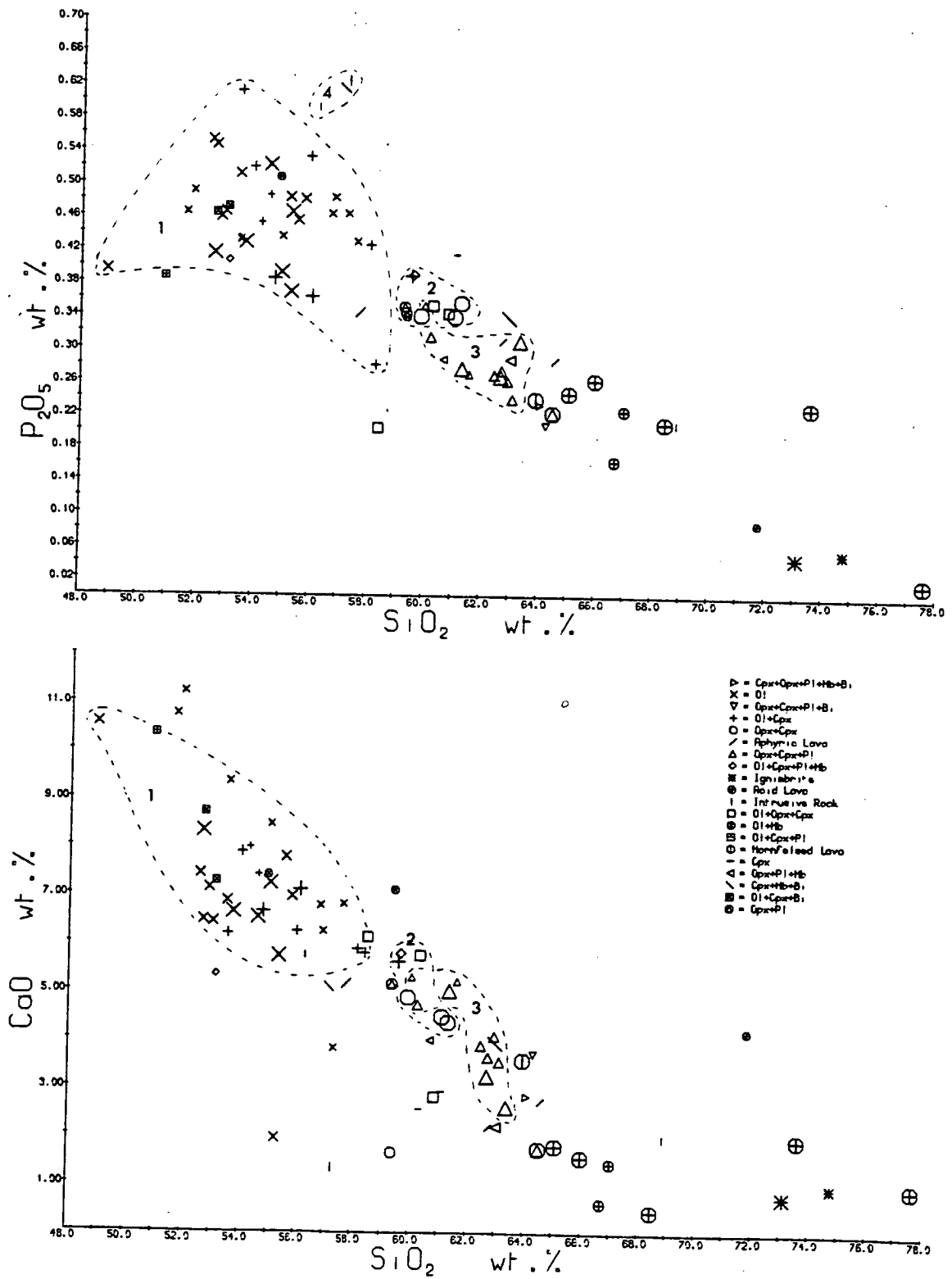


Fig. 4.2 c & d

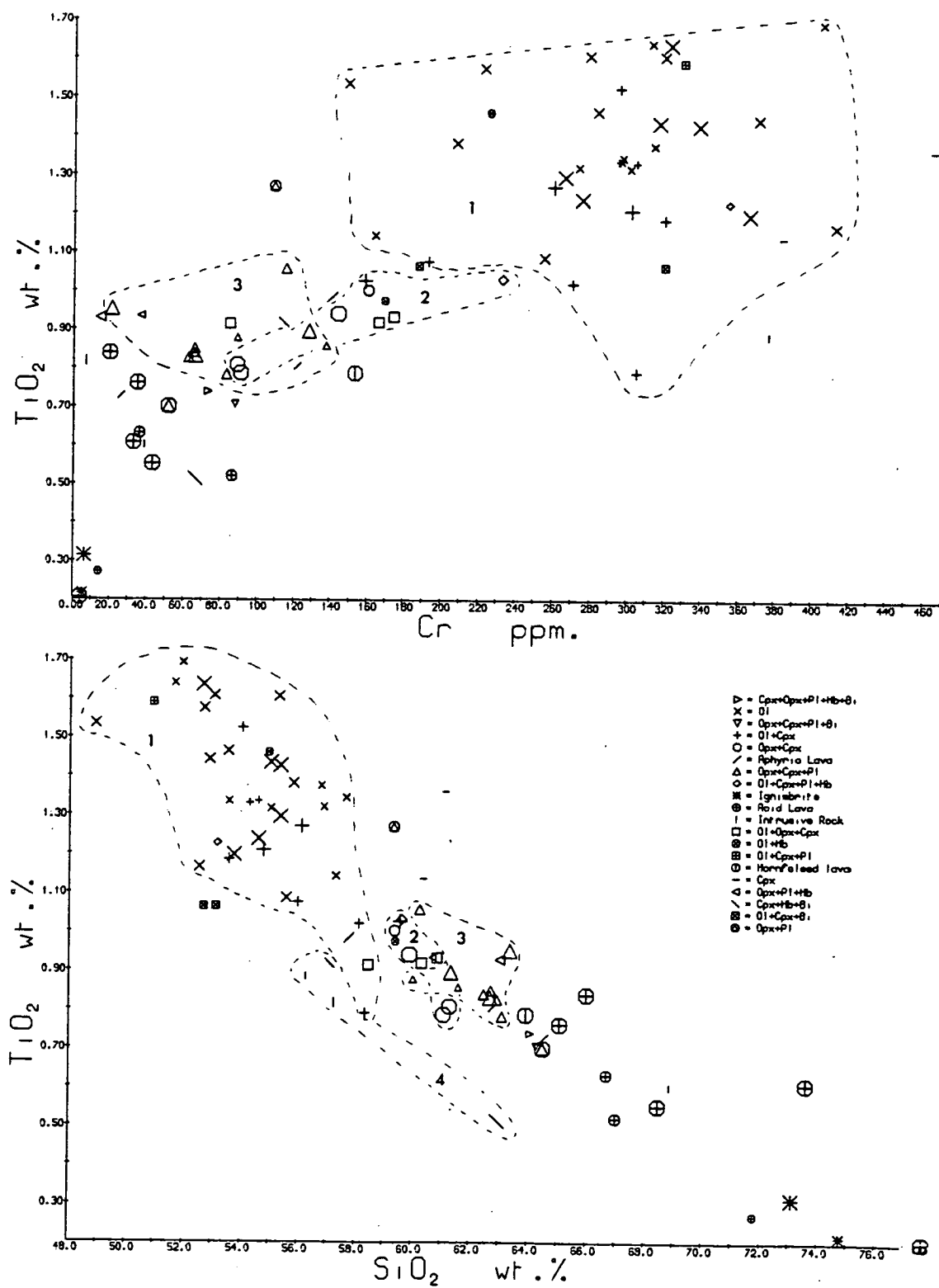
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LORNE PLATEAU

Fig. 4.2 e & f

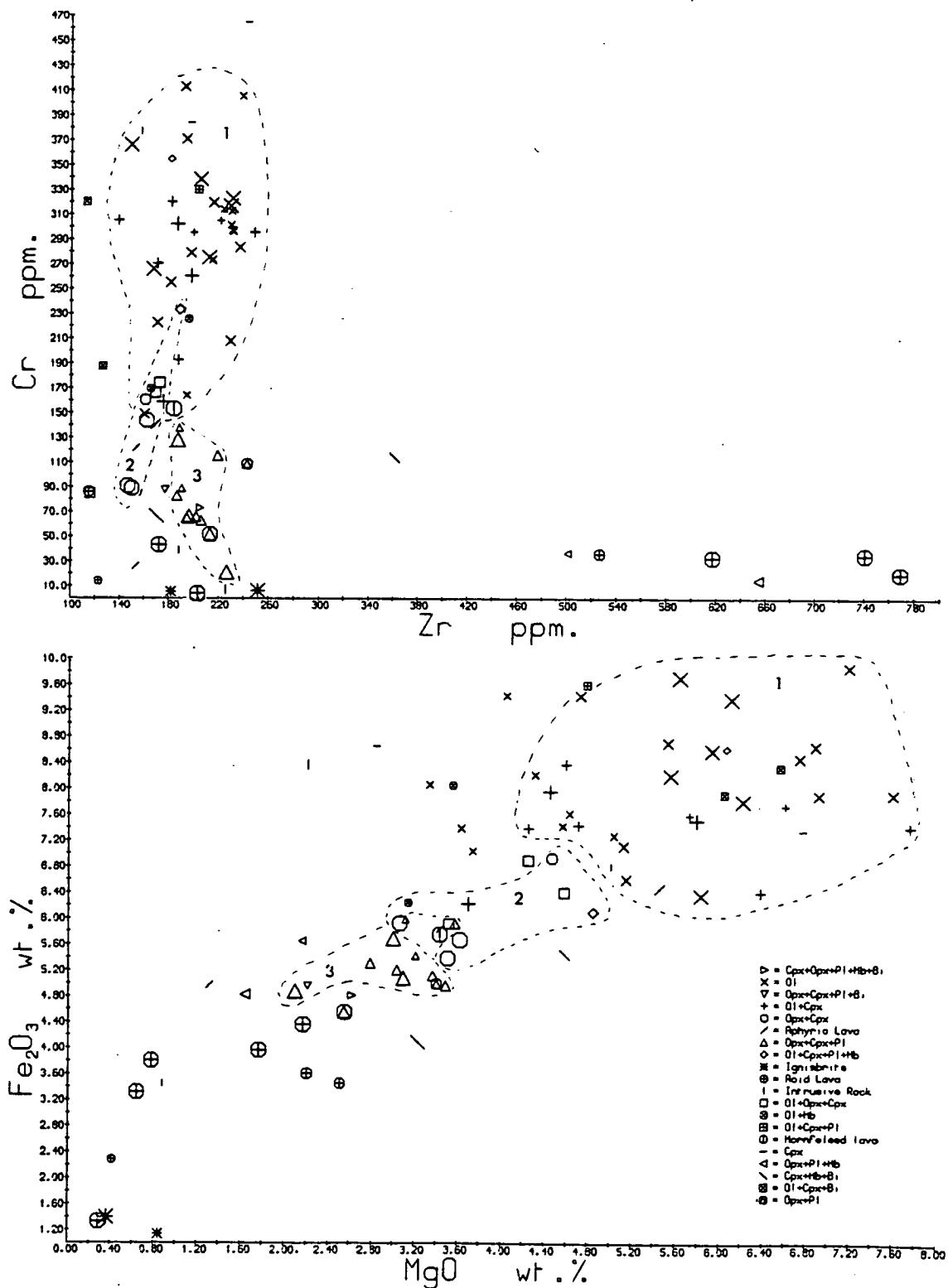
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LORNE PLATEAU

Fig. 4.2 g & h

Fields as Fig. 4.1



elements thought by Groome and Hall (1974) to show smooth variation with silica, and that the associations are not transitional with increasing silica content. The petrochemistry of the rocks in each major phenocryst association will therefore be discussed.

(b) Ol-phyric samples (a1)

Samples with olivine as the sole silicate phenocryst contain olivine pseudomorphs and occasional opaque oxide microphenocrysts in a plagioclase-augite-oxide groundmass. The rocks contain up to 15% modal phenocryst olivine, generally decreasing with increasing silica, although the most basic rock, L23, is phenocryst-poor (<1%). Silica varies from 48.9 to 57.6%, and no elements show smooth variation with silica, although general negative correlation exists for Fe, Mg, Mn, Cr and V, and general positive correlation for Rb, Nb, K and La/Y. Variation diagrams for other elements against silica show no clear trends, and are greatly scattered, despite the appearance in most cases of smooth variation when all rocks are considered (Fig. 4.2).

It is clear from Fig. 4.2 that the rocks do not lie on an olivine control line, and are therefore not genetically related by fractional crystallisation of the phenocrysts. It is apparent that samples with olivine and clinopyroxene as the only phenocrysts are not chemically distinguished from ol-phyric samples, and therefore this group will be treated prior to further discussion of the

chemistry.

(c) Ol-cpx-phyric samples (a7)

These rocks are petrographically very similar to ol-phyric samples, but additionally contain up to 3% of almost colourless augite phenocrysts. Rare samples also have opaque oxide phenocrysts, probably titanomagnetite (L155). The clinopyroxene is chemically a diopsidic augite (e.g. pyroxene analyses 1 and 12, Table C2) with low Al, Ti, Na and generally high Cr. Bulk-rock silica content varies between 53.5 and 59.5%, so that the average (Table 4.1) is more siliceous than that for the ol-phyric samples, and average concentrations of other elements differ according to the 'smooth trends' with increasing silica of Fig. 4.2. Substantial chemical overlap exists between the two groups, and the rocks show the same scattered variation in Figs. 4.1, 4.2. Variation diagrams using other elements as indices of differentiation, e.g. MgO, Cr and Zr, show a similar degree of scatter: it may therefore be concluded that no single-stage, single-source petrogenetic mechanism can create the observed variation.

The chemical variation discussed so far could be produced by a two-stage fractional crystallisation process; for example, the general variation trends of Table 4.1 may have been generated by high pressure fractional crystallisation, with scatter superimposed through lower pressure fractionation. A number of lines of evidence

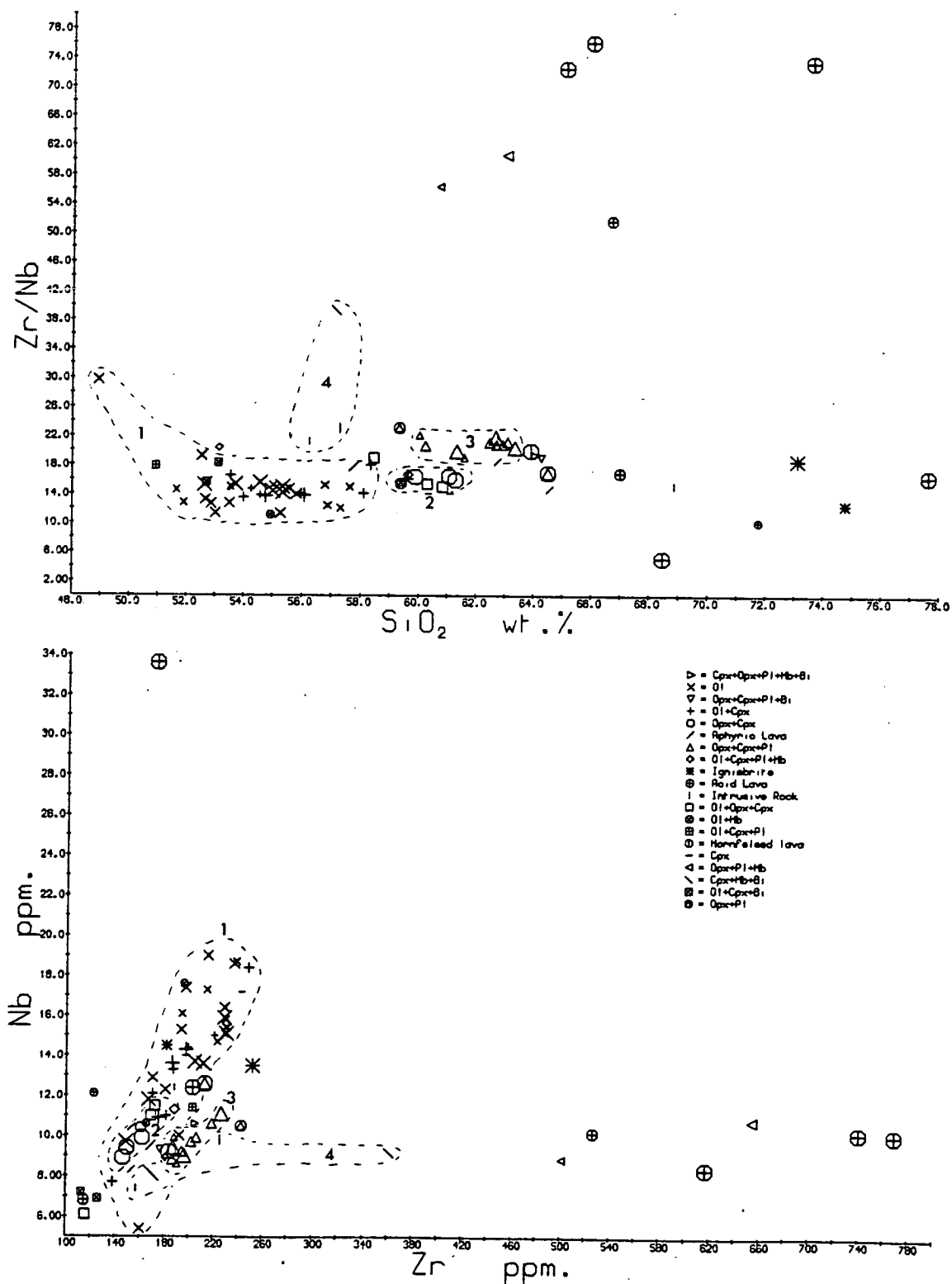
suggest that this is not the case, of which the strongest is the use of the concentrations of elements with low crystal-liquid distribution coefficients ('incompatible elements'), which, even in multi-stage fractional crystallisation, should maintain constant ratios with evolution. The identity of such elements of course depends on the composition of the crystallising assemblage, but Pearce and Norry (1979) suggest that, assuming that liquids of basaltic composition are not in equilibrium with minor phases, Zr/Nb should be insensitive to fractional crystallisation or variation in degree of partial melting.

Although there is general positive correlation between Zr and Nb for the ol- and ol-cpx-phyric samples, there is still substantial scatter (Fig. 4.3b). Fig. 4.3a demonstrates the result of this scatter on the Zr/Nb ratio: for ol- and ol-cpx-phyric samples this varies between 11 and 30, although all except three have Zr/Nb between 11 and 16. This variation is substantially greater than that for any region illustrated by Pearce and Norry (1979), although the range for Hawaiian basalts is comparable to the restricted range for the Lorne samples. The presence of biotite and resorbed amphibole in some of the basic Lorne lavas suggests that equilibration with minor phases is a distinct possibility; however, Zr and Nb content of these phases is low, and therefore a high degree of crystallisation or large variation in degree of partial melting with these phases residual would be required to generate the observed Zr/Nb variation. These mechanisms would lead to major variation

LORNE PLATEAU

Fig. 4.3 a & b : Bulk rock variation diagrams

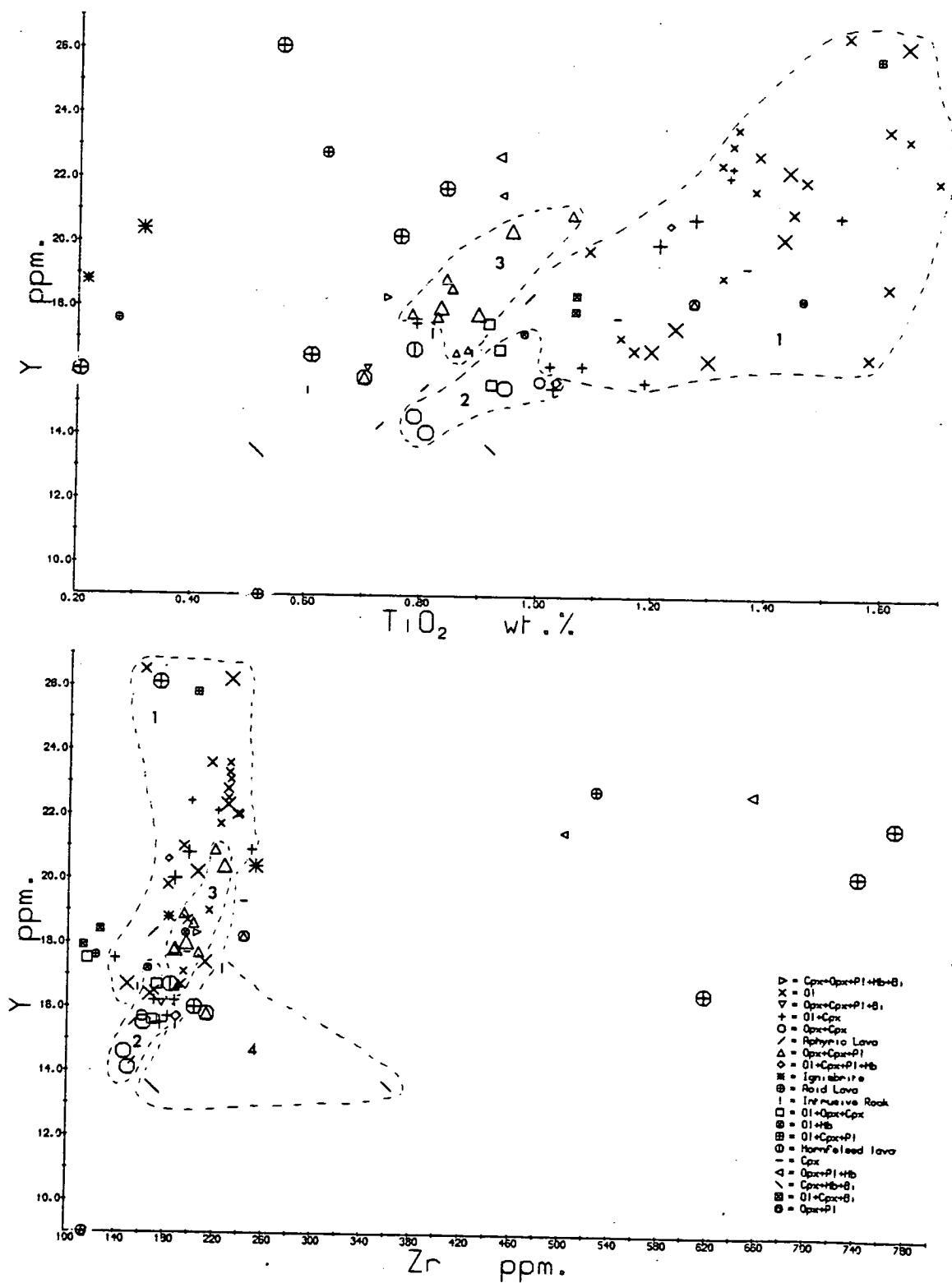
Fields as Fig. 4.1, conventions as section 3.3



LORNE PLATEAU

Fig. 4.3 c & d

Fields as Fig. 4.1



in the rest of the chemistry, particularly in Si, which would correlate with Zr/Nb variation. This is not observed (Fig. 4.3). Ilmenite has substantially higher Zr and Nb concentrations (e.g. analysis 2, Table C4) and equilibration with ilmenite-bearing assemblages could therefore lead to change in Zr/Nb (Chapter 3).

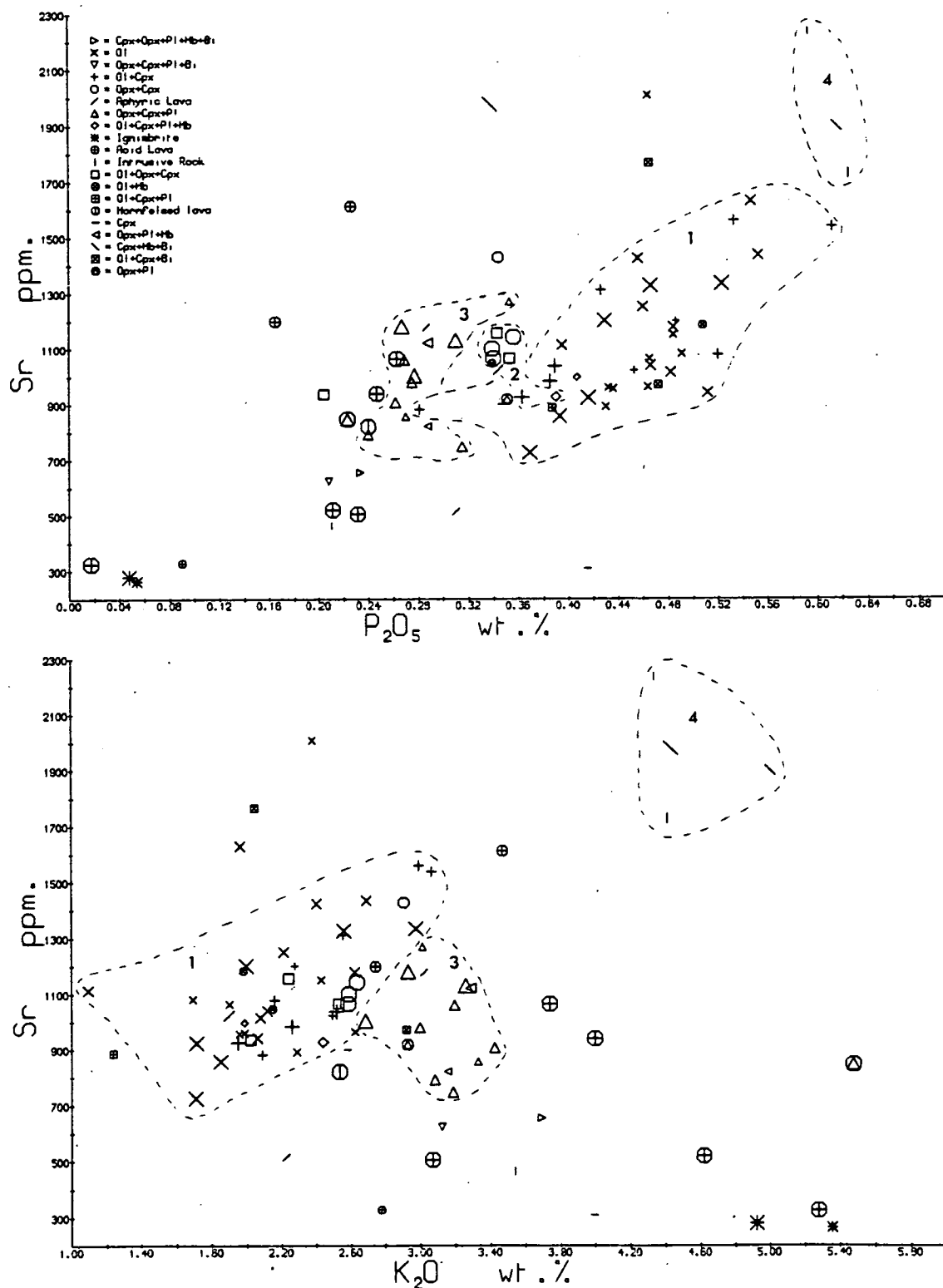
In addition to the general positive Zr-Nb correlation, there is also general positive correlation between Zr and Y, Ti and Y (Fig. 4.3), Ti and Nb and to some extent between Ti and Zr. Conversely, correlations between Zr and Ce (Fig. 4.1e) and between Ti and P are poor; Ce and P being elements which remain incompatible unless apatite is a fractionating phase.

Such Ti-Zr-Y-Nb relations, with relatively constant inter-element ratios, are commonly found in volcanic suites (Pearce and Norry, 1979), and may usually be interpreted as the products of partial melting or fractional crystallisation events. The direction of evolution on the Zr versus Nb diagram should be the direction of Cr and Ni decrease providing that plagioclase is not the sole fractionating phase, for one or both of Cr and Ni partition strongly into all mafic minerals (e.g. Gill, 1978). In these samples, there are good Sr-K, Sr-P, Sr-Ba, Sr-Rb and Sr-La/Y positive correlations (Fig. 4.4), implying that plagioclase can not be an important fractionating phase (Chapter 3). The range in Zr and Nb concentrations implies about 50% crystallisation of the parent magma if both are

LORNE PLATEAU

Fig. 4.4 a & b : Bulk rock variation diagrams

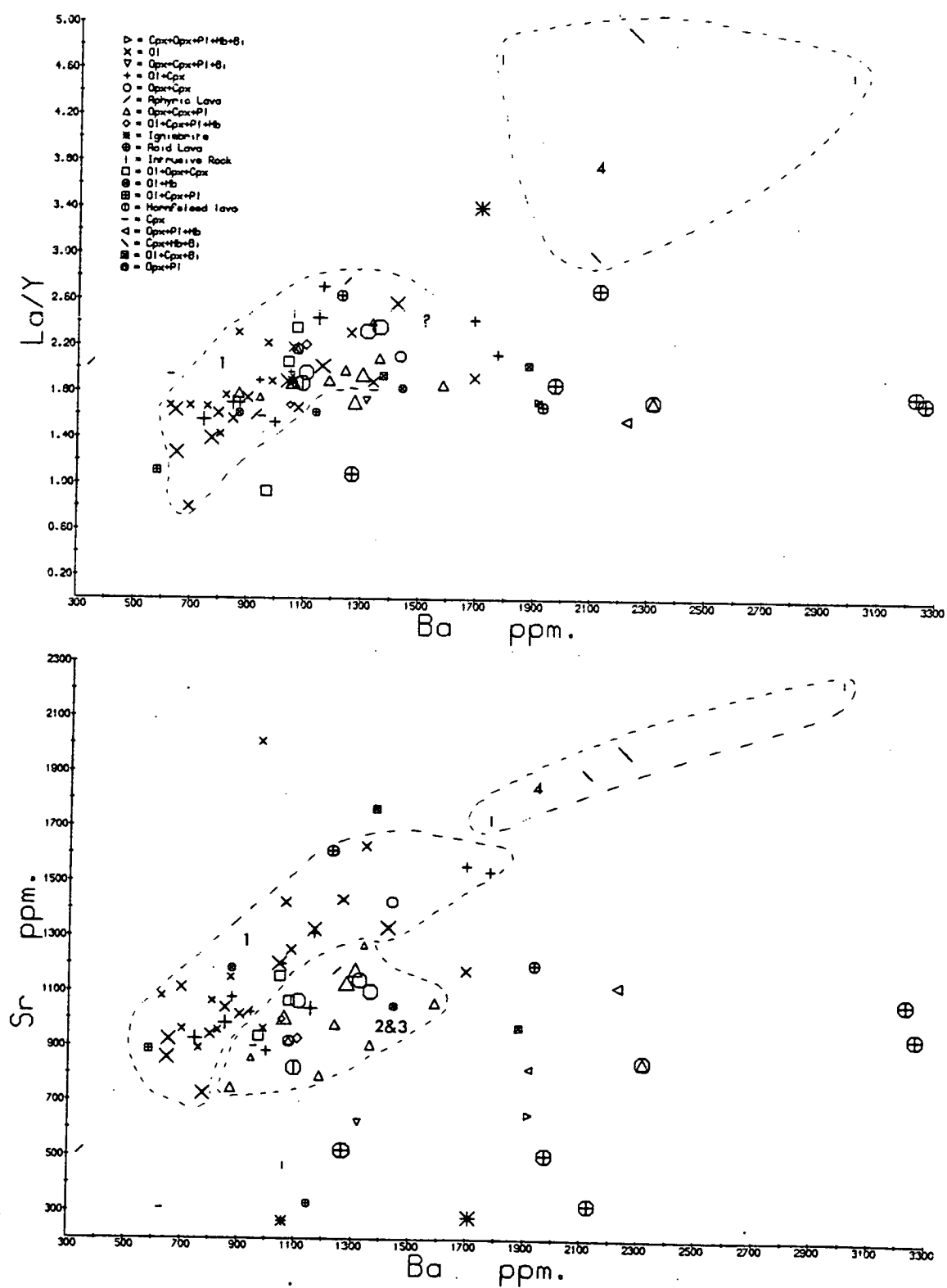
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LORNE PLATEAU

Fig. 4.4 c & d

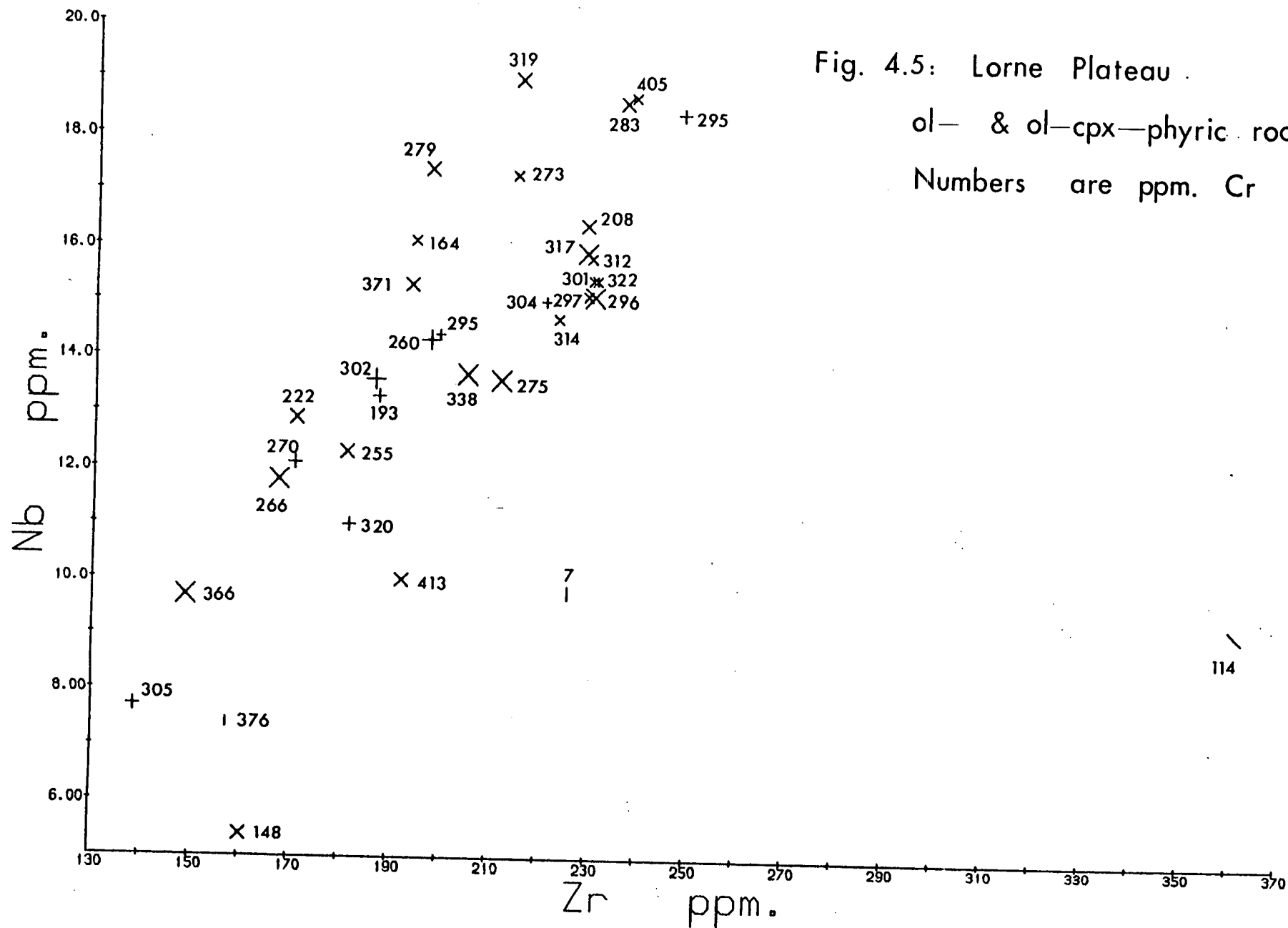
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regarded as incompatible; such a large degree of crystallisation is likely to produce substantial reduction in Cr and Ni concentrations. For example, if the bulk distribution coefficient for Cr was as low as 2, the Rayleigh equation predicts halving of the Cr content of the liquid on 50% crystallisation. The same argument applies if Zr and Nb are regarded as compatible, for it is most improbable that they could be more compatible than Cr. No systematic depletion in Cr content occurs either with increase or decrease of Zr (Fig. 4.2). If fractional crystallisation of small amounts of ilmenite (or magnetite, Pearce and Norry, 1979) produces the variation in Zr/Nb by preferentially removing Nb, then Cr and Ni will also decrease with increasing Zr/Nb, so that, at constant Nb, there should be systematic decrease in Cr with increasing Zr. No such pattern is displayed (Fig. 4.5). Zircon separation, the final possibility suggested by Pearce and Norry (1979) for change in Zr/Nb by fractional crystallisation, may be ruled out because of the improbability of early zircon crystallisation from a basalt-basaltic andesite liquid with only about 200 ppm Zr. It may be concluded that even multistage fractional crystallisation can not produce the observed chemical variation.

(d) Opx-cpx-phyric and related samples (28)

Rocks of this phenocryst association have a few phenocrysts of augite and pseudomorphed orthopyroxene in a



generally trachytoid feldspathic groundmass. Only four samples have been collected, but five other samples (L50-52, L21 and L61) show nearly identical chemistry, with the exception of substantially higher Th for samples L51 and L52 (Fig. 4.1). These two have phenocryst olivine in addition, but are not chemically transitional to the ol-cpx-phyric samples. L50 has olivine and augite phenocrysts with rare resorption pseudomorphs after amphibole and rare plagioclase, while the original nature of the phenocrysts in L61 is a little difficult to determine. L21 is the most siliceous ol-cpx-phyric sample, but has more affinities with the opx-cpx-phyric group.

Augite phenocrysts from L50 and L51 are very similar to those from the ol-cpx-phyric samples, and in particular do not have higher Fe/Mg than the pyroxenes from the more basic groups, contrary to the suggestion of Groome (1972). Single rounded crystals of quartz with a reaction rim of very low Ti, low Al augite (analysis 9, Table C2) or amphibole are very common in rocks of this group, and were interpreted as 'xenolithic' by Kynaston and Hill (1908, p.64). Groome believed them to be relatively high pressure phenocrysts, because of the lack of reaction rims around rare schist xenoliths. The absence of reaction rims around large aggregates of quartz grains (?quartzite xenoliths) and their presence around single crystal quartz in GC10 suggests that Groome's interpretation was correct, although quartzite xenoliths in the Ballachulish quartz-diorite display wide augite-hornblende coronae (Muir, 1953).

The silica range in this group is small, from 59 to 62%, but even in this range fairly smooth depletions are observed for Ti, Ca (unaltered samples), Mg, Fe, Cr, Ni, Sc and V (e.g. Fig. 4.2), contrasting strongly with the behaviour of these elements in the more mafic samples. Concentrations of these elements are lower than in more mafic samples (Table 4.1), as expected from the 'smooth' variation trends with silica for the Lorne lavas as a whole, but there appears to be a composition gap between this group and the more mafic samples, particularly evident for Nb, Ce (Fig. 4.1), Ti and P (Fig. 4.2). Zr/Nb is between 14 and 16, which is identical within analytical error and closely comparable with the average Zr/Nb of the mafic rocks (Fig. 4.3). Variation diagrams against Cr (e.g. Fig. 4.2) demonstrate that Ti, Zr, Y and Nb decrease smoothly with increasing differentiation (i.e. with decreasing Cr, Ni and increasing SiO_2). This may suggest fractional crystallisation of an assemblage including amphibole or biotite+zircon (Pearce and Norry, 1979) or possibly ilmenite. LREE may decrease slightly with differentiation, but as with Y, Nb and also Rb the amount of variation involved is close to the analytical precision limit. K_2O increases smoothly by 7% relative if the three more altered samples are ignored, Ba appears to increase by 22% relative (from about 1100 ppm in L21, 10, 50 and 51 to about 1350 ppm in L14 and L45), but Rb increases by a maximum of only 7%. This combination might suggest fractional crystallisation of a biotite-bearing assemblage (Chapter 3) rather than an amphibole-bearing one, but it should be noted that the

distribution coefficients are poorly known, and the variations in Rb, Nb and Y are close to the limits of analytical precision. Further, resorption pseudomorphs after amphibole occur in L50, suggesting that amphibole may be more plausible.

A model of fractional crystallisation of a biotite- or amphibole-bearing assemblage from a more mafic composition could therefore produce some features of the chemical variation of this group of rocks, but certain difficulties remain. Prominent amongst these are the lack of measurable Zr in amphiboles from higher Zr lavas in Glencoe, indicating $D(\text{Zr}, \text{hb}) < 0.6$; the Th concentrations of L51 and L52; and the scatter in P_2O_5 concentrations between 0.33 and 0.38% unrelated to Cr content, which is considerably greater than the scatter introduced by analytical imprecision (Table B7). It is believed that variation within this group can not be adequately explained by fractional crystallisation.

(e) Opx-cpx-pl-phyric samples (@13)

Rocks with this common phenocryst association are in general phenocryst-rich, with up to 40% plagioclase, and correspond to the hypersthene-andesites of Kynaston and Hill (1908). The feldspar is usually calcic andesine, and the clinopyroxene is an augite low in Ti, Al and Na, with Fe/Mg significantly greater than that in samples lacking phenocryst plagioclase. The pyroxene is commonly reverse

zoned. Apatite, magnetite and ilmenite are common additional phenocrysts.

Silica varies from 60 to 63.5%, and in this small range there are fairly smooth depletion trends for Fe, Ca, Cr, Ni, Sc and, with the exception of the most siliceous sample, for P, Ti and possibly Al (e.g. Fig. 4.2). The rocks fall on the smooth overall variation trends of Table 4.1, but show marked differences from the opx-cpx-phyric and related samples which are not simply related to the slightly higher average silica of the opx-cpx-pl-phyric rocks. In particular, K, Th, Rb, Sc, V, Zr and Y are substantially higher in the opx-cpx-pl-phyric rocks, while P is lower. LREE and Nb show no differences, so that Zr/Nb is higher and La/Y, and also K/Rb, are lower in the opx-cpx-pl-phyric rocks (e.g. Figs. 4.1-4.3). These differences, in particular that of Zr/Nb, strongly suggest that the two main rock groups in the 59-64% SiO_2 range are neither derived from each other nor from the same parent magma by fractional crystallisation processes. Cumulus enrichment has probably played little part in creating the chemical differences, for Al contents of the two groups are very similar, and do not increase much with increasing amount of phenocryst plagioclase (e.g. from L30, <10%, to L128, >35% phenocryst plagioclase).

Zr/Nb varies between 19 and 22, close to the range expected through analytical imprecision, and both Zr and Nb increase fairly smoothly with decreasing Cr content (Fig.

4.2), suggesting that fractional crystallisation of a Zr-, Nb-poor assemblage could explain the variation in this group. However, only one of the ol- and ol-cpx-phyric samples has Zr/Nb in this range, and therefore derivation of the group by fractional crystallisation of one of the more mafic magmas is improbable.

Y, K, and less clearly, Ce and Rb, also increase with increasing Zr and SiO_2 and decreasing Cr (Figs. 4.1-4.3), and K, Rb, Zr and Nb all show about 20% enrichment over the full Cr depletion. Ce and Y seem to be less incompatible, with only about 15% enrichment. Fractional crystallisation of the phenocryst phases could probably give rise to the main variation trends, for apatite could account for the depletion in P_2O_5 and the less than perfectly incompatible behaviour of Y and LREE (Chapter 3). This possibility is difficult to test by least squares extract calculations because of the small amount of variation involved, and the difficulty of identifying the primary major element chemistry of small numbers of samples when modified by alteration. The far from perfect linear relationships of LREE, P and Ti with silica and Cr may suggest that, again, a more complex petrogenetic mechanism should be invoked.

(f) Cpx-hb-bt-phyric samples (a15)

Only two samples of this association have been analysed, but they have very distinctive chemistry. Both have small augite phenocrysts (analysis 5, Table C2; very

similar to augites in the more mafic samples but slightly richer in K), much apatite, resorption pseudomorphs probably after hornblende but possibly after biotite, and anhedral phlogopitic mica (analysis 1, Table C2). Ilmenite microphenocrysts and augite-rimmed quartz crystals are also present in L113. Samples L54 and L55 from two minor intrusions, one of which is augite-apatite-biotite-phyric, have very similar chemistry to L113. These four rocks show K_2O/Na_2O close to or greater than 1, extremely high Sr and Ba (>2000 ppm), and very high K, P and La/Y. L125 is more siliceous than the others, and accordingly has lower P etc., but the three more basic samples plot at the high Sr, Ba, K, P, Rb, La/Y end of the positive correlations between these parameters in the ol- and ol-cpx-phyric samples (Fig. 4.4). Zr/Nb is somewhat higher than the average for mafic samples, and rocks of this group also have much lower Ti, Fe, Sc, V and lower Cr, Y and Nb than the bulk of the more mafic Lorne rocks (Figs. 4.1-4.2).

(g) Other phenocryst associations

A number of other phenocryst associations of very distinctive chemistry exist. Two samples with ?clinopyroxene as the sole phenocryst phase are siliceous (60-61% SiO_2) but have extremely high Cr (470 ppm) and very high Ni, Sc, Ti and Fe relative to other Lorne andesites (Figs. 4.1-4.2). Two basic samples with phenocrysts of olivine, augite and conspicuous pale brown phlogopite, frequently associated with calcite, have low concentrations

of Th, Nb and Zr, but relatively high LREE.

A wide variety of more acid lavas exists, of which the most conspicuous is a group very rich in Zr (up to 780 ppm), poor in Th and Nb but relatively rich in Y. The only other very Zr-rich lavas are two opx-pl-hb-phyrlic andesites; these have similarly low Th and Nb, and are low in Cr and Ni relative to other Lorne andesites. This group of high-Zr rocks has very high Zr/Nb (50-80), which, using the criteria of Pearce and Norry (1979) would suggest fractional crystallisation of magnetite. This is not confirmed by V concentrations, which are identical to those of more normal andesites. The small number of acid lavas collected does not allow detailed discussion of their possible origins, but they are undoubtedly polygenetic.

4.2 : GLENCOE

The O.R.S. rocks of Glencoe outcrop within a small elliptical area bounded by the Glencoe Boundary Fault, and were interpreted by Bailey and Maufe (1960) as a cylindrical block preserved by caldera collapse. The rocks rest on Dalradian and Moinean metasediments, and are cut by the NE-SW dyke swarm, which has created the elliptical shape of the complex by NW-SE extension. The rocks in places form a roof to the Cruachan Granite, about which there is considerable contact-metamorphism.

The O.R.S. sequence is dominated by volcanic rocks;

the stratigraphic succession (Table 4.2) and petrography have been described by Bailey and Maufe (1960) and Taubeneck (1967). There is some similarity with the Lorne sequence in that rocks with little or no phenocryst plagioclase are overlain by notably plagioclase-phyric rocks, with intervening ignimbrites and hornblende-phyric andesites. Groome (1972), however, believed that the Glencoe rocks were different, and older, on chemical and isotopic grounds. The isotopic argument was disputed by Brown (1975) who stated that the Glencoe data did not form an isochron within error. The chemical grounds noted by Groome were higher Al, Rb and lower Mg, Cr and Ni at Glencoe, and, in acid rocks, lower Fe/Mg. The new data disclose that the Lorne and Glencoe rocks are generally chemically indistinguishable, although there is a tendency to lower La/Y in the mafic rocks at Glencoe.

Table 4.2 : Stratigraphic sequence of O.R.S. rocks of Glencoe (interpretations from Taubeneck, 1967, and Roberts, 1966).

Group	Thickness ft/m	Lithologies	Interpretation
7	300/100	Hb-andesite, rhyolite, ignimbrite	Island volcano in cráter lake
6	50/15	Shales, sandstones	Caldera lake deposits
5	250/80	Ignimbrite	2nd phase of caldera subsidence
4	900/300	Hb-andesite	
3	250/80	Sandstones, breccias	Caldera deposits, talus
2	450-2000 /150-600	Rhyolite, andesite, ignimbrite	1st phase of caldera subsidence
1	1500/500	Basalts, andesites	Lorne Plateau lavas

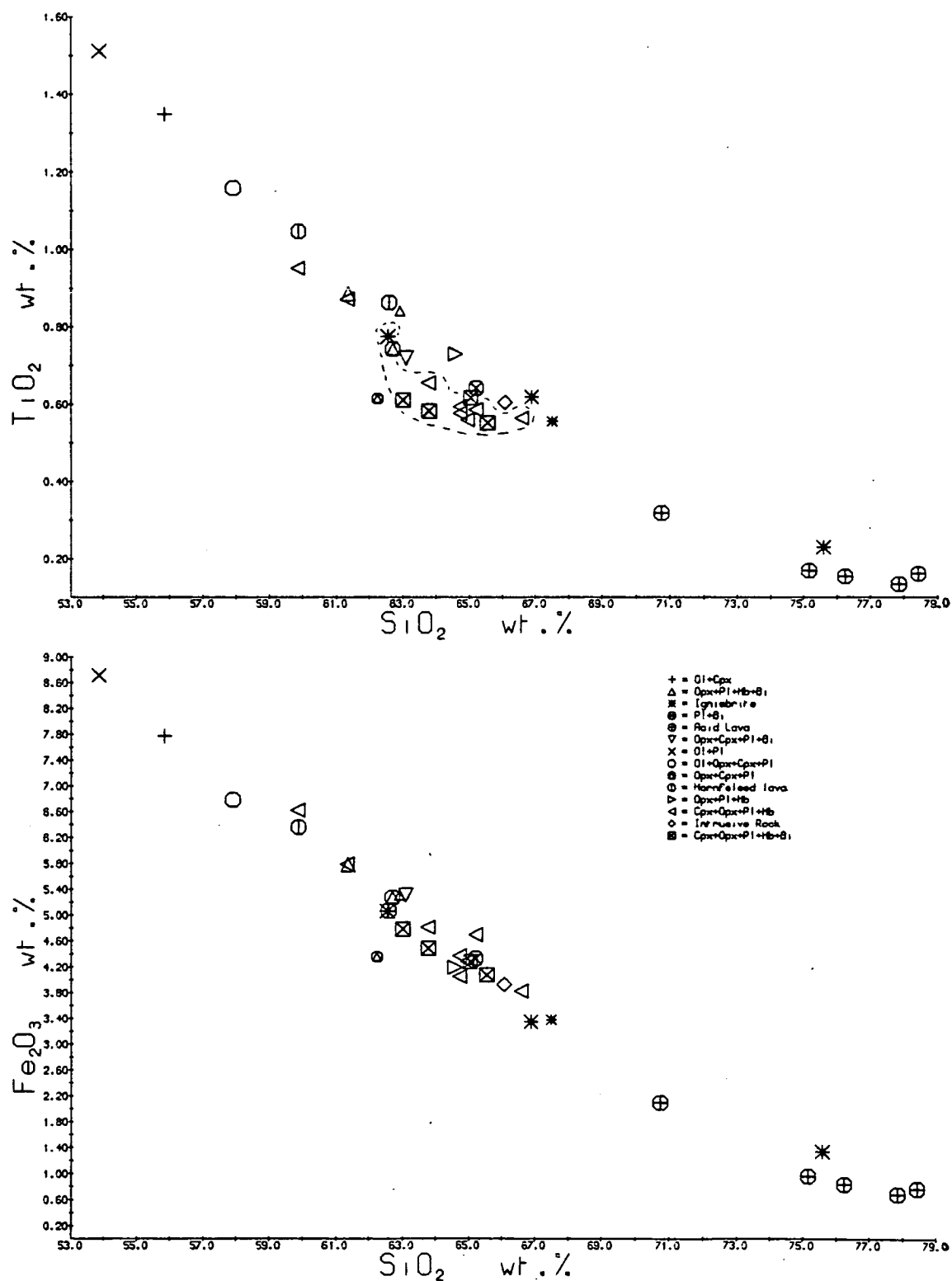
The Glencoe lavas show similar overall variation trends to those of Lorne, and there are very few deviations

from straight-line variation with silica for a number of elements (Fig. 4.6). As with the Lorne lavas, the apparently simple pattern does not hold for the LIL and high field strength elements, nor is a simple pattern produced by considering variation against Cr (Fig. 4.7). The rocks are on the whole more siliceous than those of Lorne, and the andesites of groups 1 and 2 (Table 4.2) resemble the Lorne opx-cpx-phyric group. They are phenocryst-poor, have little or no phenocryst plagioclase, and may show augite-rimmed quartz crystals and resorption pseudomorphs after amphibole. Clinopyroxenes tend to be slightly more iron-rich than those from Lorne opx-cpx-phyric samples. The andesites of groups 1 and 2 however show much greater variation in SiO_2 and Zr/Nb than the opx-cpx-phyric rocks of Lorne (Fig. 4.7).

The hornblende-andesites of group 4 are not directly comparable to any Lorne rocks, and have phenocrysts of andesine-labradorite, slightly resorbed pargasite-hastingsite, pseudomorphed orthopyroxene, magnetite, apatite and sometimes biotite or augite, closely similar to Lorne augites (analysis 16, Table C2). They have higher Zr, LREE, Y and Zr/Nb than the group 1 and 2 rocks (Fig. 4.7), and show no evidence of cumulus enrichment (e.g. higher Al_2O_3). It is noteworthy that the two petrographically similar rocks from Lorne also have much higher Zr than average Lorne rocks, but do not show higher than average LREE. The group 5 ignimbrites are again high Zr, Ce, Y rocks, but the one andesite analysed from group 7, and a later porphyritic microdiorite dyke, may represent a return to the lower Zr of

GLENCOE AND BEN NEVIS

Fig. 4.6 a & b : Bulk rock variation diagrams
 Field marked for Ben Nevis lavas
 Conventions as section 3.3



GLENCOE AND BEN NEVIS

Fig. 4.6 c & d

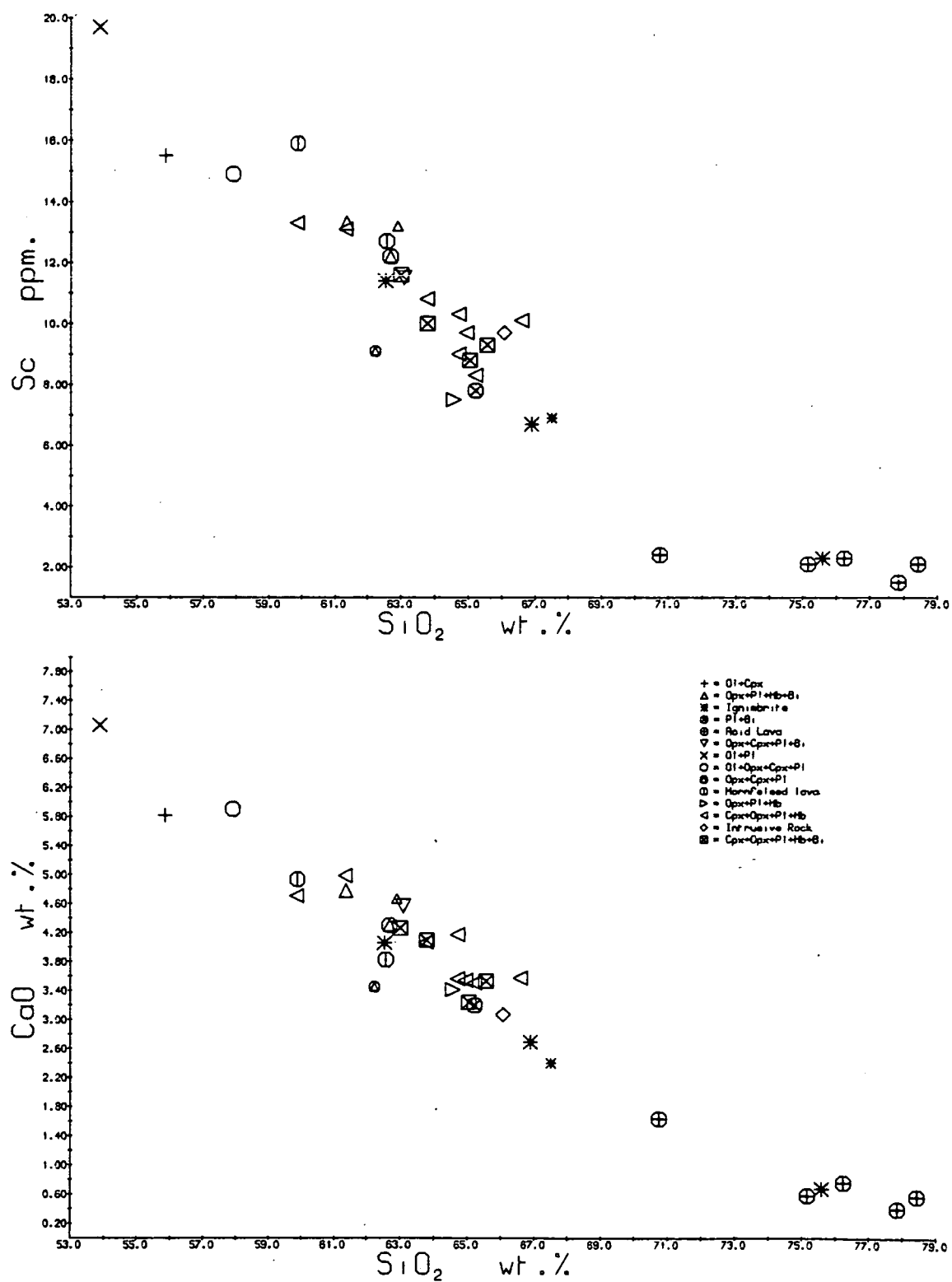
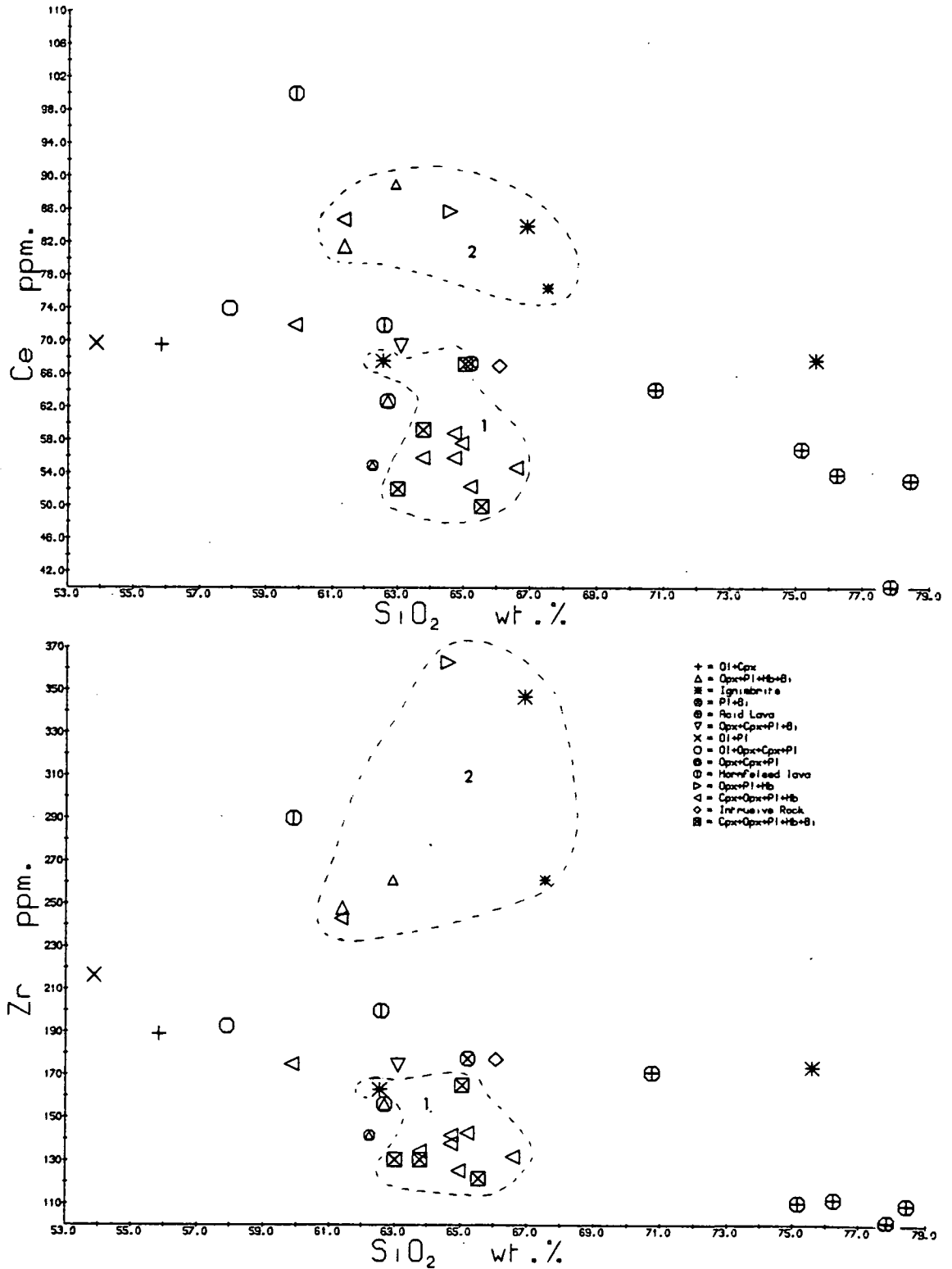


Fig. 4.7 a & b : Bulk rock variation diagrams. Fields are:

1 = Ben Nevis lavas

2 = Samples from groups 4 & 5, Glencoe

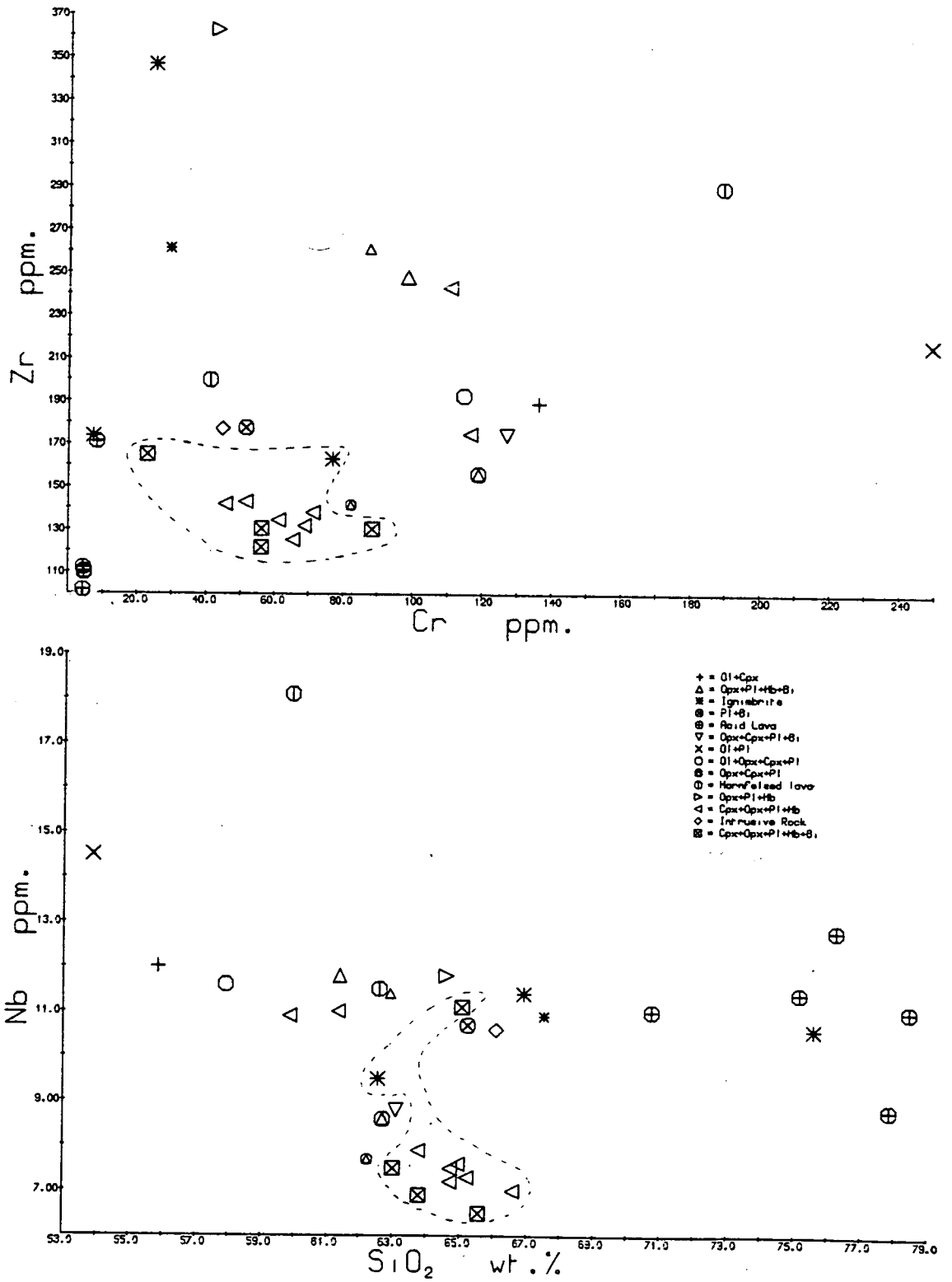
Conventions as section 3.3



GLENCOE AND BEN NEVIS

Fig. 4.7 c & d

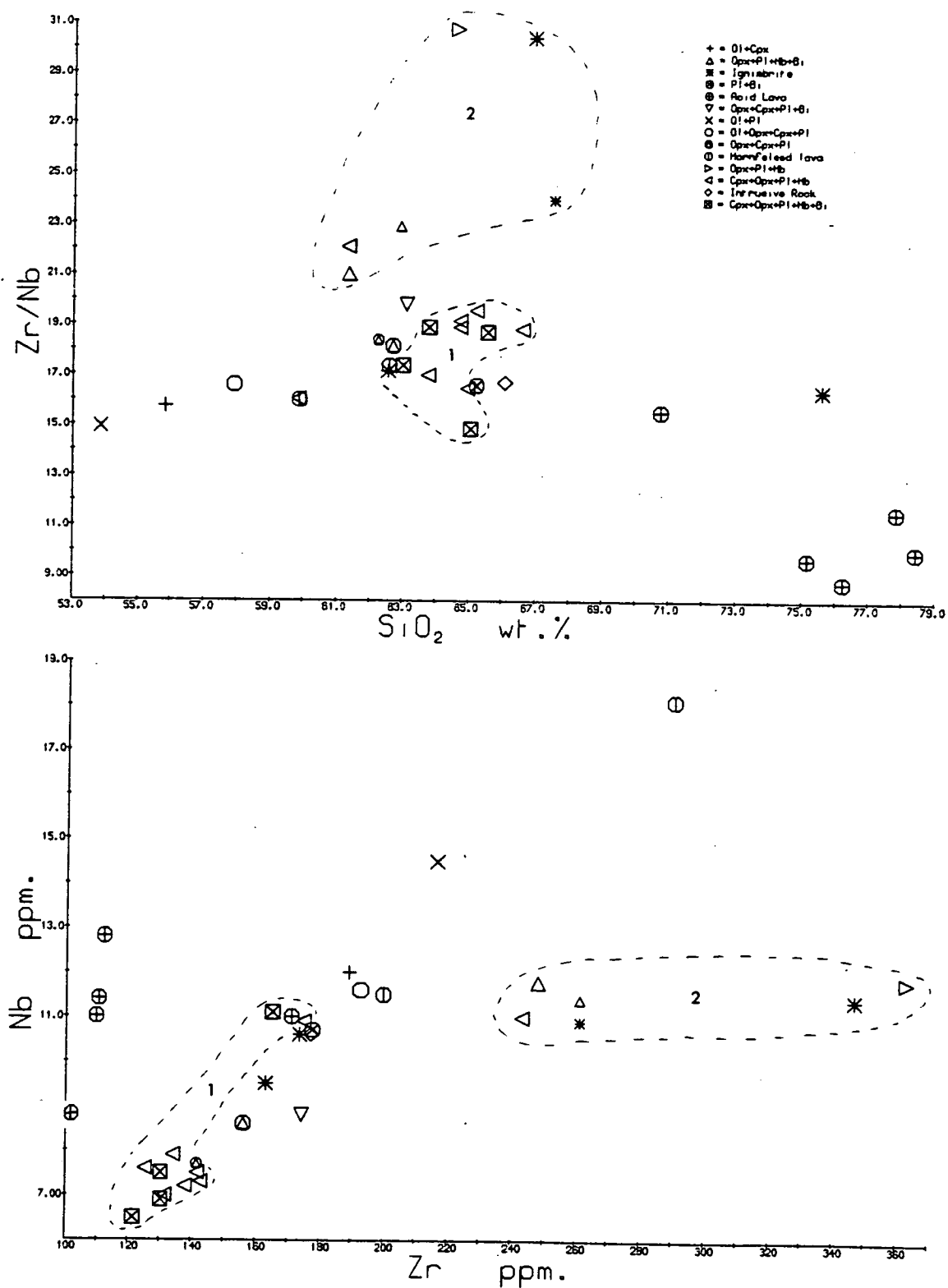
Field is for samples from Ben Nevis



GLENCOE AND BEN NEVIS

Fig. 4.7 e & f

Fields as Fig. 4.7 a & b



groups 1 and 2.

There appears to be a measure of stratigraphic control on chemistry, although it should be noted that a hornfelsed group 1 lava (GC19) shows group 4 levels of Zr, Y and LREE, and therefore the apparent stratigraphic control may be the result of the small number of samples collected. General similarity between the Glencoe and Lorne lavas is very strong, and it is believed that volcanism in the two areas was closely related in time and petrogenesis. Again, multistage fractional crystallisation can not account for all of the chemical variation, and even the groups 1 and 2 andesites, despite having a narrower range in Zr/Nb than the full sample population, show much variation in detail.

4.3 : BEN NEVIS

In common with the rocks of Glencoe, the O.R.S. of Ben Nevis was thought by Bailey and Maufe (1960) to be preserved as a cylindrical block downfaulted during caldera collapse. The rocks rest on Dalradian metasediments, and are metamorphosed by the Ben Nevis Inner Granite. The sequence is about 2000 ft (600 m) thick (Bailey and Maufe, 1960) and consists mainly of hornblende-andesite lavas and agglomerates with thin basal conglomerates and shales.

All samples collected have phenocrysts of slightly resorbed pargasite-hastingsite, andesine-labradorite, titanomagnetite, apatite, actinolite after clinopyroxene and

rare chlorite after orthopyroxene. A few show a small amount of phenocryst biotite in addition. Quartz phenocrysts are absent. Plagioclase is slightly poorer in Or than Glencoe plagioclase, but amphiboles are similar in both areas, with much variation in Ti, Al and K.

The petrochemistry of the Ben Nevis plutonic complex has been described by Haslam (1968), who suggested that the lavas formed part of the same magmatic suite. The samples collected have a small silica range (62.5 to 67%), and fall on the Glencoe variation trends for Al, Mg, Fe, Ca, Na, Mn, Ni, Cr, Zn, Sr, Sc, V and Ba (e.g. Fig. 4.6), although variation within the Ben Nevis range is seldom systematic. Ti and P are slightly lower in the Ben Nevis samples than in Glencoe acid andesites, and all other 'incompatible' elements are substantially lower (Table 4.1, Fig. 4.7). K/Rb is higher at Ben Nevis, but some Glencoe rocks have closely comparable Zr/Nb.

The higher K/Rb and lower Rb of the Ben Nevis samples suggest that they are less evolved than the Glencoe andesites, unless biotite was a fractionating phase. In either case identical Cr, Ni and Sr content of the Glencoe and Ben Nevis acid andesites precludes derivation of one from the other by fractional crystallisation (Chapter 3). Derivation of the Ben Nevis samples from the more basic Glencoe rocks would require fractional crystallisation of a biotite-, amphibole- or ilmenite-bearing assemblage to produce the lower Zr and Nb. However, intermediate points

on Fig. 4.7f include BN1 and BN2, and it is reasonable to infer that these would represent intermediate positions in any suggested fractional crystallisation scheme. However, their major element and compatible trace element chemistry is nearly identical with the rest of the Ben Nevis lavas (Fig. 4.6), suggesting that such a scheme is most unlikely. Further, Ben Nevis amphibole and biotite have Zr below the microprobe detection limit of about 150 ppm, and no zircon has been observed in thin section. The Zr analyses do not confirm the 4000 ppm reported from a Ben Nevis hornblende by Haslam (1968).

Variation of LIL and high field strength element concentrations within the Ben Nevis samples is not related to their Cr content (Fig. 4.7), but the biotite-bearing samples, excepting BN1, are the poorest in Zr and Nb. Again, therefore, the apparently simple genetic relationships suggested by smooth compatible element variation are not confirmed by the behaviour of the 'incompatible' trace elements.

4.4 : SW HIGHLANDS - CONCLUSIONS

Despite much variation in detail, the Old Red Sandstone volcanic rocks of the SW Grampian Highlands are very similar in broad outline.

(a) Petrography and mineral chemistry

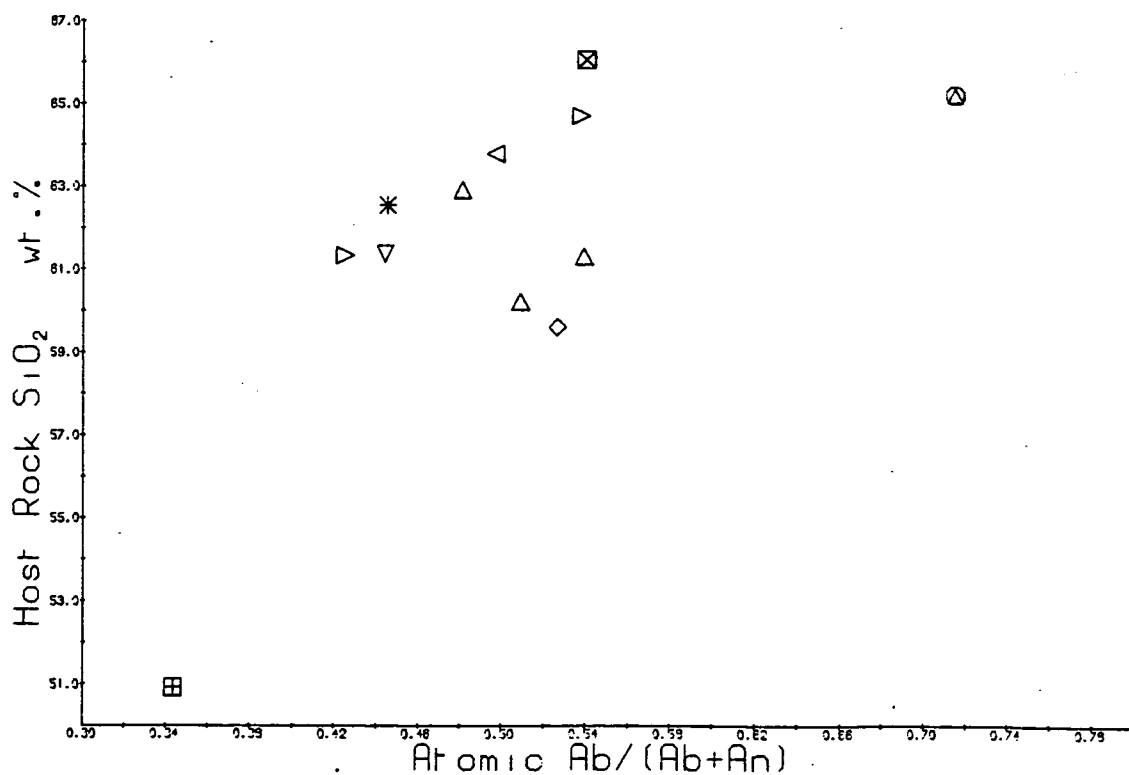
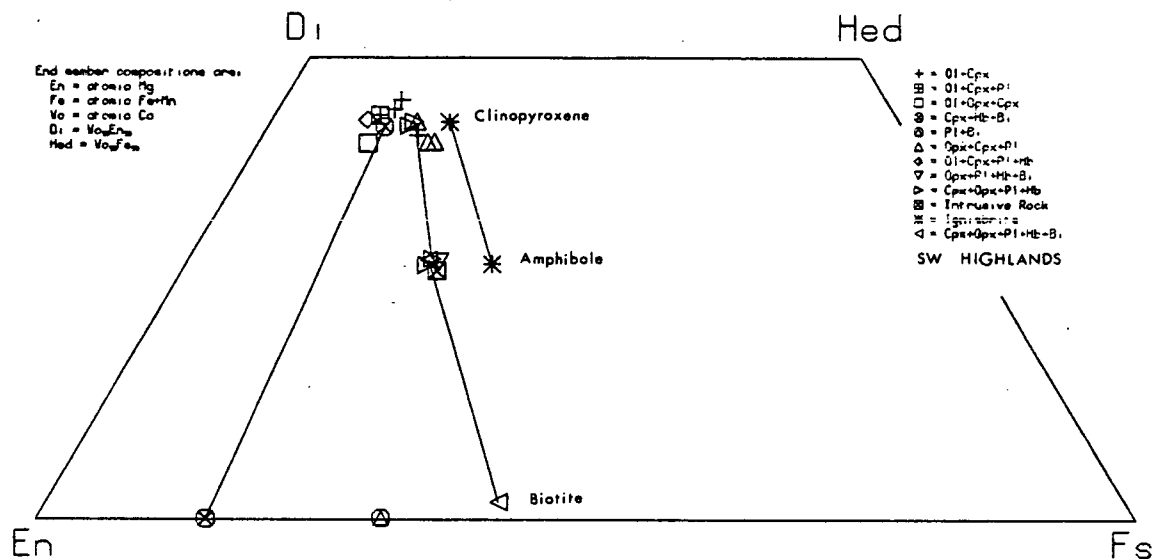
Rocks more basic than 60% silica are characterized by the paucity of phenocryst plagioclase, and all rocks without phenocryst plagioclase have a low total phenocryst content. Quartz, believed to be a high pressure phenocryst phase (section 4.1d), is often present in rocks without phenocryst plagioclase, within the silica range 57.1 to 64.6%. At the basic end of this silica range, quartz is perhaps only a near-liquidus phase above 10 kb (Green and Ringwood, 1968), suggesting a sub-crustal source for the magmas. Phenocryst clinopyroxene is a diopsidic augite, with a little variation in Fe/Mg uncorrelated with host rock silica (Fig. 4.8). Ti and Al contents vary greatly within a single phenocryst, and do not correlate with host rock Ti and Al. All averaged clinopyroxene analyses fall within the tholeiitic (subalkaline) field of Le Bas (1962) for TiO_2 and tetrahedral Al. Na content is low and variable. Rocks rich in phenocryst plagioclase do not show good correlation between silica content and %Ab in the feldspar (Fig. 4.8), although the only plagioclase-phyric basalt (L73) has a calcic labradorite, unlike the normal labradorite-andesine. Or content of plagioclase may be a function of host rock K_2O , but the few alkali feldspars analysed occur in medium-grained aggregates with plagioclase (L68) which may be xenolithic or autolithic. Orthopyroxene phenocrysts are in general restricted to more siliceous rocks.

Fig. 4.8 a & b : Phenocryst chemistry of SW Highland O.R.S. lavas

a = atomic Ca, Mg, Fe for pyroxenes, amphiboles and biotites

b = the composition of plagioclase as a function of host
rock silica

Average core compositions only plotted.



(b) Normative characteristics

Six of the samples collected have small amounts of normative nepheline, if a wt% $\text{Fe}_2\text{O}_3/(\text{FeO}+\text{Fe}_2\text{O}_3)$ ratio of 0.2 is chosen, but of these, five have $\text{LOI} > 3.3\%$, and the introduction of calcite or alkalis during alteration may explain the undersaturation. The sixth, L141, is fresh, and the 0.65% normative nepheline may be original. 21 rocks are olivine-hypersthene normative; while a number of these are altered it is probable that most were originally olivine-normative. There is some evidence that olivine-normative rocks may have higher Sr and LREE. However, most of the rocks are quartz-normative, and they clearly do not resemble alkali basalt differentiation series. Almost all samples with more than 66% silica are peraluminous, a frequent feature of calc-alkaline rocks.

(c) Chemical characteristics

Groome and Hall (1974) noted that the lavas of northern Lorne show a typical calc-alkaline trend of little relative iron enrichment on an FMA diagram, and the data presented here for all the SW Highland volcanics follow a similar trend, and plot in the calc-alkaline field of Miyashiro (1974) on an SiO_2 - Fe/Mg diagram. High alumina concentrations are often thought to be typical of calc-alkaline basic rocks, but the SW Highland rocks plot in the low-Al, tholeiitic, field of Irvine and Baragar (1971). Alkali contents are high, and place the rocks in the

alkaline field of Kuno (1968), but they are transitional between high-K calc-alkaline and shoshonitic (Fig. 9.1) on the classification of Peccerillo and Taylor (1976). Use of Ti, Zr, Y, Nb and Sr as suggested by Pearce and Cann (1973) to determine the tectonic setting of basaltic rocks suggests that the rocks are non-alkaline to transitional ($Y/Nb > 1$), but the very high Sr, high Zr and low Y cause them to plot outside the fields given by Pearce and Cann (1973) on Ti-Zr-Y and Ti-Zr-Sr diagrams. In both cases, however, the SW Highland rocks plot close to the fields for calc-alkaline basalts. The unusual Zr-Nb relationship, in which more siliceous rocks frequently show lower Zr and Nb, was only recognized by Pearce and Norry (1979) in some Andean-type volcanic arc rocks.

The bulk of the evidence favours classification of the SW Highland volcanics as high-K calc-alkaline, and they are best compared with Andean-type volcanic arc rocks, in which comparably high levels of Ba, Sr and LREE have been reported (e.g. western U.S.A., Ewart, in press). The very high Ni and Cr are most unusual features for high-K calc-alkaline suites (e.g. Jakes and White, 1972), although concentrations little lower are again reported from the western U.S.A. (Ewart, in press). The high Ni and Cr imply that little fractional crystallisation of mafic minerals, particularly olivine, can have occurred during ascent. Fractional crystallisation of olivine or other mafic minerals would lead to higher Al_2O_3 and lower Ni and Cr comparable with most calc-alkaline volcanic suites.

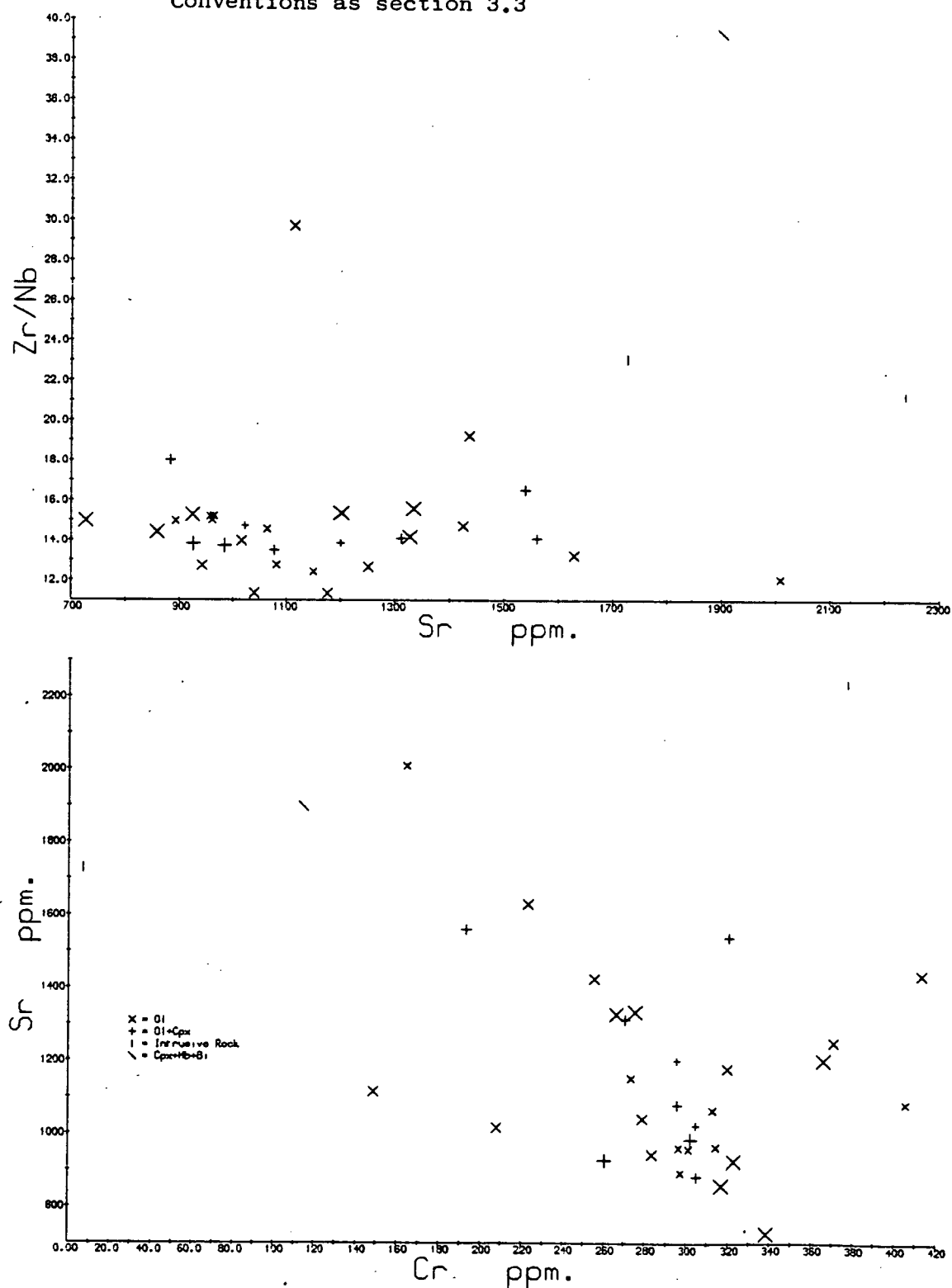
(d) Source of magmas(i) More basic rocks of Lorne

The high Ni and Cr content of the lavas must imply a mantle contribution, and the very high La/Y could imply equilibration with garnet. The elements Ba, Sr, P and LREE are probably incompatible with any mantle mineral assemblage below the plagioclase-spinel lherzolite transition zone, which is likely to have been shallower than the Moho below the O.R.S. mountains. The positive correlation between these elements, with K and Rb (Fig. 4.4) is not the result of fractional crystallisation of the magmas, for there is no correlation between depletion in Cr, Ni and increase in LILE (e.g. Fig. 4.9). The lack of correlation suggests that variable degrees of partial melting of a single source is also an unlikely mechanism, for Ni and Cr would increase and the LILE decrease with increasing degree of partial melting. The relatively high degrees of partial melting implied by the highest Cr and Ni contents would also require extremely high LILE contents in the mantle prior to melting. For example, a rough calculation may be made on the amount of Ce which must be removed from the column of mantle directly underlying the Lorne Plateau to form a 2000 ft (600 m) sequence of lavas with an average 80 ppm Ce. Assuming that melt will not have coalesced from a much wider area than the present lava outcrop, a 30 km high column of mantle with an initial 1.5 ppm Ce must have had its entire Ce content removed. Since no partial melting mechanism is this efficient, a much deeper column of mantle must have been

LORNE PLATEAUFig. 4.9 a & b : Bulk rock variation diagrams

Lorne ol- and ol-cpx-phyrlic samples,
cpx-hb-bi-phyrlic samples and related intrusions

Conventions as section 3.3



involved: it seems implausible that conditions could be favourable to melting over such a large thickness of mantle, and that melt could be created over the substantial depth range required without much modification to the compatible element chemistry. Furthermore, variation in Zr/Nb suggests that a single source model is not viable, and lack of correlation between Zr/Nb and LILE (e.g. Fig. 4.9) suggests that a simple binary contamination model between a mantle derived melt and a substance with different Sr and Zr/Nb is also untenable.

The chemistry therefore implies three separate controlling processes: a mantle source region controlling Cr and Ni, a process to provide LILE (e.g. a LILE-rich contaminant) and a process to provide two-fold variation in Zr and Nb, with some variation in Zr/Nb ratio. Derivation of the high levels of Sr by crustal contamination is thought to be unlikely because of the low initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7044 determined for Lorne (Brown, 1975). The conclusion that the Sr is of mantle origin, however, prevents the use of the initial ratio as a control on the degree of crustal contamination. A large crustal contribution with moderate Sr and high $^{87}\text{Sr}/^{86}\text{Sr}$ would be swamped by the high levels of mantle Sr. Brown (1975) reports somewhat higher initial $^{87}\text{Sr}/^{86}\text{Sr}$ at Glencoe (0.7049), and suggests that this may be the result of crustal contamination.

Since Sr correlates with K, Rb, Ba, La/Y and P, it is probable that the high level of all these parameters is of

mantle origin. The lack of correlation with Zr/Nb or with Zr could, however, be produced by contamination by crustal Zr and Nb.

(ii) More siliceous lavas

With minor exceptions, the more siliceous lavas of Glencoe, Ben Nevis and the opx-cpx- and opx-cpx-pl-phyric rocks of Lorne lie on smooth variation trends with silica for the major elements and the compatible trace elements, which extend from the most basic to the most acid volcanic products. The variation of LIL and high field strength elements precludes the conclusion that all are related by a single fractional crystallisation model, and suggests that they are better considered as a number of small groups. Variation within these groups might in some cases be ascribed to fractional crystallisation of biotite- or amphibole-bearing assemblages but this is not borne out by detailed examination of whole rock and mineral chemical data. Furthermore, significant crystal settling in such siliceous and hence viscous magmas is improbable, particularly in the case of such phases as biotite. Volcanic rocks possibly parental to the siliceous suites have not been identified, despite the abundance of basic rocks at Lorne. There is no control over the degree of crustal contamination that these rocks may have suffered, although the Ni, Cr and Sr contents appear to be mantle derived. Since no parental magmas can be identified, it would appear that andesites with silica well in excess of

60% may be direct melts of a sub-crustal source.

The chemistry of the SW Highland volcanic rocks is thus extremely complex in detail, although they may be considered as high-K calc-alkaline to shoshonitic. The range in magma compositions implies that the existence of separate magma generations for the intrusive rocks, as suggested by Groome and Hall (1974) is more than likely, and the rocks should not be viewed as the differentiation products of a single 'Devonian parent magma' (Bailey, 1958). The bulk of the volcanic rocks appear to have been produced in the mantle by processes including partial melting, mixing and contamination, but do not appear to have been significantly modified by fractional crystallisation.

CHAPTER 5 : NORTH MIDLAND VALLEY

Lower Old Red Sandstone rocks outcrop in a number of inliers near the southern margin of the Midland Valley of Scotland, and continuously from Stonehaven to Arran along the northern margin. In the north the rocks are dominantly conglomerates and sandstones but considerable thicknesses of volcanic rocks are interbedded with the sediments. The O.R.S. sequences overlap the Highland Boundary Fault Zone onto the Dalradian metasediments of the Highlands and onto the Cambro-Ordovician Highland Border Series. The Lower O.R.S. outcrop is disposed about a broad NE-SW trending paired anticline-syncline, and is bounded to the south by the Upper Old Red Sandstone unconformity or by the Ochil Fault. The crest of the Ochil-Sidlaw Anticline is faulted into a graben in the Carse of Gowrie, which is occupied by Upper O.R.S. sediments.

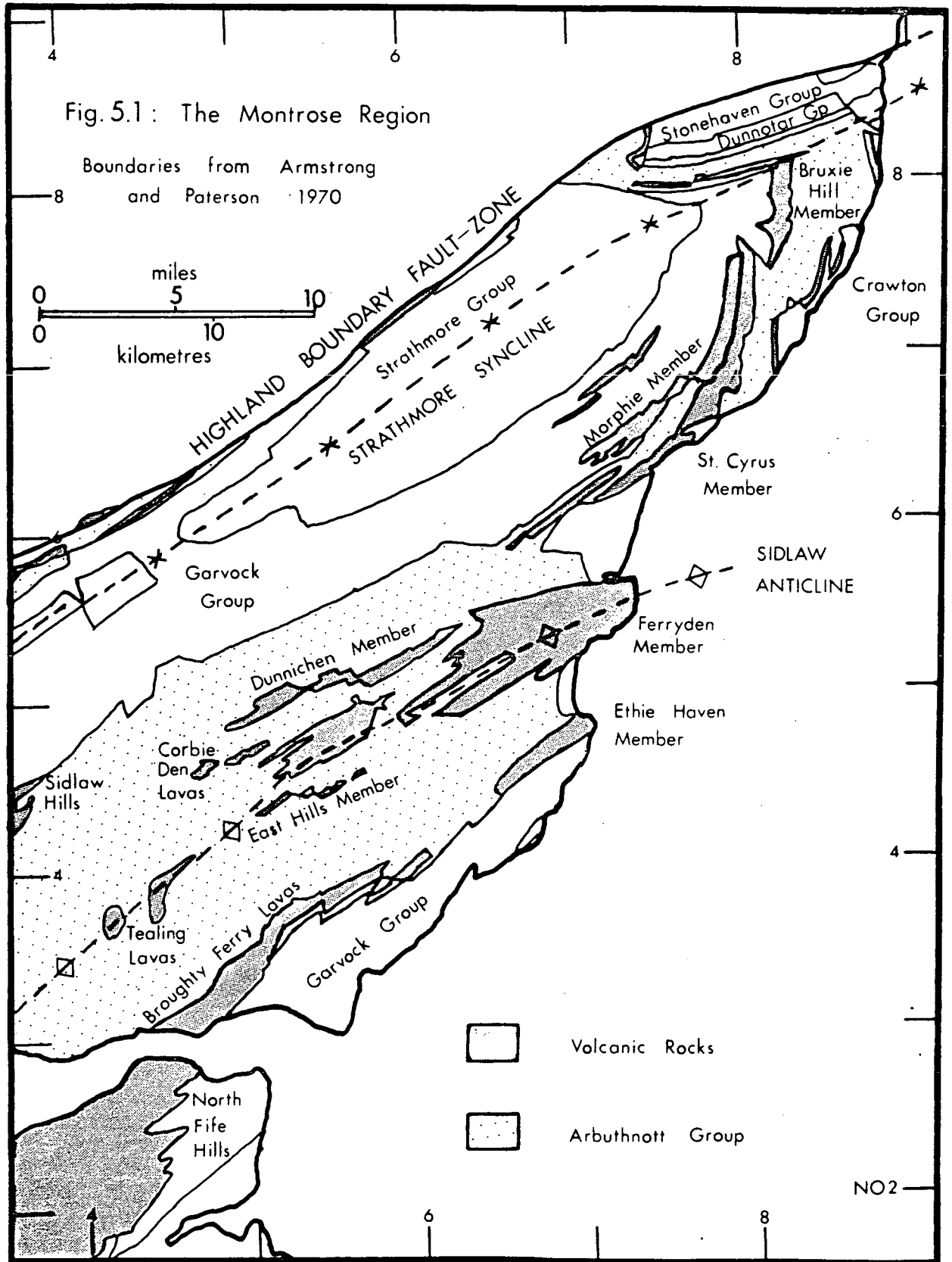
Armstrong and Paterson (1970) described six major lithostratigraphic groupings in the Lower Old Red Sandstone of the northern Midland Valley, of which all but the youngest contain volcanic rocks. The stratigraphy is summarized in Table 5.1.

The rocks of the Ochil Volcanic Formation have been somewhat arbitrarily divided for collecting purposes into three areas: the Sidlaw Hills and Moncreiffe Hill, the western Ochil Hills, and the hills of northern Fife.

Table 5.1 : Lower Old Red Sandstone stratigraphy of the northern Midland Valley, with location of volcanic horizons (after Armstrong and Paterson, 1970). Figures are thicknesses in ft/m.

Group	Stonehaven -St. Cyrus	S of Montrose	Dundee	Perth	Highland Border
Strathmore 6500/2000	no volcanic rocks				
Garvock 5000/1525	Garvock lavas 800/250				
	Morphie or Bruxie Hill Member 800/250				
Arbuthnott 7000/2100	St. Cyrus Member 2000/650	Ethie Haven Member 1000/320	Broughty Ferry lavas 1200/400	Ochil Volcanic Formation 8000/2400	Volcanic rocks of Glenisla and Blairgowrie. Conglomerate with volcanic clasts
	Dunnichen Member 500/150	East Hills Member 500/150	?Tealing lavas 300/100		
	Ferryden Member 1300/400				
Crawton 2200/670	Crawton Volcanic Formation Conglomerates and sandstones with acid volcanic clasts and 2 thin lavas			100/30	Lintrathen Porphyry 500/150
Dunnottar 5450/1660	Tremuda Bay Volcanic Formation Conglomerates and sandstones with volcanic clasts and 2 thin lavas				
Stonehaven 5100/1550					

The Sidlaw Hills are separated from the rest of the outcrop by a wide tract of alluvium, but the Ochil and North Fife Hills have continuous outcrop. The division here was placed at Glen Farg, for Geikie (1900, pp.25,32) suggested that the paucity of pyroclastic rocks in Glen Farg may be due to its distal position relative to centres of activity in the Ochil and North Fife Hills. In these three areas it is not yet possible to use stratigraphic subdivisions of the volcanic sequence of more than very local significance, but in the remainder of the Midland Valley, the Montrose region, a detailed stratigraphic-geographic subdivision may be employed (Fig. 5.1).



5.1 : MONTROSE REGION

The stratigraphy and petrography of some of the Old Red Sandstone volcanic rocks of the Montrose region have been described by Campbell (1913) for Kincardineshire, by Jowett (1913) for the coast between Montrose and Red Head (Ferryden and Ethie Haven Members) and by Robson (1948) for the inland area south of Montrose. Robson (1948) noted that the Montrose volcanic sequence lacked acid members, in contrast to the Old Red Sandstone volcanic sequence of the Ochil Hills.

(a) Rocks older than the Arbuthnott Group

Very coarse conglomerates dominate the pre-Arbuthnott Group strata, and most of the volcanic rocks occur as clasts in these, although there are a few lava flows. The latter are predominantly basic in composition, and contrast with the more siliceous nature of the volcanic clasts noted by Armstrong and Paterson (1970), which range from hypersthene-, hornblende- and biotite-andesites to rhyolites. The bulk of the clasts in the conglomerates are, however, Highland-derived (Campbell, 1913), and Waterston (1965) believed that the contrast was the result of interdigitation of acid Highland material with more basic flows originating in the Ochil-Sidlaw region.

Samples SC1-9 were collected from clasts in these conglomerates. They are mineralogically very varied,

although all have phenocrysts of a hydrous mineral. One sample has augite-rimmed quartz ?phenocrysts (SC4), and the rocks are similar to some of the Western Highland acid andesites. Silica varies from 60 to 77%, and the rocks are mostly corundum-normative, although this may in part be an effect of alteration. Trace element concentrations are very variable, and the rocks are most unlikely to be simply genetically related. This is indicated by the occurrence of acid rocks ($>70\% \text{SiO}_2$) with both low and high concentrations of elements such as Zr, Nb, Y, and LREE, and by very variable Zr/Nb at constant Cr (c.f. SC6 and SC7). Despite this variability, it is notable that these samples have considerably less Sr, and, in general, less Ba, than otherwise comparable acid andesites from Lorne and Glencoe. Further collection of volcanic clasts may provide useful petrogenetic information, but at present they are important in that they demonstrate that very high Sr concentrations in Highland volcanic rocks are restricted to the west.

In situ volcanic rocks older than the Arbuthnott group in Kincardineshire comprise a few thin andesite flows, of which one in the Dunnottar Group is a bi-opx-cpx-pl-phyric andesite (SC10), chemically similar to some of the clasts; and the Tremuda Bay and Crawton Volcanic Formations. Four samples (SC11-14) have been collected from these latter formations. Each is petrographically distinctive, especially the type Crawton Basalt (SC13), with large tabular plagioclase phenocrysts in addition to the olivine $\pm$ augite of the other three. The samples are basic (51-53%

SiO₂), olivine-hypersthene normative and moderately high-alumina (16%). The one evolved sample (SC13) shows substantial iron enrichment relative to Mg, and plots in the tholeiitic field of Miyashiro (1974). Although the rocks have Y/Nb > 1, suggesting sub-alkaline affinities (Pearce and Cann, 1973), they have concentrations of Nb, Ti, P and LREE comparable with those of many alkali basalts. All four samples have Zr/Nb almost identical at about 13, but SC11, despite relatively low Cr and Ni, has lower Zr and Zr/Y and is thought to be less closely related than the other three.

The three more closely related samples show variation trends which may probably be accounted for by fractional crystallisation of the phenocryst phases olivine, plagioclase and clinopyroxene, although some minor opaque oxide may be involved. Zr, Th, Nb, LREE and P all show about 80% increase from SC14 to SC13, suggesting that SC13 represents about 40% crystallisation. Ni, Mg, Cr and Mn decrease and K, Rb, V, Ba, and Y all increase, while most other elements show a stepped change consistent with removal of olivine from SC14, followed by clinopyroxene and plagioclase. The small number of samples does not permit verification of this hypothesis by least squares extract calculations. The minor difference in Al contents between the three samples suggests that the chemistry of SC13 has not been significantly affected by plagioclase accumulation.

The one remaining in situ volcanic rock in pre-Arbuthnott Group strata is the Lintrathen Porphyry,

which was shown to be an ignimbrite by Paterson and Harris (1969). The sample collected is rich in crystal clasts of quartz, plagioclase, biotite, hornblende, apatite, muscovite and phlogopite, and is unusual for the presence of three micas, although it is probable that at least one of these is an accidental xenocryst. It is strongly LREE enriched ($La/Y = 2.5$, approximately the same as the Crawton lavas) and has high Th, Nb, K, Rb but low Zr ($Zr/Nb=6$).

(b) Dunnichen/East Hills Members

Lavas belonging to these members of the Montrose Volcanic Formation are typically nearly aphyric, and show a few pseudomorphs after olivine and rarer labradorite (analysis 16, MT4) in a feldspathic groundmass, with opaque oxides and subophitic or intersertal augite. The one exception, MT5, has apatite phenocrysts with a few haematitic pseudomorphs possibly after olivine, and is chemically very similar to a number of apatite-phyric rocks from the Ferryden Member. This group of rocks, the "trachyandesites", will be treated together in section 5.1(e).

The rocks collected are silica-poor (52.6-55.3%), alumina-rich (>17.8%), poor in Ni and Cr (<27, <10 ppm respectively) and are quartz- or very slightly olivine-normative except where modified by alteration. They have fairly high Fe/Mg, but all fall within the calc-alkaline field of Miyashiro (1974). In common with the

SW Highland and pre-Arbuthnott Group volcanics, they show concentrations of LIL elements comparable to those in alkali basalts, although Sr and Ba are substantially lower than at Lorne. There are no significant chemical differences between the Dunnichen samples and MT1 and 3, and Zr/Nb is identical within precision, between 18 and 20. MT4 has substantially higher concentrations of LIL elements than the rest of the group, and Rb and P show greater enrichment than Y, Zr, Nb, K and LREE. The enrichment in Rb could be produced by about 30% crystallisation of a liquid with composition MT1, assuming that Rb was incompatible in the crystallising phases. Ni, Sc, Ti and particularly V show substantially lower concentrations in MT4, suggesting that fractional crystallisation of an assemblage including either amphibole or an opaque oxide could explain the observed variation. Again, the small number of samples and the altered nature of two of them does not permit the quantification of such a hypothesis by least squares extract calculations.

(c) Ethie Haven Member

Samples collected from Ethie Haven are rich in olivine and augite phenocrysts. All except MT42 have infrequent bytownite-labradorite microphenocrysts. Olivines are magnesian (Fo82-86, anal. 1, MT45) and Ni-rich; calculation using the data of Roeder and Emslie (1970) suggests that this is not far from the equilibrium olivine, and it is probable that the chemistry of MT45 has not been

seriously modified by olivine accumulation. Clinopyroxene phenocrysts are low-Na diopsidic augites (e.g. anal. 18 and 21; MT45, 42), but include some plotting within the alkaline field of Le Bas (1962). However, these latter include both core and rim compositions, and both TiO_2 and tetrahedral Al vary substantially between phenocrysts in the same rock, although the average augite analyses from the two rocks are nearly identical. It is believed that this is the result of localized melt heterogeneities arising during rapid crystallisation. The samples are quartz- or slightly olivine-normative, have SiO_2 from 53.8 to 55% and high MgO (6.5-9%), Ni (>150 ppm) and Cr (300-540 ppm), with moderate alumina (about 16%). These are much higher MgO, Ni and Cr concentrations than in the Dunnichen/East Hills samples, and the Ethie Haven rocks also have higher concentrations of Ca and Sc, and slightly lower Fe, Ti, Sr and many other LIL and high field strength elements. This suggests that the two groups could be related by fractional crystallisation processes, with olivine and clinopyroxene as the major crystallising phases. This possibility will be further discussed in section 4.1(i).

Zr/Nb varies within the limits of precision, and does not rule out an origin of the chemical variation within the Ethie Haven samples by fractional crystallisation, or by olivine accumulation, for the most magnesian sample, MT42, has the greatest quantity of modal olivine. The latter possibility is difficult to test. If MT42 is assumed to represent a liquid composition, then the increase in Zr

shown by the other samples implies roughly 9% crystallisation of this. A somewhat higher degree of crystallisation is implied by LREE data (about 16%) and somewhat lower by data for Y (7%). K and Rb concentrations appear to have been changed by alteration, but Ba suggests about 20% crystallisation. No element shows systematic variation in the three more evolved samples, and variation in many of the major elements is unrelated to the more magnesian nature of MT42. While it may not be conclusively demonstrated, it is thought unlikely that fractional crystallisation was the only process operating to produce chemical variation in these rocks.

(d) St. Cyrus Member

The volcanic rocks of the St. Cyrus Member were thought by Armstrong and Paterson (1970) to be at the same stratigraphic level as the Ethie Haven Member. Two of the samples collected have olivine and occasional feldspar phenocrysts, and are more magnesian and less siliceous than the third, which is phenocryst rich and has additional phenocryst ortho- and clinopyroxene. The overall chemistry of the rocks is similar to that of the Ethie Haven samples, but St. Cyrus samples have much lower Zr/Nb (Fig. 5.2), and since MgO, Cr and Ni concentrations are little different, the St. Cyrus lavas are most unlikely to be related to those of Ethie Haven by fractional crystallisation processes. Variation within the St. Cyrus Member is not simple, for although MT23 has the highest Zr, Y, Ti, Nb, P, and Al and

lowest Ni and Cr, it has lower LREE than the other samples, and is high in MgO.

(e) Ferryden Member

The members of the Montrose Volcanic Formation previously discussed display a high degree of chemical individuality, well expressed by a constant distinctive Zr/Nb for each member (Fig. 5.2). The Ferryden Member displays a greater range of lithologies and chemistries, and has a range of Zr/Nb from 14 to 22. Alumina also shows a wide range, and it is possible to divide the rocks of this member using Al content (Table 5.2).

Table 5.2 : Petrochemical characteristics of alumina-based subdivisions of the Ferryden Member.

Al ₂ O ₃	Samples	Silica range	Cr	Phenocrysts	Zr/Nb
18.4-.8	24,25,35	53.7-54.5	7-8	rare ol, pl	17.5-18.2
17.9	9,27,29	60.3-62.2	6-12	rare ap,ol,pl	22
				("trachyandesites")	
17.8	26	52.2	113	ol,pl	20
16.9-17.3	38-40	54.6-55.8	114-127	ol,pl	14.5-15.5
16.5	41	59.9	232	opx,pl	16.2
15.8-16.1	36,37	57.6-.7	298-321	ol,opx,pl	14-14.8

Rocks of the high-alumina group have many similarities with those of the Dunnichen/East Hills Members, but have significantly lower Zr/Nb, lower Fe, Ti, P, Sc, V, Zr, Y and LREE and higher Ni, Al and Sr. These two groups are unlikely to be derived from each other by fractional crystallisation processes because of their identical concentrations of K, Rb and Ba. Derivation by separate

fractional crystallisation events from a similar parent is, however, possible (section 5.11).

Most of these Al-based divisions have distinctive Zr/Nb ratios, and therefore derivation from each other by processes of fractional crystallisation is unlikely. For MT36-40, Zr/Nb varies within the range of analytical error, and does not therefore preclude derivation of MT36 and 37 from the other three or vice versa by fractional crystallisation. If this were the case, the positive correlation between Cr, Ni and silica could only be generated by crystallisation of a very siliceous assemblage (>58% silica; MT36,37 parental) or of an assemblage with perhaps >80% plagioclase (MT36,37 derivative). No plausible combination of phases can produce such a siliceous crystallising assemblage, and furthermore, both K and Zr also correlate positively with silica, Cr and Ni. If Cr is incompatible in the crystallising assemblage (i.e. >80% plagioclase), then over 60% crystallisation is implied by the increase in Cr content. No other element, normally incompatible, shows such an increase. It is thought most unlikely that any of the Al-based subdivisions of the Ferryden Member could be derived from another by fractional crystallisation processes.

The high-alumina, apatite-phyrlic, relatively siliceous samples described as "trachyandesite" are worthy of special note. The name "trachyandesite" was given because of the resemblance of these rocks to ones so named

by Francis et al. (1970) in the Ochil Hills. It is, however, recognized that they are no more alkaline than many other rocks in the Northern Midland Valley, and certainly do not display normative or pyroxene characteristics of alkaline rocks. Three samples of the Ferryden Member and one of the East Hills Member have been classified as "trachyandesite". They are nearly aphyric, and therefore their high alumina content may not be ascribed to plagioclase accumulation. Zr, Nb and Th are very high, with concentrations in excess of 600, 27 and 21 ppm respectively. It is notable that such high concentrations of Th are comparable to those found in peralkaline rhyolites (Macdonald and Bailey, 1973) although in these Zr and particularly Nb are substantially higher. Sc and V are much lower than in the more mafic rocks of the region, and Ni is further reduced from the low levels of the high-alumina basic andesites (Dunnichen Member etc.). Sr is also considerably lower, suggesting substantial fractional crystallisation of plagioclase. Enrichment factors for the LIL and high field strength elements relative to the high alumina rocks are given in Table 5.3, and are consistent with the derivation of the "trachyandesites" by fractional crystallisation of a plagioclase-rich assemblage with accessory apatite.

Table 5.3 : Enrichment factors for LIL and high field strength elements in the "trachyandesites" relative to high-alumina basic andesites, Montrose.

K	Rb	Ba	Th	Zr	Nb	La	Ce	Nd	Y	P	Sr
2.2	3.2	1.5	3.3	2.6	2.2	1.9	1.9	1.6	1.2	1.0	0.6

The lack of rocks intermediate on these possible fractional crystallisation trends prevents deduction of the particular mafic suite of the Montrose Volcanic Formation from which these "trachyandesites" may be derived and this precludes the use of least squares extract calculations to quantify a model. It is not impossible that the 70% crystallisation of one of the mafic liquids calculated from the Rb enrichment could result in increase of the Zr/Nb ratio by a small amount (Pearce and Norry, 1979). A number of elements show systematic variation within the "trachyandesites" with increasing silica and decreasing MgO. The Ferryden samples show increases in La, Rb, Zr and K, constant Ce and decreasing P with increasing silica, but comparable changes in other 'incompatible' elements are not significant relative to the analytical precision. The decrease in P implies that apatite is a fractionating phase. The sample from East Hills is relatively rich in V and particularly Fe (Fig. 5.2), and may be derived from a parent with a somewhat different composition, but by the operation of similar fractional crystallisation processes.

(f) Morphie/Bruxie Hill Member

The seven samples collected from this member are all

phenocryst-rich and five have phenocryst orthopyroxene, in addition to small quantities of olivine. Orthopyroxene may mantle olivine or vice versa. Pyroxenes are magnesian and Cr-rich, orthopyroxene being bronzite and clinopyroxene the diopsidic augite low in Na, Ti and Al that is typical of the province (e.g. anal. 19 and 20, MT10). Phenocryst plagioclase is variable, but generally labradorite. All seven samples are quartz-normative, fairly siliceous (55-57.7%), and have moderately low alumina (15.9-16.5%). Ni and Cr are high (110-208 and 193-343 ppm respectively). No systematic relationships exist between element concentrations and silica or MgO content, and the most magnesian, least siliceous sample has the highest concentrations of Ni, Cr, P, Ti, K, Ba, Sr, Zr, Nb and LREE. Zr/Nb varies from 14.5 to 17.5, and does not correlate with Zr or Cr. It is highly unlikely that such a suite of rocks could be related by fractional crystallisation nor is there any evidence suggesting a genetic relationship with any other member of the Montrose Volcanic Formation.

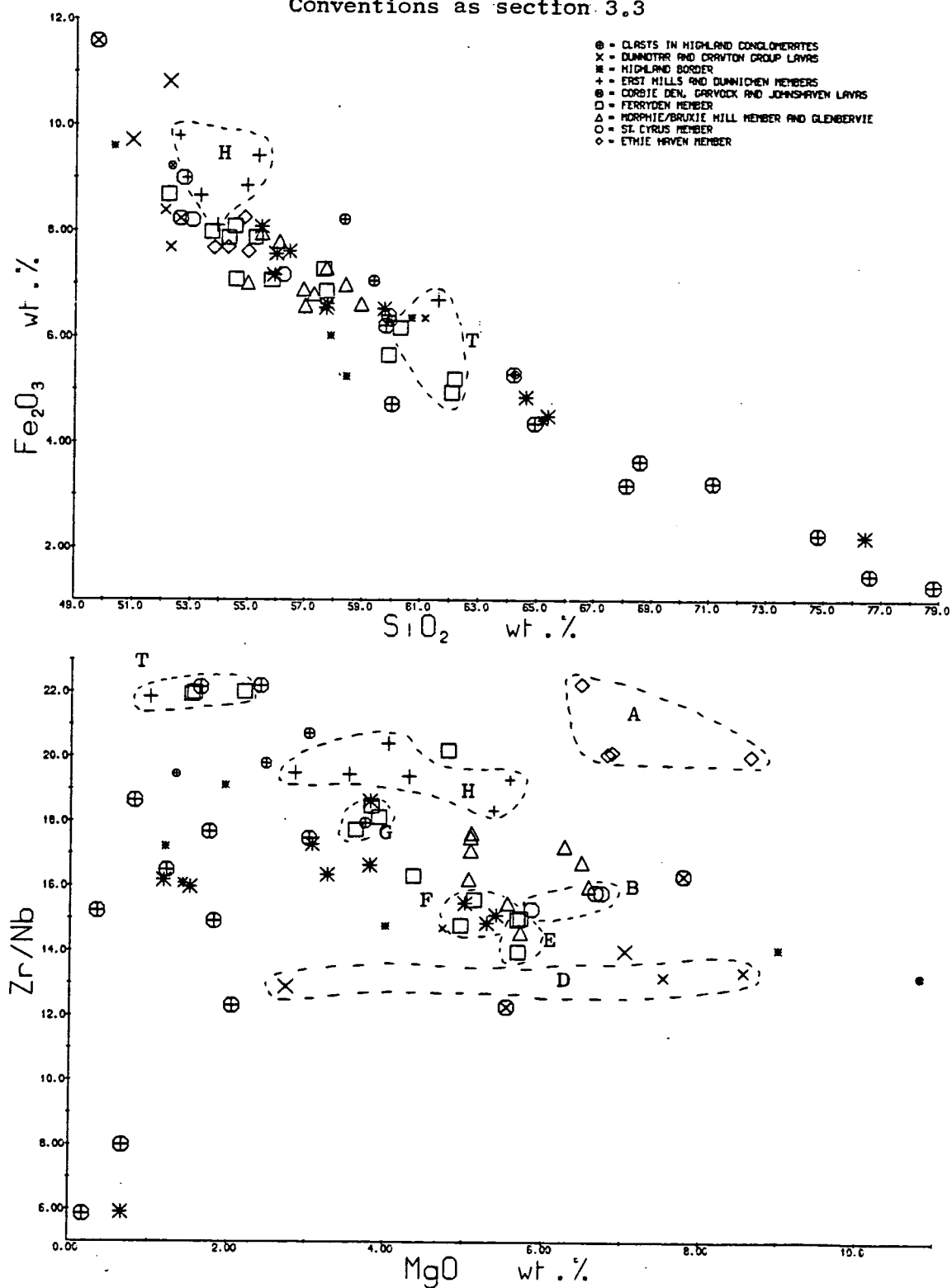
The samples collected from Glenbervie, on the NW limb of the Strathmore Syncline, are opx-cpx-pl-phyric andesites similar in many ways to the Bruxie Hill lavas, but detailed examination of Table B17 discloses some differences e.g. lower P. The low K of the Glenbervie samples is attributed to hydrothermal alteration of the groundmass glass (Chapter 2). These lavas were thought to be part of the Bruxie Hill Member by Campbell (1913), but Armstrong and Paterson (1970) believe that they are the approximate equivalents of the

MONTROSE REGION

Fig. 5.2 a & b : Bulk rock variation diagrams

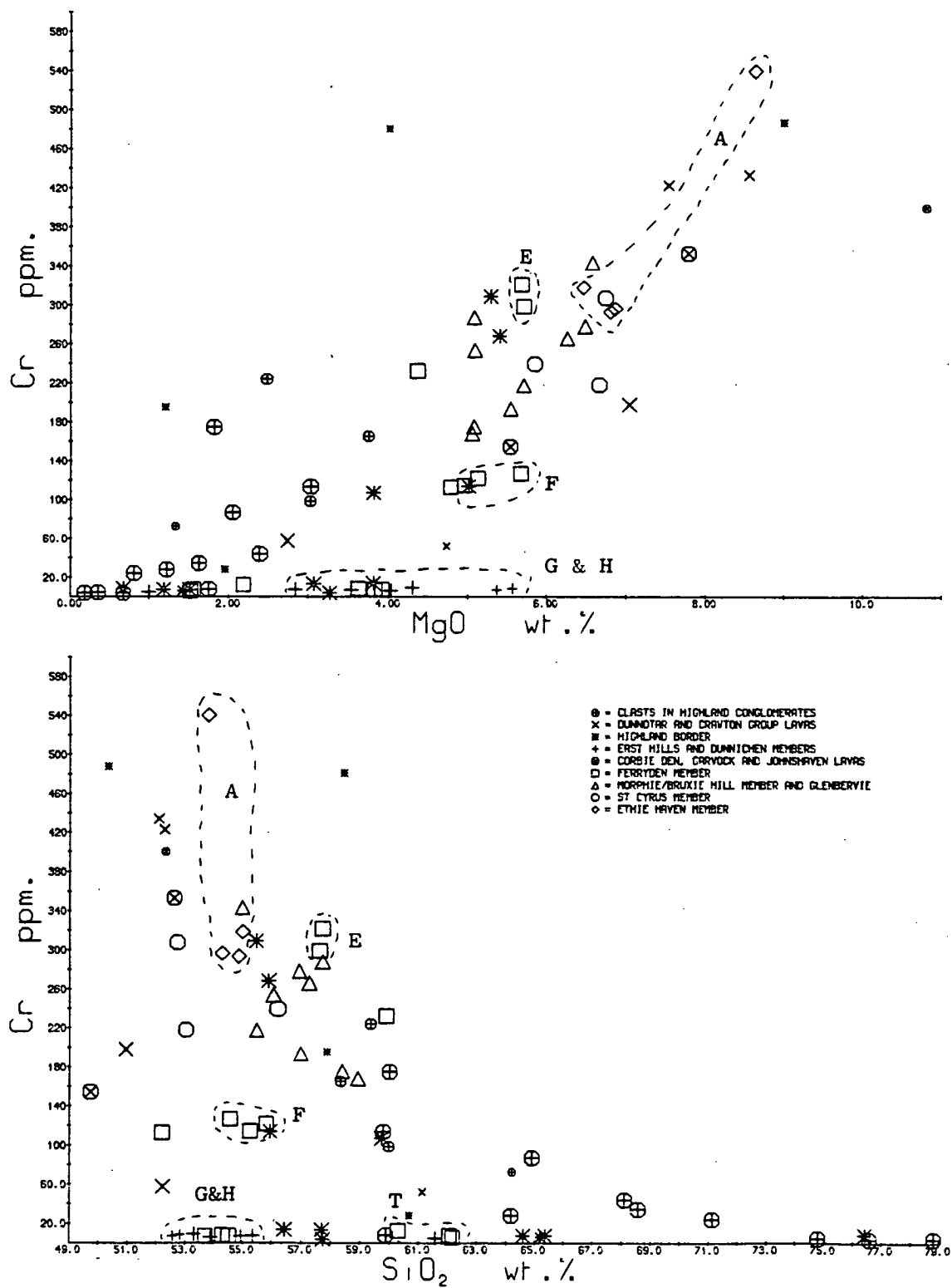
Lettered fields refer to the major rock groups of Table 5.4,
field T to the "trachyandesites" (Table 5.2).

Conventions as section 3.3



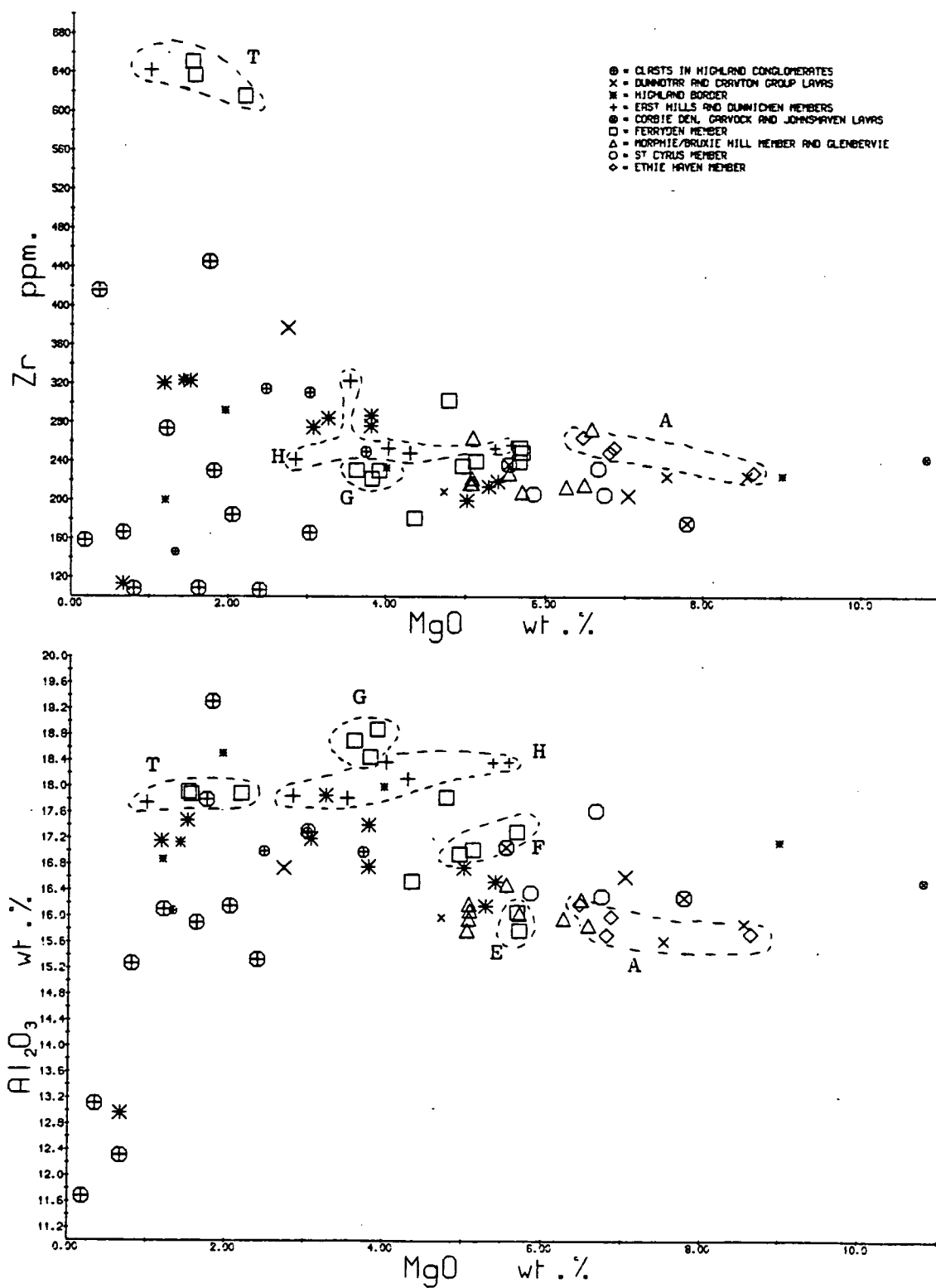
MONTROSE REGION

Fig. 5.2 c & d



MONTROSE REGION

Fig. 5.2 e & f



St. Cyrus Member.

(g) Highland Border Lavas

Volcanic rocks assigned to the Arbuthnott Group by Armstrong and Paterson (1970) outcrop at a number of places on the steeply dipping NW limb of the Strathmore Syncline, in close proximity to the Highland Boundary Fault. The main area of outcrop is between Kirriemuir and Dunkeld, with smaller areas near Crieff, Callander and Aberfoyle. All samples collected are quartz-normative, except for one highly altered sample from near Callander. They are very variable, and range from olivine-phyric basic rocks to hornblende-biotite dacites. The rocks from the Kirriemuir-Blairgowrie area frequently contain augite-rimmed quartz ?phenocrysts, and MT53 shows aggregates of pyroxenes and opaque minerals, possibly resorption pseudomorphs after amphibole. None of the rocks with less than 59% silica show much phenocryst plagioclase. Only one of the more basic samples has high alumina (MT33), and this is nearly aphyric, and has very low Ni and Cr. Wide variation in Zr/Nb exists, and it is unlikely that any of the rocks can be related by fractional crystallisation processes, although the number of samples available is too small to verify this.

Conglomerates containing volcanic and Highland metamorphic clasts are common in the Arbuthnott Group of the NW limb of the Strathmore Syncline. Four volcanic clasts have been collected from these conglomerates, all

plagioclase-phyric andesites. They are less variable than those from the Kincardineshire conglomerates, and have relatively low Al and Sr (400-600 ppm), and high concentrations of Th, K and Rb.

(h) Garvock Lavas

The one sample collected from the thin, ill-exposed volcanic rocks of the Garvock Group is an olivine-normative ol-phyric basalt. It has a high Fe/Mg ratio, believed to be primary, and falls in the tholeiitic field of Miyashiro (1974) on an SiO_2 -Fe/Mg diagram. Despite this, concentrations of other elements are not abnormal, although Ti and P are relatively high.

(i) Montrose Region : Discussion and Conclusions

The volcanic rocks of the Montrose region have many general chemical similarities to those of the SW Highlands, particularly in being a quartz- or slightly olivine-normative suite of rocks with concentrations of LIL elements, Ti, Zr and Nb comparable to those of many alkaline suites. The stratigraphy, in conjunction with phenocryst mineralogy, Zr/Nb, Al, Ni and Cr allows the identification of a large number of petrochemically distinct rock groups. Each group shows relatively little compositional variation; in some cases such variation as exists may be explained by fractional crystallisation hypotheses (e.g. Dunnichen/East Hills Member, "trachyandesites") and in others can not

(e.g. St. Cyrus, Bruxie Hill). The groups therefore form tight clusters of points on variation diagrams, although the overall impression of these is of highly scattered calc-alkaline trends (Fig. 5.2).

Use of MgO instead of silica as an index of variation gives greater separation of the samples with less than 60% SiO_2 , and is therefore preferred. Most importantly, it indicates that the high alumina samples are more evolved than samples with lower Al, a distinction not brought out by the use of silica as an index of variation, for silica concentrations of these are relatively low.

It is clear that the groups of samples, or even the least evolved sample from each group, do not lie on the same liquid line of descent from a common parent. The following interrelationships are possible between the various groups:

- 1/ Each group represents a position along a unique liquid line of descent from a common parent. Different groups therefore represent different combinations of phases crystallising from the same parent, at, for example, different P, T.
- 2/ Each group represents a stage on a liquid line of descent controlled by crystallisation of the same phases, but derived from a different parental liquid.
- 3/ A combination of 1 and 2, in which each group represents a stage on a unique liquid line of descent from a unique parent magma.
- 4/ Each group represents different degrees of partial

melting of the same source, possibly including disequilibrium melting.

5/ A more complex mechanism, possibly involving the melting of several sources, followed by crystallisation, contamination or magma mixing during ascent.

The chemical parameters believed to be most relevant to these possibilities are listed in Table 5.4.

Consideration of the first possibility requires the identification of possible parental liquids. The high Cr of group A rocks, in particular MT42, suggests that they are mantle-derived, and that little fractional crystallisation of mafic minerals can have occurred since separation of the melt from its mantle source. This is also true for groups B-E, Table 5.4. Fractional crystallisation of plagioclase is not precluded, however.

It was noted in Chapter 4 that Zr/Nb may only be changed during fractional crystallisation (of phases excluding ilmenite, magnetite and zircon) if the degree of crystallisation is high, for the differences in distribution coefficients between Zr and Nb are small for olivine, pyroxenes, amphiboles, biotite, garnet or plagioclase (Pearce and Norry, 1979). Further, fractional crystallisation of ilmenite- or magnetite-bearing assemblages can only lead to change in Zr/Nb with substantial depletion in V and Cr, elements which have high crystal-liquid distribution coefficients for these phases. Fractional crystallisation of zircon is most unlikely in

TABLE 5.4 : Chemical characteristics of the major lava groups of the Montrose region.

Evolved samples omitted. Oxides in wt.%, trace elements in ppm.

Group	SiO ₂	Al ₂ O ₃	K ₂ O	Sr	P ₂ O ₅	Ce	La/Y	TiO ₂	Zr	Zr/Nb	Cr
A - Ethie Haven	54-55	15.7-16.2	?	560-630	0.36	62-76	1.2-1.3	1.29-1.34	228-264	20.0-22.5	300-560
B - St. Cyrus	53-56	16.3-17.6	1.9	580-690	0.33-.39	59-66	0.9-1.5	1.28-1.71	205-232	15.5	210-310
C - Morphie/Bruxie Hill	55-58	15.9-16.5	2.0	457-546	0.29	59-71	1.1-1.5	1.12-1.40	208-264	14.5-17.5	200-290
D - Crawton	52	15.6-15.9	1.7-1.9	770-830	0.50	93-112	1.8-2.1	1.50-1.66	224	13	430
E - Ferryden (MT36,37)	57.5	15.8-16.1	2.3	564	0.35	70-73	1.4-1.5	1.3	249-254	14.0-14.8	310
F - Ferryden (MT38-40)	54-56	17.0-17.3	21.9	666-737	0.37	70-75	1.2-1.5	1.48-1.54	235-240	14.5-15.5	120
G - Ferryden high-alumina	53-55	18.5-18.9	2.0	690-740	0.37	67-70	1.0-1.1	1.53-1.56	222-230	17.5-18.2	410
H - East Hills/ Dunnichen	53-55	17.8-18.4	2.0	634-673	0.44	71-80	1.0-1.1	1.70-1.76	241-256	18.0-20.2	410

these basic andesites. It is therefore clear that groups A, B, D of Table 5.4 may not be derived from a common parent. The higher Si and K of groups C and E suggests that these could be derived by the fractional crystallisation of plagioclase-rich assemblages from magmas of groups A, B or D. Zr/Nb, and the difficulty of creating lower La/Y except by major apatite crystallisation, precludes derivation of groups C and E from either of groups A and D. The data given in Table 5.4 do not prevent group B liquids from being parental to those of groups C and E, but since both groups B and C are believed to be polygenetic (sections 5.1 d and f), and show wide spreads in La/Y and, for group C, Zr/Nb, it is clear that discussion of a liquid line of descent is meaningless.

It has been previously demonstrated that group F may not be derived from group E by fractional crystallisation processes (section 5.1e). Since there is only moderate depletion in Cr and no Zr enrichment relative to the more Cr-rich groups A-E, Zr/Nb ratio precludes derivation of group F from groups A and D. Therefore, group F may only be derived by fractional crystallisation from groups B and C, and by the argument of the previous paragraph, discussion of a liquid line of descent is meaningless.

It was noted in section 5.1(e) that groups G and H are not part of the same liquid line of descent. The low Cr, Ni and high alumina of these samples suggest that these groups could have been derived by fractional crystallisation

of olivine and clinopyroxene from a magma represented by one of the more mafic compositions of the area, comparable, for example, with the model of Gandy (1973a) for the derivation of high-alumina basalt from olivine-tholeiite by the fractional crystallisation of olivine and clinopyroxene. This can not have involved a high degree of crystallisation, for K, Zr and Ce contents are little, if at all higher than in the more mafic rocks of the region. Substantial magnetite or ilmenite separation is precluded by comparable, or higher, V contents in these high-alumina rocks. Therefore Zr/Nb is unlikely to have changed substantially from that of the parent liquid: groups G and H may therefore not be derived by fractional crystallisation of magmas from groups B, D, E and F, and Zr/Nb for groups A and C is also distinctly different. Further, derivation from group A would imply at least 23% crystallisation (Ti data); Zr, which is only an important minor constituent of Ti-rich phases such as ilmenite, would suggest <11% crystallisation of MT42. Group G shows a smaller increase in Ti, but no increase in Zr at all from MT42. It is very difficult to decrease Zr/Ti by fractional crystallisation of any phase except zircon (Pearce and Norry, 1979). Further evidence against fractional crystallisation comes from the relatively large enrichment in P, but very small enrichments in LREE.

It seems highly probable that no group of lavas in the Montrose region can be related to another by a fractional crystallisation process.

The second hypothesis for interrelationships between the groups, derivation of each group by the same fractional crystallisation process from different parental liquids, is extremely difficult to test by geochemical argument, for it is impossible to recognize the phase assemblage crystallised. Instead, less satisfactory arguments based on volume relationships must be resorted to. The individual group chemistries previously discussed require at least 6 different mafic magma bodies all differentiating more or less simultaneously, with only two of these mafic magmas (MT42 and SC14) being sampled in the present collection. This is most unlikely, and is made more unlikely by the difficulty of generating eight unrelated primitive magmas at roughly the same place.

The third hypothesis can combine the better features of the first two, but suffers from most of the difficulties of the second, and it becomes harder still to test. Different degrees of partial melting of the same mantle source, and the possibility of disequilibrium melting, are also difficult to test, for much depends on the phase composition of the source region. However, Zr/Nb is unlikely to vary much in the different partial melts, unless there is a residual Zr-rich phase, for example ilmenite.

The chemical variation of the rocks of the Montrose region clearly requires a very complex genetic mechanism. There are a number of parallels here with the complexities of the SW Highland volcanics: it is thought, however, that

further discussion should be postponed until after the description of the Ochil Volcanic Formation. It is possible that this formation contains mafic magmas not represented in the smaller outcrops at Montrose.

5.2 : THE SIDLAW HILLS

To the SW of the Montrose region, volcanic rocks appear at the junction between the Arbuthnott and Garvock Groups near Glamis and thicken to the south and west to form the volcanic sequence of the Sidlaw Hills, lying on the northern limb of the Sidlaw Anticline (Fig. 5.1). The stratigraphy and petrography of the rocks of various parts of the Hills have been described by Harry (1956,1958), Davidson (1932) and Gandy (1973a). These authors described a volcanic sequence dominantly composed of basalt and basic andesite, with very subordinate andesites and a "trachyandesite" at Craighead (Harry, 1956). No in situ acid rocks occur, but the conglomerates overlying the volcanic rocks near Perth are rich in acid clasts. A few horizons of sandstone are intercalated in the volcanic sequence.

In the course of the current research, a selection of the samples collected by Gandy (1973a) has been reanalysed, together with a number of new samples from the Moncreiffe Hill - Perth area.

(a) Ol-phyric, ol-pl-phyric, ol-cpx-pl-phyric and aphyric samples (a1, a11, a12, a20)

None of the samples are truly aphyric, and those classified as aphyric lavas have occasional microphenocrysts of olivine and plagioclase. These are the dominant phenocryst phases in the Sidlaw lavas; clinopyroxene is seldom abundant, and only occurs in the most phenocryst-rich rocks. These phenocrysts are set in a plagioclase-rich groundmass, with intersertal opaque oxide and either subophitic or intersertal clinopyroxene. Many rocks contain groundmass chlorite, which may be replacing both glass and, in some rocks, olivine. Gandy (1973b) has shown that olivine and plagioclase are the liquidus phases of the lavas at atmospheric pressure, and suggested that the chemical variation of the entire Sidlaw suite was controlled by fractional crystallisation of these, with minor ilmenite and possibly clinopyroxene, at low pressure. High scatter on the variation diagrams (Gandy, 1973a) was attributed to phenocryst accumulation and to a range of immediately parental high alumina basalt magmas.

Olivine has not been found fresh, but phenocryst clinopyroxenes are the low Na, Ti, Al diopsidic augites characteristic of the province. They show substantial variation within each rock in Ca, Mg, Ti and Al, not readily correlated with zoning. Plagioclase is labradorite, and neither plagioclase nor clinopyroxene composition is closely related to host rock chemistry.

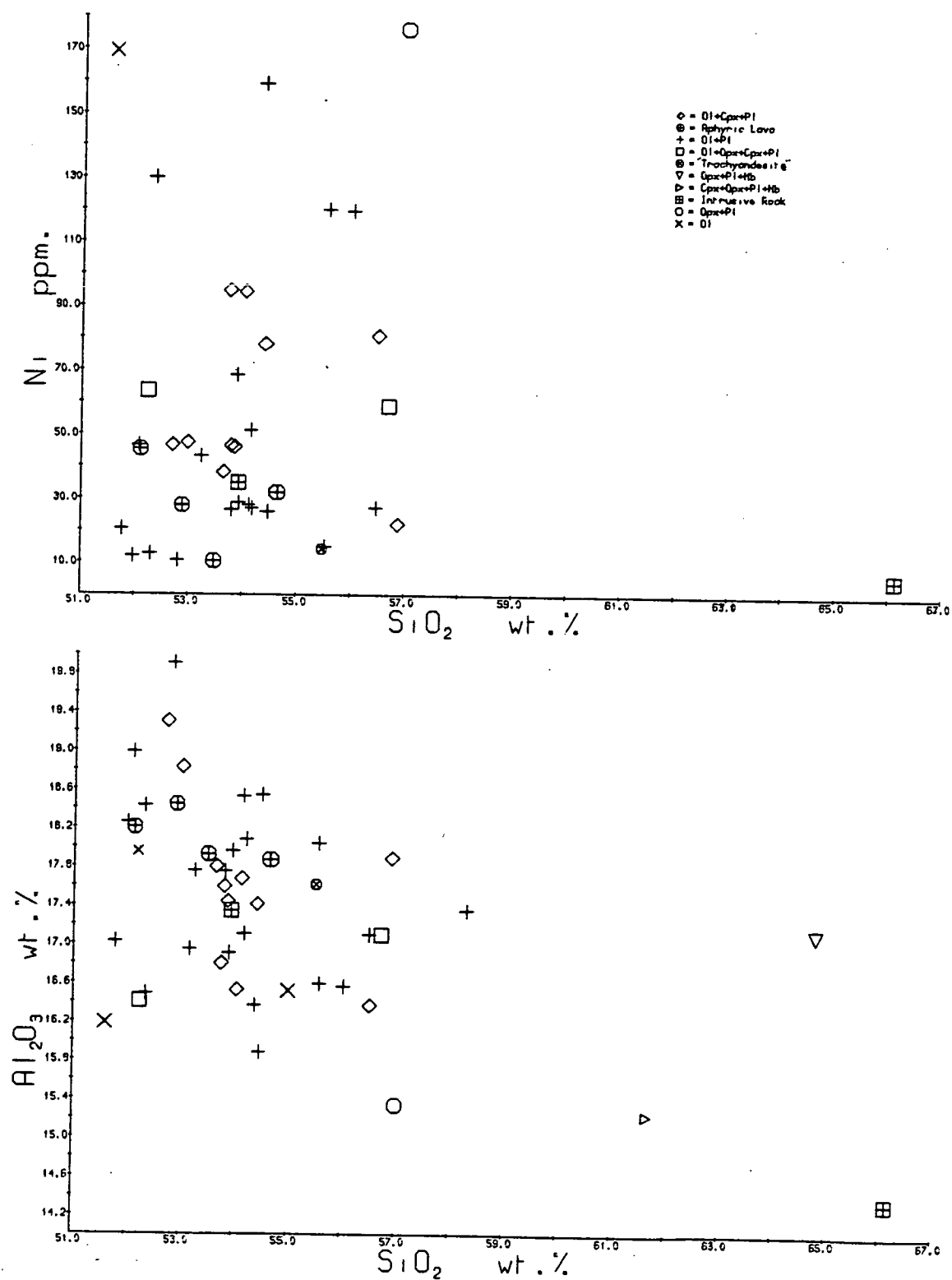
The rocks are mainly quartz-normative, although a few contain minor normative olivine (up to 4%). Silica varies from 51.5 to 58.5%, although most rocks have less than 56% silica. Few elements show unscattered variation with silica (Fig. 5.3); in particular, the lack of a systematic relationship with Ni strongly suggests that olivine-dominated fractional crystallisation can not give rise to the variation in silica content. Further, separation of 40% olivine, 60% clinopyroxene from olivine-tholeiite to produce a range of high-alumina basalts as suggested by Gandy (1973a) followed by further olivine separation would be most unlikely to produce basic andesites with >100 ppm Ni.

Use of MgO as an index of evolution as at Montrose provides better separation of the basic andesites on variation diagrams (Fig. 5.4). Although there is considerable scatter, it will be noted that there are broad increases in Al and Ti with decreasing Cr and MgO, contrasting with the predictions of the petrogenetic model of Gandy (1973a) involving fractional crystallisation of olivine, plagioclase and minor ilmenite. There is little correlation between Al content and amount of phenocryst plagioclase (ol-cpx-pl-phyric rocks are generally richest in phenocryst plagioclase), suggesting that plagioclase accumulation has not played an important part in generating the scatter.

Incompatible elements in general increase with

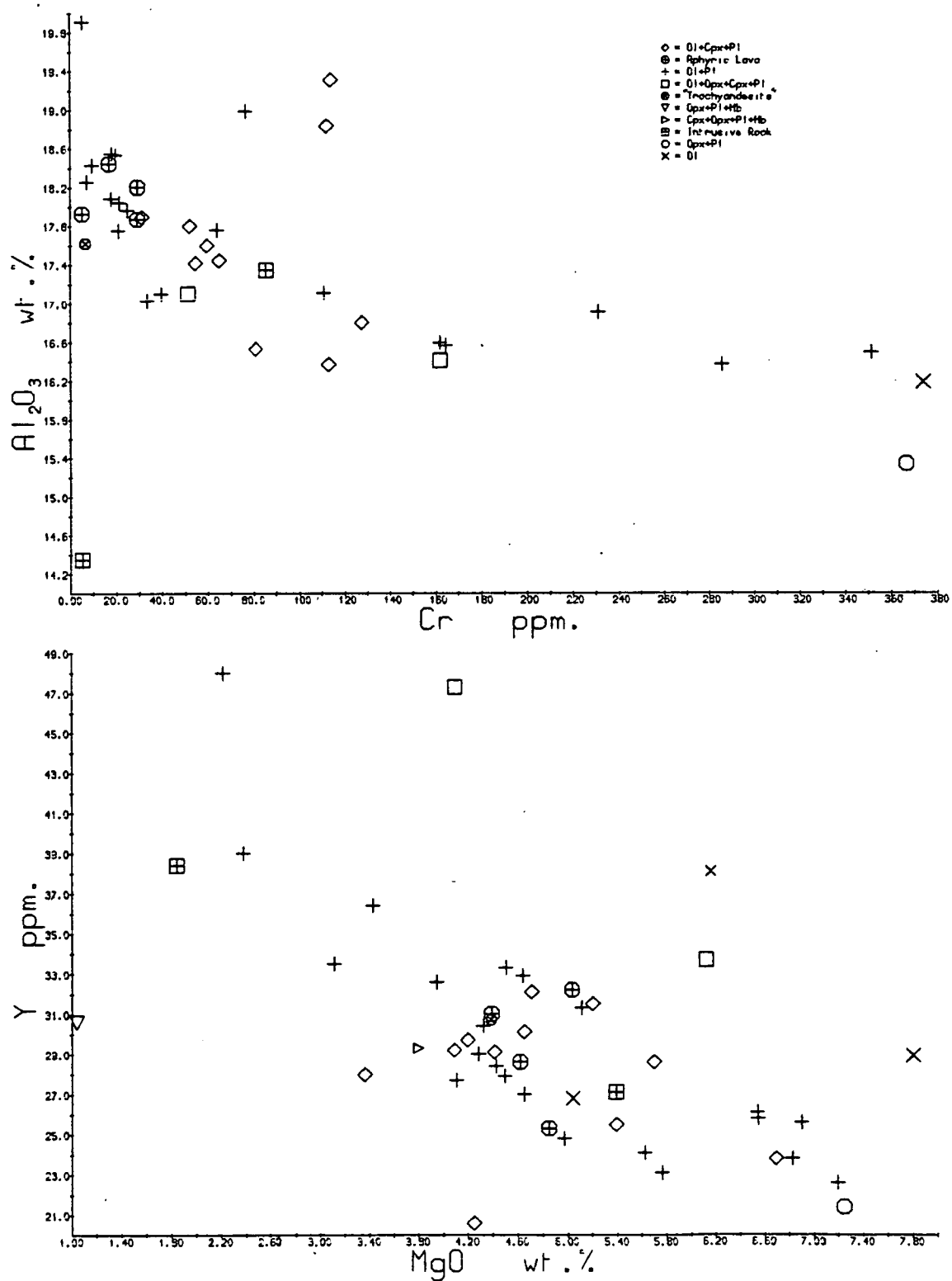
SIDLAW HILLSFig. 5.3 a & b : Bulk rock variation diagrams

Conventions as section 3.3



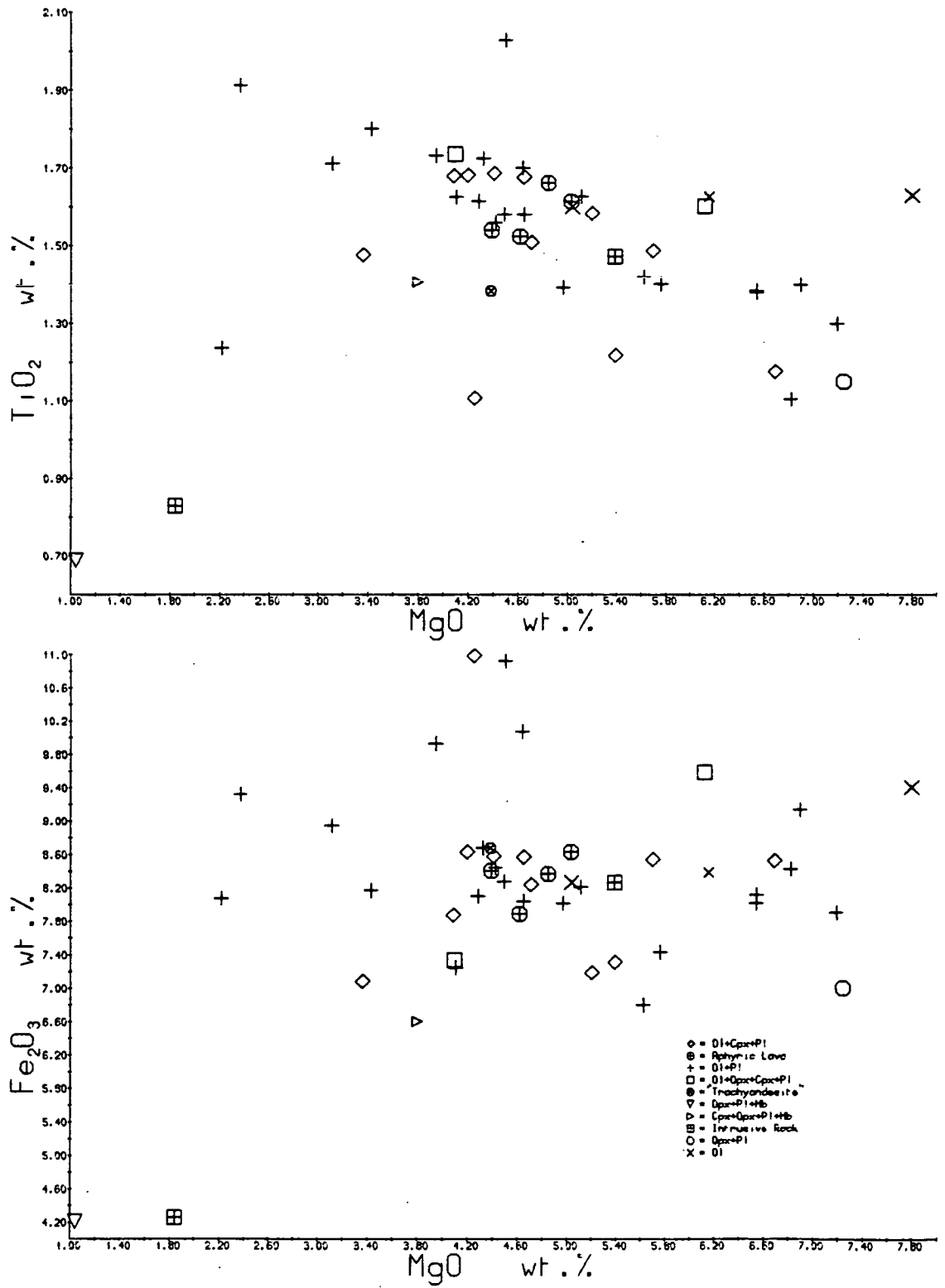
SIDLAW HILLSFig. 5.4 a & b : Bulk rock variation diagrams:

Conventions as section 3.3



SIDLAW HILLS

Fig. 5.4 c & d



decreasing MgO, (Figs. 5.4, 5.5), but there is much scatter, reflected in wide variation in Zr/Nb ratio from 14.5 to 29. Correlation of 'incompatible' element concentrations with Cr is poor, although in general the most Zr, Nb enriched samples have low Cr. Zr/Nb does not correlate with Cr, and again it may be concluded that the Sidlaw lavas may not be derived by multistage fractional crystallisation or partial melting processes from a common source.

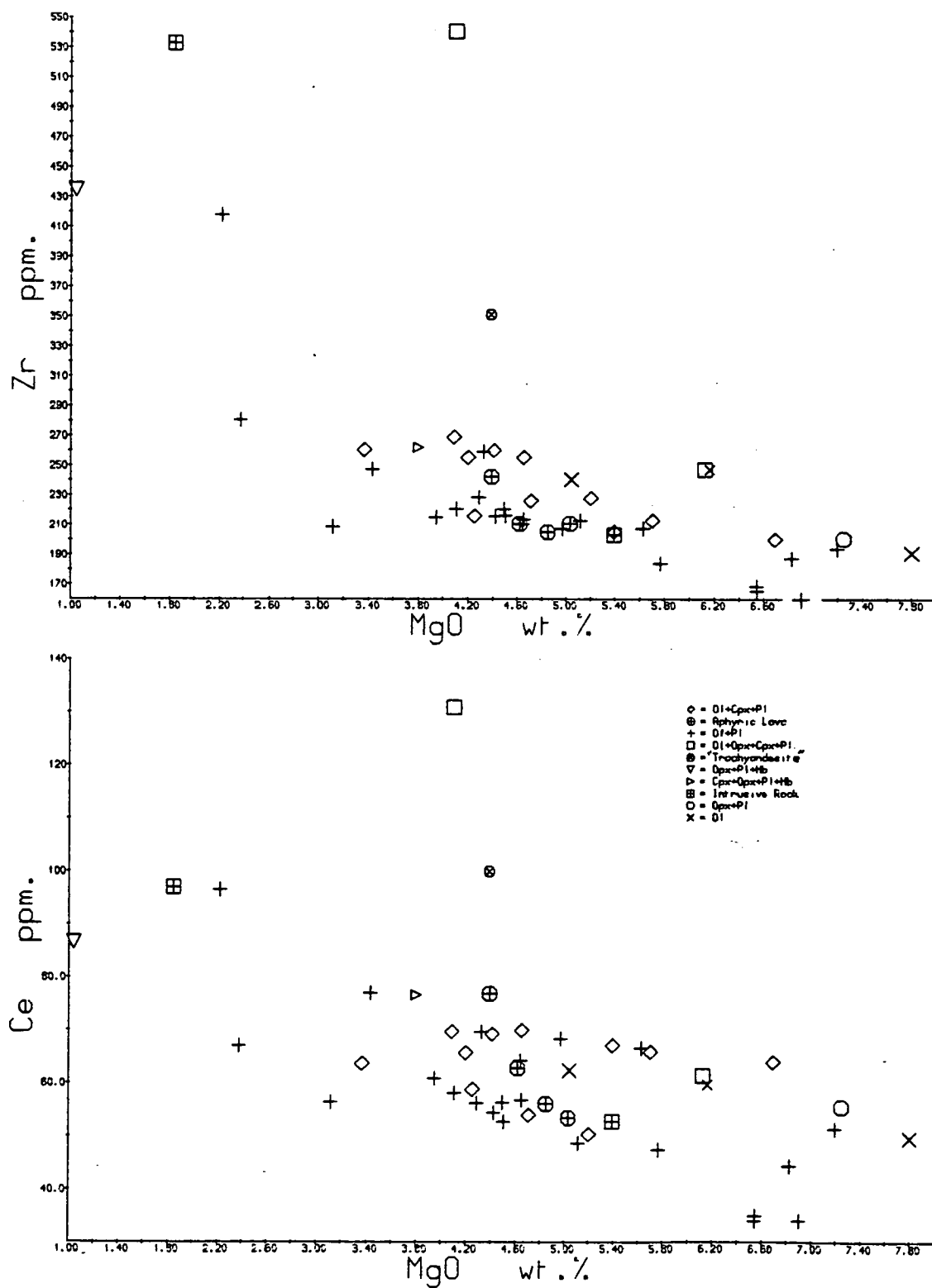
Because of the lack of an external criterion by which to divide the rocks, it is very difficult to investigate whether individual groups of rocks can be derived from others by fractional crystallisation processes. Comparison with the variation diagrams for samples from the Montrose region shows that the Sidlaw lavas cover the full range of chemistries displayed by individual members of the Montrose Volcanic Formation. No basic andesite with <4.6% MgO has <17% alumina: at Montrose, only the Highland Border rocks have alumina in this region. A few samples have substantially higher alumina than the Dunnichen/East Hills rocks, but also have higher Ni (40 ppm) and Cr (100 ppm). It is clear that derivation of all high-alumina rocks by simple fractional crystallisation of olivine and clinopyroxene from a common parent is not a viable hypothesis.

(b) Orthopyroxene-bearing samples (@5, @10)

Phenocryst orthopyroxene is present in three samples

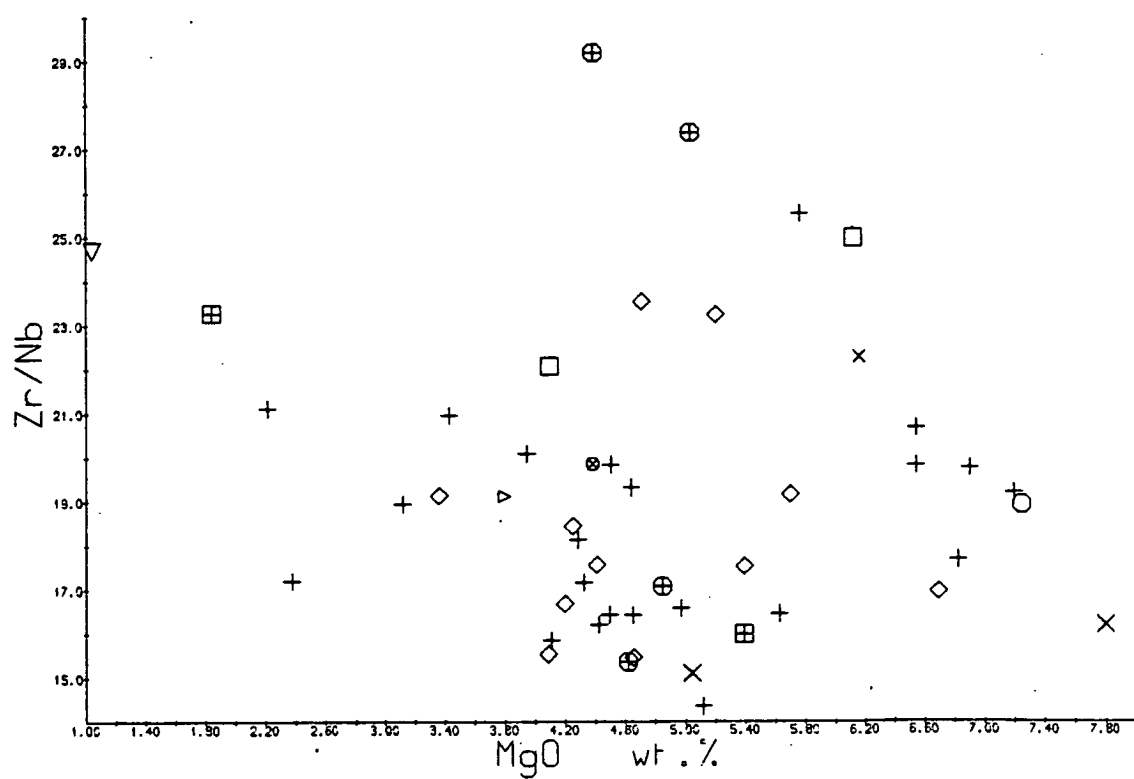
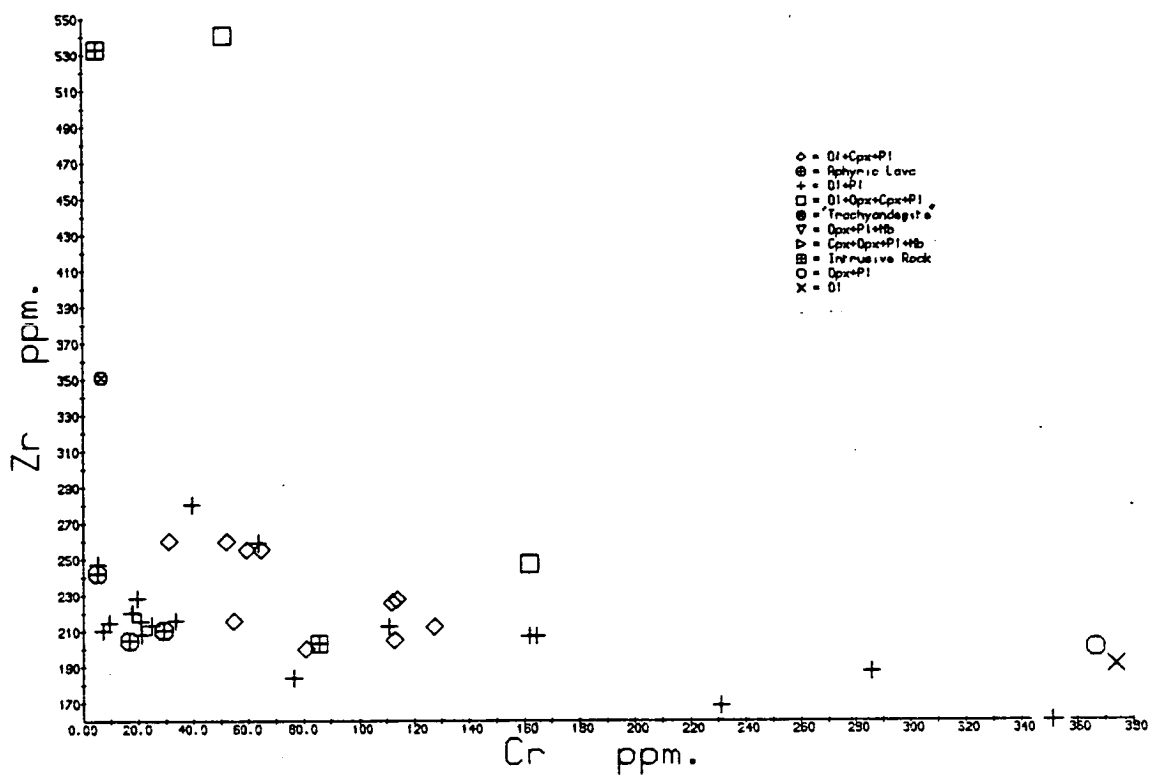
SIDLAW HILLSFig. 5.5 a & b : Bulk rock variation diagrams

Conventions as section 3.3



SIDLAW HILLS

Fig. 5.5 c & d



from the Sidlaw Hills. In one of these, it is a magnesian bronzite rich in Ni and Cr (anal. 22, S44), and is associated with sodic labradorite (anal. 19, S44). This sample was described by Gandy (1973a) as an orthopyroxene-phyric andesite, for it contains 57% silica, but it is one of the most Ni-, Cr-, Mg-rich rocks in the Sidlaw Hills. It is also rich in K and Rb, and for its MgO content, relatively rich in other generally 'incompatible' elements. It has therefore a number of similarities to the Ferryden samples MT36,37, but differs from these in detail, e.g. Zr/Nb ratio. Sr content is greater than that of other comparably mafic Sidlaw lavas, and therefore fractional crystallisation of a plagioclase-dominated assemblage can not produce the incompatible element enrichment. Fractional crystallisation of mafic minerals would reduce Ni and Cr: it may be concluded that no other Sidlaw composition could produce S44 by fractional crystallisation.

The two other orthopyroxene-bearing samples contain olivine and clinopyroxene in addition. Orthopyroxene is Cr-poor hypersthene (anal. 25, S52), plagioclase is labradorite-andesine and clinopyroxene the typical diopsidic augite low in Ti, Na and Al (Table C2, anal. 24 and 26, S13 and S52). Plagioclase is considerably richer in Or, and clinopyroxene in Fs, than those from the ol-cpx-pl- and ol-pl-phyric samples. Orthopyroxene is frequently mantled by clinopyroxene or by small olivines. The two samples are strongly enriched in Y (Fig. 5.4) relative to rocks with comparable MgO, and are also enriched in Zr (Fig. 5.5). S13

is also strongly enriched in other generally incompatible elements, with Ba the only exception. Sr is depleted relative to the bulk of the rocks; it is probable that fractional crystallisation of plagioclase-rich assemblages can explain the incompatible element enrichment, but, again, identification of a parental magma is very difficult. The difference in Zr/Nb between S13 and S52 suggests that these are not cogenetic, but S13 has comparable Zr/Nb to the Montrose "trachyandesites". Zr, Nb, Ce and several other elements show linear relations with MgO between S13 and the Montrose "trachyandesites", possibly suggesting that S13 is immediately parental in a fractional crystallisation process. Major elements, in particular Al and Ti, suggest that this can not be a simple process, however.

(c) "Trachyandesite"

The Sidlaw "trachyandesite", or "high-K andesite" of Gandy (1973a) is very different, both mineralogically and chemically, from the Montrose "trachyandesites". It is quite strongly sericitized, and use of K as a major classificatory parameter is therefore unsatisfactory. The sample is, however, highly enriched in Zr, LREE, Ba, P and Rb relative to rocks with comparable MgO (Figs. 5.4, 5.5), and depleted in Sc and Ca. Y is not enriched, and the sample is probably not related to S13 and S52@10. The sample may be a product of a further process of fractional crystallisation operating in the Sidlaw Hills.

(d) Sidlaw Hills : Conclusions

The chemical variation of the lavas of the Sidlaw Hills may not be generated by fractional crystallisation of olivine, plagioclase and minor ilmenite from a range of high-alumina basalts, themselves generated by olivine and clinopyroxene separation from a primary olivine-tholeiite, as proposed by Gandy (1973a). The chemistry of the Sidlaw Hills lavas is very variable, and encompasses the full range of variation of the samples collected from the Montrose region. Despite this variety, the Sidlaw lavas display the high levels of 'incompatible' elements characteristic of the rest of the province, and demonstrate calc-alkaline trends with little relative iron enrichment. Since it is not possible to separate the Sidlaw samples on a satisfactory stratigraphical or geographical basis, it becomes impractical to demonstrate that fractional crystallisation processes may not generate some of the compositions observed from other sampled compositions. By analogy with the Montrose region, it is believed that no extensive liquid line of descent could be recognized within the Sidlaw samples.

While the Sidlaw lavas include rare compositions appropriate for the genesis of the high-Al, low-Ni, -Cr lavas of East Hills/Dunnichen by olivine-clinopyroxene separation, there are several other high alumina samples in the Sidlaw Hills subtly different from those of Dunnichen. A number of these have relatively high Ni and Cr contents.

It is not possible to determine whether all high-alumina rocks are the products of such fractional crystallisation processes, and it remains possible that they have been generated by the partial melting of a source poor in Ni and Cr.

5.3 : THE WESTERN OCHIL HILLS

The Old Red Sandstone volcanic rocks of the Ochil Hills west of Glen Farg outcrop on both limbs of the Ochil-Sidlaw Anticline. The base of the volcanic sequence is not seen, but it is overlain by and intercalated with sediments belonging to the Garvock Group on the northern limb of the anticline. Overlying sediments on the southern limb are not seen, for the volcanic sequence is truncated by the Ochil Fault in the west, and by the Upper Old Red Sandstone unconformity in the east. Total thickness of volcanic rocks is believed to be in excess of 8000ft (2400m; Francis et al., 1970). The volcanic rocks are cut by a number of intermediate and acid dykes, and by a variety of sills, bosses and laccoliths thought to be closely related to the volcanism. There are larger diorite bodies close to the Ochil Fault near Tillicoultry.

Geikie (1900) and Francis et al. (1970) have described the field occurrence and petrography of the volcanic rocks. A wide variety of rock types has been recorded, both lavas and pyroclastic rocks, and Francis et al. (1970, p.25) noted that the different lava-types were

distributed in an almost random manner both laterally and vertically. Hornblende-andesites were, however, believed to be restricted to the lower parts of the volcanic pile, and the coarsest agglomerates to areas close to the Ochil Fault. This latter feature was thought to imply proximity to a line of vents along or close to the Fault (Francis et al., 1970, p.27).

The rocks collected show strong similarities, both chemical and petrographic, to the rocks of the Sidlaw and Montrose areas. They differ mainly in the greater development of siliceous rocks, including opx-cpx-pl- and hb-opx-cpx-pl-phyric andesites, "trachyandesites" and the acid lavas of Craig Rossie. There is a corresponding paucity of Ni- and Cr-rich rocks, although many rocks are again considerably richer in these than the average andesite of Jakeš and White (1972). A wide range of phenocryst associations is present, but very few rocks lack phenocryst plagioclase, and over half the samples collected have phenocryst orthopyroxene, in contrast to the statement by Taylor (1972) that orthopyroxene was 'very uncommon' in the volcanic rocks south of Dunning.

Taylor (1972) described a trimodal distribution of silica content from the volcanic rocks of the Ochil Hills south of Dunning. This is not evident when rocks from a wider area are considered, and it is believed that this trimodality results from the unrepresentative collection inevitable in this small, poorly exposed area.

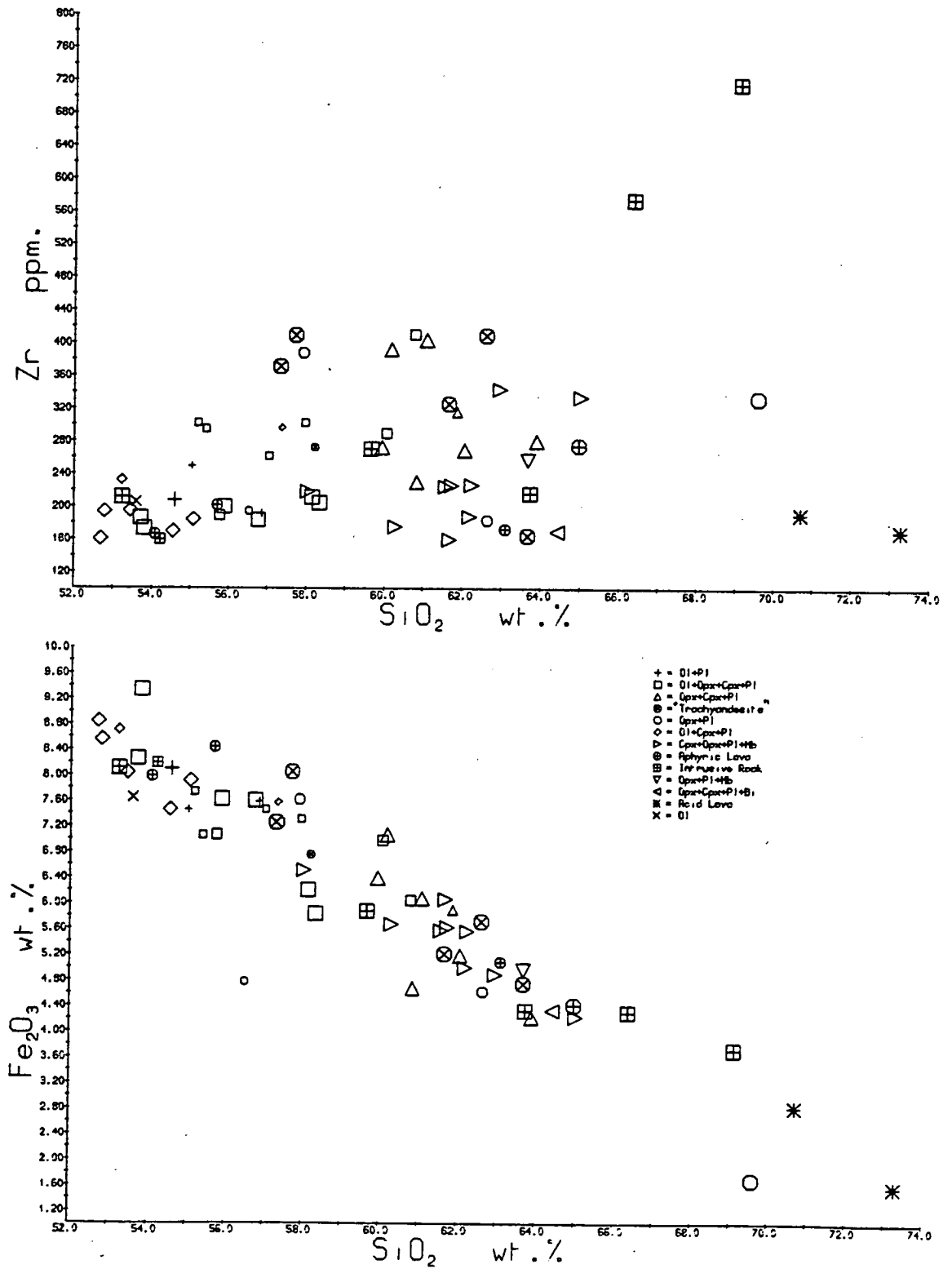
(a) Olivine-bearing samples

Only one sample with olivine as the sole phenocryst has been collected; all other olivine-bearing samples have phenocryst plagioclase, and many contain both orthopyroxene and clinopyroxene. Only one of these has fresh orthopyroxene. This is a bronzite, and the host rock, OC15, although siliceous (56.8%), is the most Cr-rich rock collected in the area. There are therefore some parallels with S44@5 (section 5.2b). Clinopyroxenes are the typical diopsidic augites low in Na, Ti and Al, and again there is much variation within the phenocrysts of a single rock, including, on rare occasions, pyroxenes plotting within the alkaline field of Le Bas (1962). This is again thought to be due to localized melt heterogeneity arising during rapid crystallisation (section 5.1c). Plagioclase is usually labradorite or andesine. Little correlation exists of phenocryst association and chemistry with host rock chemistry.

These rocks show a very wide range in chemistry not related to MgO or silica content (Fig. 5.6), even greater than that shown by the Montrose or Sidlaw volcanic rocks, although again, all rocks are quartz- or slightly olivine-normative. As discussed in previous sections, the high variability of Zr/Nb (15-36) suggests that derivation of the suite by fractional crystallisation of a common parent is most improbable, but as no non-chemical means of subdivision exists, it is difficult to rule out an origin by

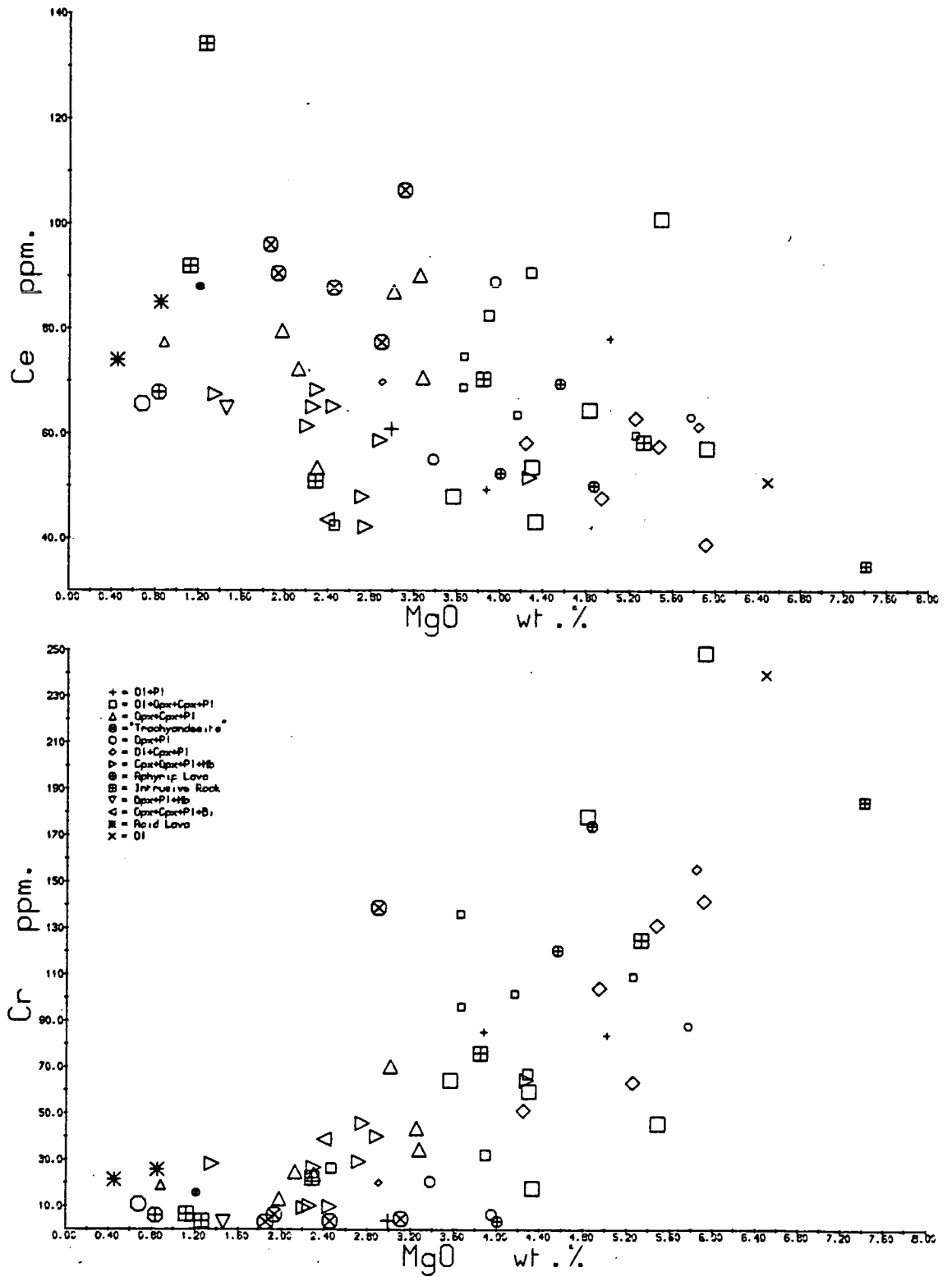
Fig. 5.6 a & b : Bulk rock variation diagrams

Conventions as section 3.3



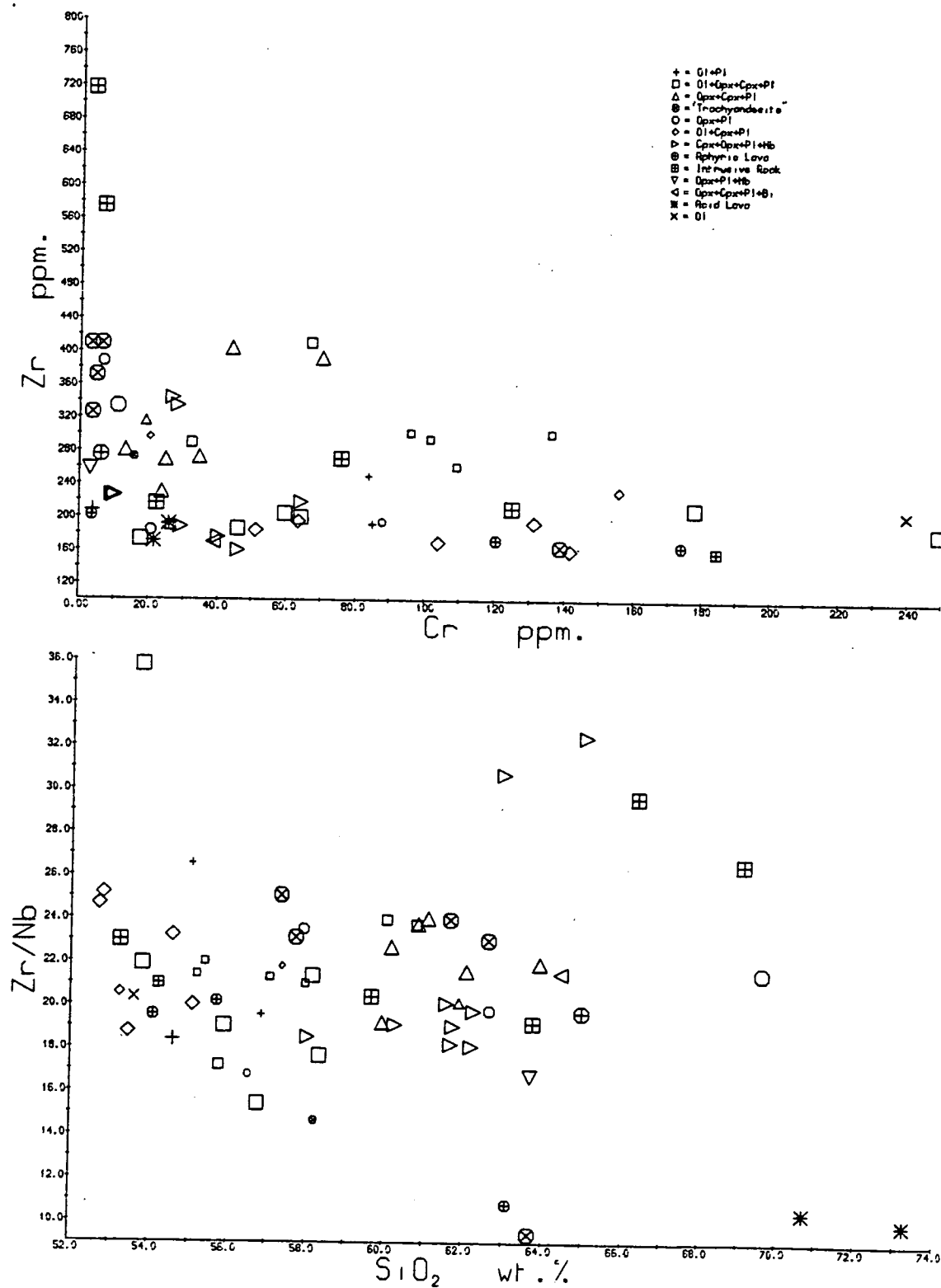
WESTERN OCHIL HILLS

Fig. 5.6 c & d



WESTERN OCHIL HILLS

Fig. 5.6 e & f



fractional crystallisation for small groups of samples. Small groups of samples which behave coherently may be recognized e.g. 0C7, 8, 10. It should be noted that the ol-opx-cpx-pl-phyric samples are not as strongly enriched in generally incompatible elements as Sidlaw ol-opx-cpx-pl-phyric samples.

(b) Opx-cpx-pl-phyric samples (@13)

All samples with this phenocryst association have between 59.9 and 64% silica, 1.9 and 3.3% MgO (excluding one altered sample) and between 10 and 30 ppm Ni. Despite this apparently restricted composition, Zr varies from 220 to 400 ppm, Y between 19 and 40 and Ce between 55 and 90 ppm. The two samples with the highest incompatible element concentrations (0C7,8) also have high Ni, Cr, Sc and V relative to other opx-cpx-pl-phyric samples, but lower Sr and Al. This could suggest fractional crystallisation of an assemblage dominated by plagioclase, but it is unlikely that this could lead to increases in Ni and Cr. Furthermore, CaO concentrations are little different and Zr/Nb variation is outside the limit of analytical error. It may be concluded that the opx-cpx-pl-phyric rocks are unlikely to be all related to each other by fractional crystallisation processes. The phenocrysts are chemically comparable with those of the olivine-bearing samples, and the association may have apatite and magnetite in addition.

(c) Hornblende-andesites (a16)

As noted by Taylor (1972), phenocryst amphibole is absent from the basalts and basic andesites and it is never common in more siliceous rocks. The hornblende-andesites also contain phenocrysts of orthopyroxene, clinopyroxene, plagioclase and titanomagnetite. Some samples also have phenocryst apatite, and one contains rare pseudomorphs after olivine central to large aggregates of pseudomorphed orthopyroxene. The amphibole is a pargasitic hornblende, clinopyroxene is the typical low Ti, Al, Na diopsidic augite and orthopyroxene is bronzite-hypersthene. Plagioclase is labradorite or andesine, although two crystals partly enclosed in amphibole in OC67 zone from An84 inside the amphibole out to An50. Plagioclase is poorer in Or than that from samples with olivine-bearing associations.

With the exceptions of OC65 and OC67, the rocks have Zr/Nb within the range of analytical error. These two rocks are strongly enriched in Zr and Rb, slightly enriched in P, La, K, Si and depleted in Na, Y, Fe, Mg and Ti relative to other hornblende-andesites. The closely similar values of Cr, Ni, V, Sc and Sr strongly suggest that the two groups may not be derived by fractional crystallisation of a common parent. The most mafic sample, OC23, has substantially higher levels of Ni and Cr, but also has more Zr and Nb than many of the remaining five. These five show a good linear increase in Zr and Nb with decreasing Cr (Fig. 5.6). It seems possible that these five are related by fractional

crystallisation of a common parent, but as previously, the small variation does not permit the use of extract calculations to deduce the possible crystallising assemblage. Any parental magma must have been significantly poorer in Zr and Ce than any other composition analysed in the region.

(d) "Trachyandesites" (@18)

Rocks described as trachyandesites by Francis et al. (1970) and classed as dacites by Taylor (1972) form yet another petrographically and chemically heterogeneous group. They are generally sparsely porphyritic with a groundmass dominated by a subtrachytic arrangement of plagioclase laths. Phenocrysts include calcic andesine, diopsidic augite with slightly higher Na, Ti and Al than average (anals. for OC27, Table C2), but well within the tholeiitic (subalkaline) field of Le Bas (1962), titanomagnetite, orthopyroxene, hornblende and apatite in various combinations. The rocks are not notably more alkaline than many other rocks described as andesites by Francis et al. (1970), and the term "trachyandesite" is therefore a misnomer; it is still useful to refer to them as a group, and the term has therefore been retained in quotes.

The "trachyandesites" vary from 57 to 64% silica, and most of them are poor in Ni and Cr, with $Ni > Cr$, like the "trachyandesites" of the Montrose region. The one relatively Ni-rich sample is also the most siliceous, and,

together with one more altered sample (OC24) has very much lower Zr/Nb (10-15) than the remaining four samples (Zr/Nb=23-26). These four samples are themselves chemically very variable, and one (OC63) is much poorer in V, Ti, Y and also Zr and Nb than the remainder. This could possibly suggest fractional crystallisation of an ilmenite-rich assemblage, but this can not satisfactorily explain the silica variation. In addition, OC63 has much lower K and Rb than the other three. It seems likely that at least three magmas differing in 'incompatible' element ratios are required to generate the Ochil "trachyandesites". They show some broad similarities to the Montrose and Sidlaw "trachyandesites", particularly in their strong enrichment in P relative to most Midland Valley samples, but 'incompatible' element concentrations differ in details which may not be attributed to fractional crystallisation.

(e) Western Ochil Hills : Conclusions

It is clear from the preceeding discussion that Taylor's (1972) model for the petrogenesis of rocks with <63% silica by the wet partial melting of quartz-eclogite at 27-30kb can not explain the variations in Ni and Cr or in 'incompatible' element ratios, unless the eclogite was extremely heterogeneous. He believed that more siliceous rocks were derived by the fractional crystallisation of plagioclase, clinopyroxene and amphibole from wet andesitic magma. While a wide variety of andesitic magmas was apparently available, the very low Zr/Nb of the Craig Rossie

'rhyodacites' precludes their derivation from most of the andesites of the Western Ochil Hills by fractional crystallisation of zircon-free assemblages (Chapter 3). Early crystallisation and settling of zircon from liquids with only about 250 ppm Zr is thought to be unlikely.

The rocks of the Western Ochil Hills are very similar to those of the Sidlaw Hills and the Montrose Volcanic Formation, for they again show great chemical variety within broad calc-alkaline trends. Since no satisfactory non-chemical method of rock classification exists, it is again impractical to deduce whether individual rock groups can be related by fractional crystallisation processes to the more mafic lavas of the area or to a small number of parental magmas. Where a rock group may be delineated using petrographic and chemical criteria, for example, five of the hornblende-andesites, no other composition in the Ochil Hills can be immediately parental. Comparison with the Montrose region suggests the conclusion that no extensive liquid line of descent controlled by fractional crystallisation exists in the Ochil Hills.

5.4 : NORTH FIFE HILLS

Old Red Sandstone rocks of the Ochil Volcanic Formation outcrop in a range of hills along the south side of the Firth of Tay from Glenfarg to Newport-on-Tay, and cross the Tay at Dundee as the Broughty Ferry Lavas. These rocks are all on the southern limb of the Ochil-Sidlaw

Anticline. The volcanic sequence is thinner than in the western Ochil Hills, and in general thins to the east. The volcanic rocks are underlain by and intercalated with sandstones containing a Lower Old Red Sandstone fauna (Geikie, 1902, p.30) and are unconformably overlain by Upper Old Red Sandstone sediments. Only a few small intrusions are present south of the Tay, but there is a large suite of basic intrusions, probably mainly sills and plugs, near Dundee. The thick sill at Newburgh noted by Geikie (1900, p.30) is now believed (M.A.E. Brown, pers. comm., 1979) to be at least one lava flow. A K-Ar date of 394 ± 5 Ma was reported by Evans *et al.* (1971) for some lavas near Tayport.

Geikie (1900,1902) and Harris (1928) have described the stratigraphy and petrography of the rocks south of the Tay and of the Broughty Ferry lavas respectively. There is again wide variety in lithology, and Geikie (1902, p.48) noted that there was no rational pattern in distribution of different petrographic types with position in the volcanic sequence. Most of the lavas contain phenocryst plagioclase (labradorite-andesine), almost always coexisting with one or more of the following: forsteritic olivine (up to Fo86), bronzitic orthopyroxene, titanomagnetite and low Na, Ti, Al diopsidic augite. Hornblende-andesites comparable to those of the western Ochil Hills are lacking, and pseudomorphed amphibole phenocrysts have only been observed in an acid lava clast from an agglomerate at Broughty Ferry, and from some nearly aphyric lavas akin to the "trachyandesites" at Auchtermuchty. These latter lavas contain an abundance of

coarse-grained xenoliths, which will be described later. Phenocryst biotite is restricted to the "dacites" of Geikie (1902).

The samples analysed show a range in silica from 50 to 80%, but there is a marked composition gap between the dominant lavas with <62% silica and the "dacites" of Geikie (1902) with >70% (Fig. 5.7). The only sample analysed in this gap was from a clast in an agglomerate (OC89). Only one nepheline-normative sample exists, and this may be due to secondary introduction of calcite. Most of the rocks are quartz-normative, although some of the most magnesian are slightly olivine-normative. They are all rich in LILE, high field strength elements and often in Ni and Cr relative to the average andesite of Jakeš and White (1972), and are thus closely comparable to the rocks of the province described previously.

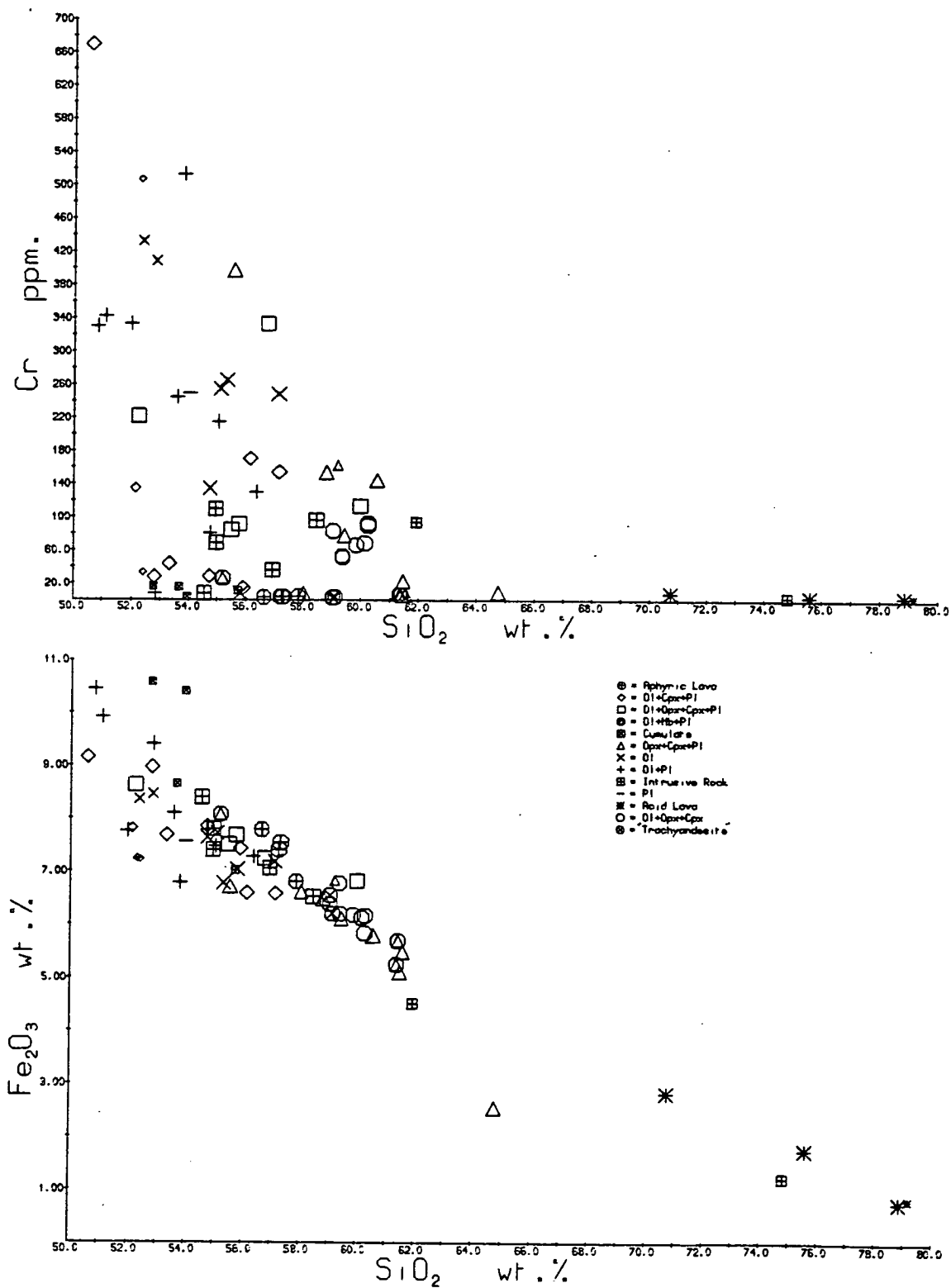
As elsewhere in the northern Midland Valley, few elements show good linear correlation with increasing silica, although a number show general increases (K, Rb, Th, LREE) or general decreases (Fe, Mg, Ca, Ti, Sc and V). Other elements, particularly Al, P, Ni, Cr and Zr, are very highly scattered. Variation diagrams with MgO show little improvement in scatter, although Al and Na show broad increases, and Cr and Ni decreases, with decreasing MgO (Fig. 5.7).

Zr/Nb is very variable at all silica concentrations

NORTH FIFE HILLS

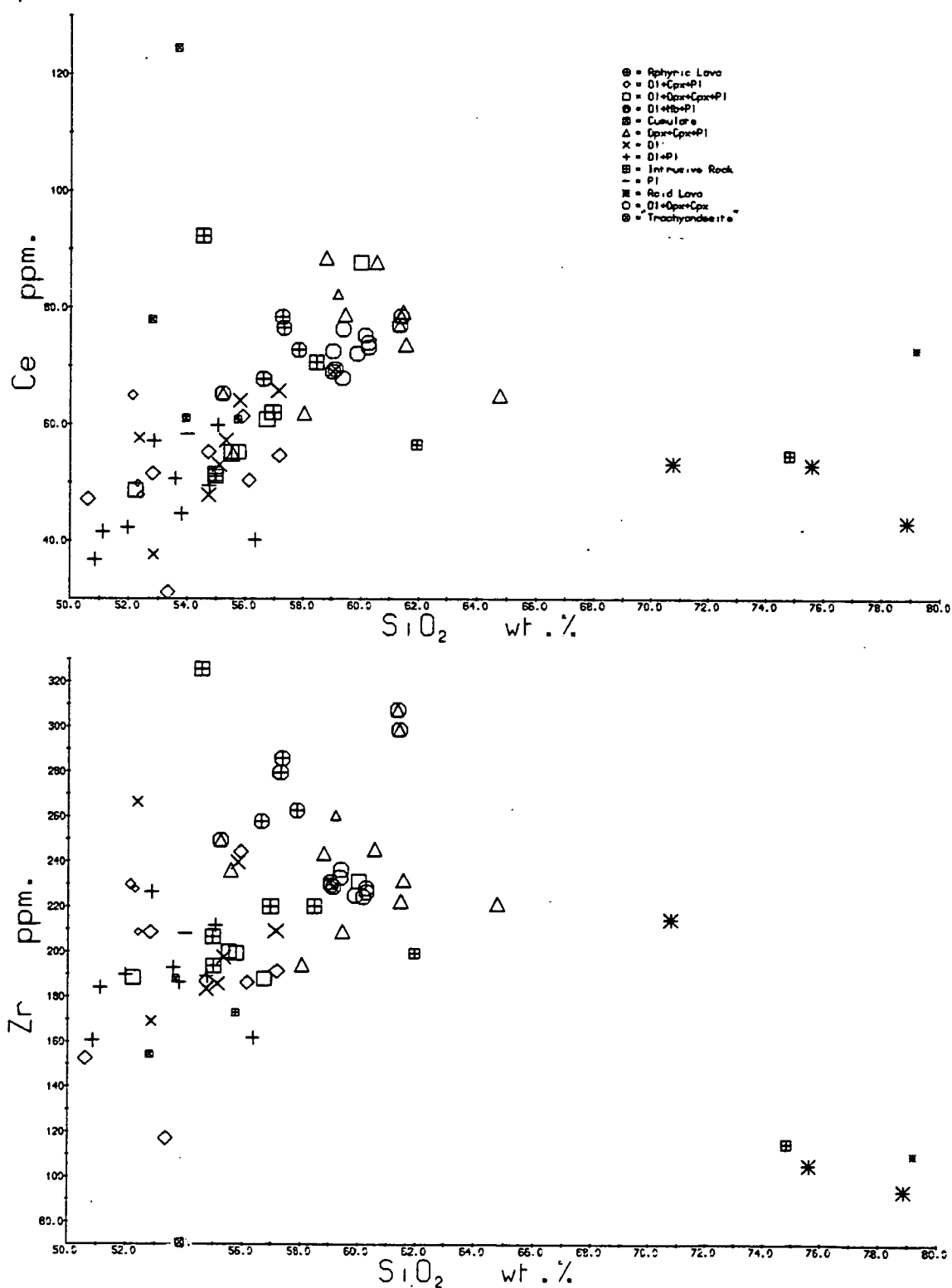
Fig. 5.7 a & b : Bulk rock variation diagrams

Conventions as section 3.3



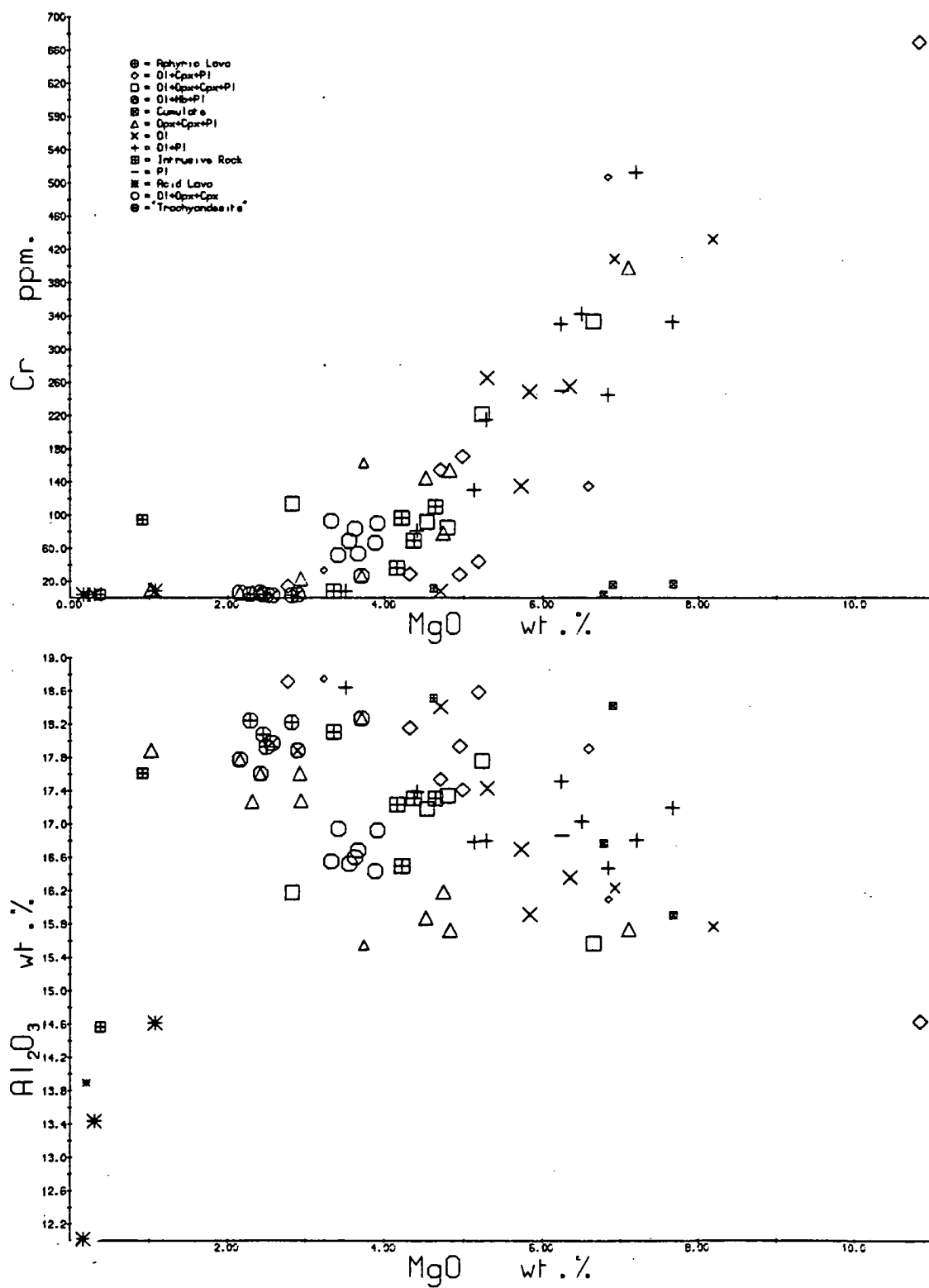
NORTH FIFE HILLS

Fig. 5.7 c & d



NORTH FIFE HILLS

Fig 5.7 e & f



(Fig. 5.8), with a range between 14 and 30 for mafic samples, and correlations between Zr and Nb, Cr and Zr and Cr and Nb are poor: it may therefore be concluded that most of the volcanic rocks of the North Fife Hills may not be related to each other by fractional crystallisation processes. As with the Sidlaw and west Ochil Hills, however, it is not possible to subdivide the rocks by stratigraphical or geographical criteria, and therefore the recognition of small groups of samples of roughly constant Zr/Nb, for which hypotheses of fractional crystallisation may be tested, is impractical. By analogy with the Montrose region, it is again believed that no large suite of rocks conforming to a liquid line of descent is likely to be found.

Use of phenocryst assemblage as a method of classification indicates that a few of the more siliceous assemblages have constant Zr/Nb, and that therefore the rocks with these assemblages might be related by fractional crystallisation.

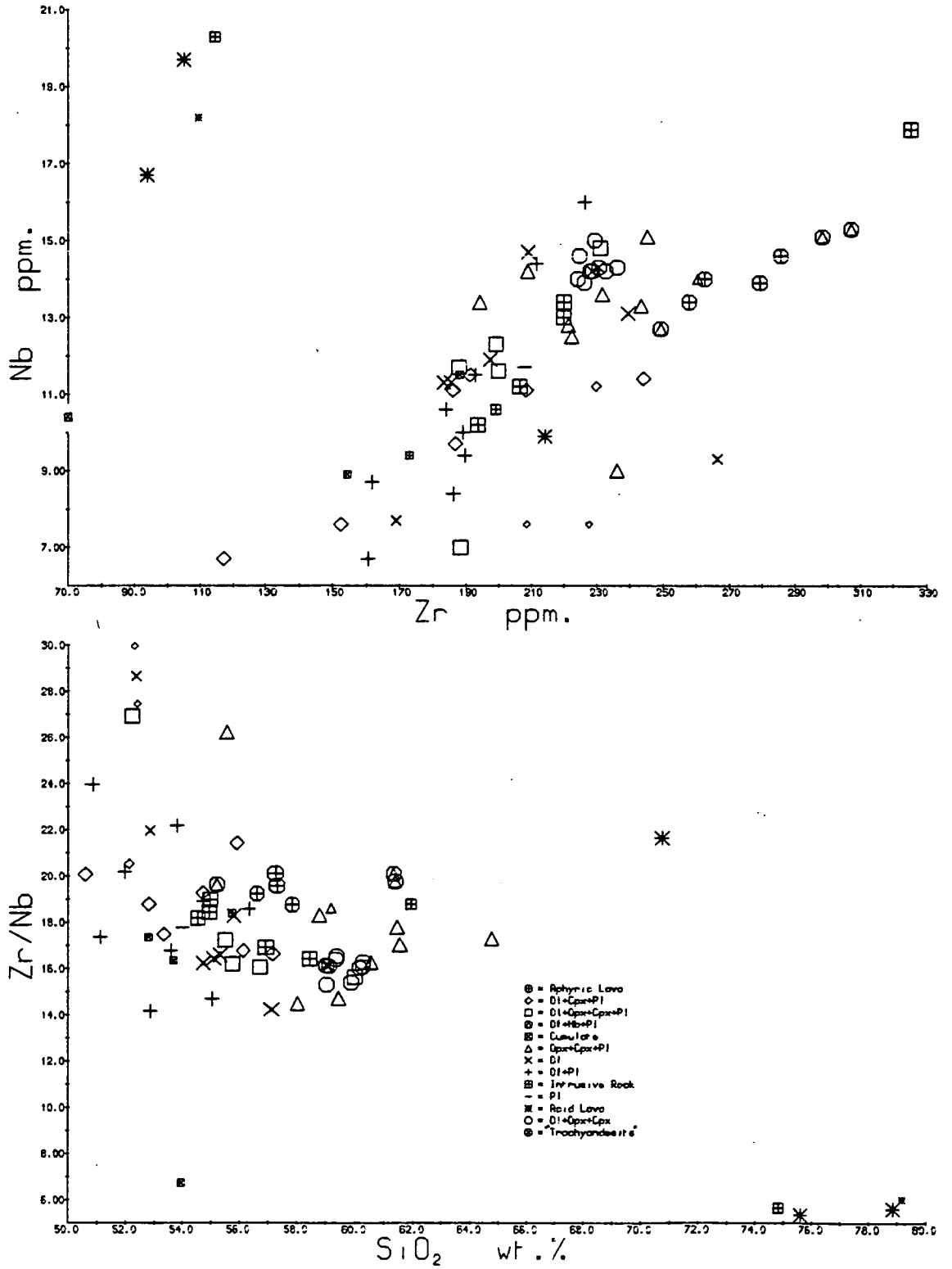
(a) Acid Lavas (@19)

The three acid lavas collected from the "dacites" of Geikie (1902), together with the Lucklaw Hill ?intrusion, also described by Geikie (1902) as a "dacite", have closely similar Zr/Nb, much lower than that of any other rock collected from the area. This is due to their low Zr content. Reduction of Zr/Nb with evolution by fractional

NORTH FIFE HILLS

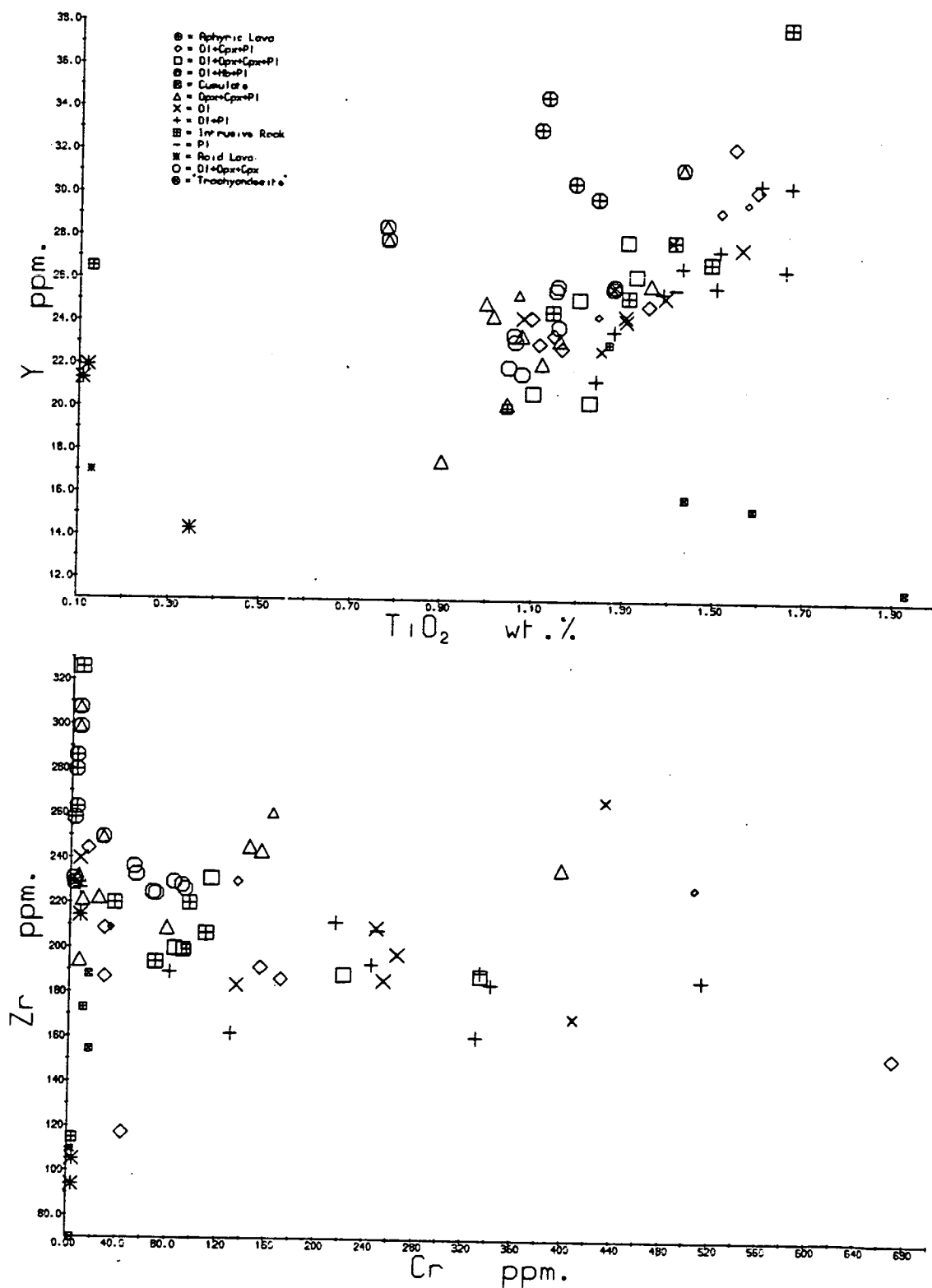
Fig. 5.8 a & b : Bulk rock variation diagrams

Conventions as section 3.3



NORTH PIPE HILLS

Fig. 5.8 c & d



crystallisation would require the separation of zircon (Pearce and Norry, 1979). This is believed to be a most improbable mechanism, for Zr contents of the rocks are low, and Th would probably also be substantially reduced by zircon separation. Further, no intermediate rocks exist in such a fractional crystallisation scheme, and therefore it is believed that the "dacites" may not be generated by fractional crystallisation of any of the more mafic lavas of the area. Within the group, excepting the more altered sample, Zn, Fe, Zr, Nb, Y and LREE all decrease slightly with increasing silica content. This variation may not be significant, however, for a small number of rocks probably affected by secondary silicification.

(b) Aphyric and Ol-hb-pl-phyric samples (a20, a38)

Both of these groups outcrop in geographically restricted areas. The lavas classified as aphyric are all from the horizon described as a sill by Geikie (1900), and have very rare phenocrysts of plagioclase and magnetite in a groundmass of subtrachytoid plagioclase with intersertal ortho- and clinopyroxene. The ol-hb-pl-phyric lavas are restricted to the top of the sequence near Auchtermuchty, and are again nearly aphyric, but are most unusual for the province in containing an abundance of coarse-grained xenoliths. Elsewhere the only inclusions in the lavas are medium-grained aggregates with mineralogy similar to that of their host rocks, which may be interpreted as autoliths; or rarely, inclusions of country rock (e.g. phyllites at Lorne

and shales in the Cheviot Hills). At Auchtermuchty inclusions are abundant and show great variety. The commonest contain large crystals of pseudomorphed amphibole, plagioclase (An50 zoned to An40), a low-Cr, low-Al titanomagnetite, pleochroic apatite and rare oxidised biotite, set in a sparse matrix of devitrified glass (anal. for OC88A, Table C2). Examples of this are OC88A and D, while OC88E is a finer-grained variety with the same mineral assemblage. The host lava is very altered, but contains phenocrysts of the same minerals with additional pseudomorphed olivine. The overlying flow is xenolith-free and in addition has phenocryst diopsidic augite, whose cores are Ti- and Al-rich relative to most of the other analysed clinopyroxenes, plotting in the alkaline field of Le Bas (1962). However, it should be noted that the host rock is no more 'alkaline' than many other samples from the North Fife Hills. The similarity of the inclusion mineral assemblage and the host rock phenocrysts suggests that the xenoliths are cognate.

Other xenoliths contain pseudomorphs after olivine, orthopyroxene and (?) clinopyroxene in addition to the phases noted previously, with the possible exception of biotite. Examples of these are OC88B and OC87A (not analysed); plagioclase in OC88B zones from An84 to An57, with the more sodic plagioclase rimming partly carbonated euhedral cores. These xenoliths are sometimes layered, and may be interpreted as fragments of a layered cumulate. Accidental xenoliths include a rounded fragment of

quartzite, most probably derived from underlying O.R.S. conglomerates, and a fragment containing large elongate alkali feldspar crystals in a coarse quartz-rich mosaic. No metamorphic fragments comparable to those described by Graham and Upton (1978) from a number of localities in Carboniferous volcanic rocks have been found either at Auchtermuchty or anywhere else in the Old Red Sandstone.

Relative to other rocks of the area with comparable MgO, both groups of lavas are low in K, Th, Rb, Ba, Ce, Ni, Cr, Sc and high in Al, Fe, Ca, P, Ti, Zr and Y: there are therefore some similarities with the "trachyandesites" elsewhere in the northern Midland Valley. While the two groups of lavas have many similarities, they do not belong on the same liquid line of descent: this is particularly clear on a Ti-Y diagram (Fig. 5.8c), where Y increases with evolution of the 'aphyric' lavas, but decreases with evolution of the ol-hb-pl-phyric samples. Three of the coarse-grained amphibole-rich cognate xenoliths from Auchtermuchty have been analysed in an attempt to identify a possible bulk fractionating composition. While the compositions of the three analysed show marked differences, especially for the more mobile elements, they are all much lower in Zr, Nb and Y than the host lava, and Zr/Nb is slightly lower, in accord with the suggestion of Chapter 3 that Zr/Nb should never decrease with fractional crystallisation unless zircon is involved. The xenoliths are also very poor in Ni and Cr, which, since they contain phases with high crystal-liquid distribution coefficients

for these elements, implies that they crystallised from Ni- and Cr-poor magmas, such as their host rocks, but not OC86. It is clear from Fig. 5.8c (Ti-Y) that fractional crystallisation of the assemblage represented by these xenoliths could not generate the chemical variation of the ol-hb-pl-phyric rocks.

In contrast, the Y/Ti variation for the 'aphyric' lavas intersects the field of the xenoliths, and their variation in Ti-Y-Nb-Zr could be explained by fractional crystallisation of the xenoliths. This is not true for P, however, and it is unlikely that the assemblage of the xenoliths could crystallise from the 'aphyric' lavas. The four samples of 'aphyric' lava may be separated chemically into two pairs: in OC97 and OC99 V is much lower (60 ppm) and P_2O_5 substantially higher (0.6%) than in OC80 and 95 (115 ppm and 0.44% respectively). Other differences are: Higher in 99 and 97: Na, Mn, Nb, Zn, Zr, Y, Nd, Zr/Nb, K/Rb, and possibly Ce, La and Sr.

Lower in 99 and 97: Ni, Sc, Ti, Ca, Al, Cu, Ba, K, Rb and possibly Th.

OC97 and 99 appear to be the most evolved: if the evolution is to be explained by fractional crystallisation then biotite must be a major crystallising phase. This is thought improbable for reasons previously stated, and in particular because it is unlikely that biotite would crystallise from a magma poor in K relative to many others in the area. The Auchtermuchty xenoliths are therefore probably only related to their host rocks, and have no

general significance, for there are no rocks which could be generated by separation of these xenoliths from a parental magma. No layered olivine-bearing xenoliths of sufficient size for analysis have been found, and it is possible that these would have more petrogenetic significance.

(c) Ol-opx-cpx-phyrlic samples (29)

Rocks with this phenocryst association, together with the two North Fife "trachyandesites", outcrop on both sides of the Tay, and their close chemical similarity suggests that direct correlation could be made across the Tay. These two groups are relatively low alumina, high Cr, Ni rocks, contrasting with the "trachyandesites" of the rest of the Midland Valley. While chemically closely similar, they still display an unsystematic internal scatter for many elements (e.g. Fig. 5.8c), and it is thought most unlikely that they could be derived by fractional crystallisation of the same parent.

(d) Dundee Intrusions

The rocks of the intrusions around Dundee have between 54 and 59% silica, and show a range in Zr/Nb between the two groups described above. Even at constant Zr/Nb there is substantial chemical variation e.g. between OC137 and OC150. It is again thought that they are not very closely related.

(e) North Fife Hills : Conclusions

The Old Red Sandstone volcanic rocks of the North Fife Hills are similar to those throughout the northern Midland Valley. Again they display very varied petrography and chemistry, particularly well expressed by variation in Zr/Nb. General correlations exist between many elements and silica or MgO, but scatter on variation diagrams is probably the result of superposition of a number of chemically coherent rock groups. Identification of these groups is not practical and, by analogy with the Montrose region, it is believed that very few compositions could be related by fractional crystallisation processes. The unusual occurrence of xenoliths of cumulate appearance at Auchtermuchty probably has no general petrogenetic significance.

In previous sections the possibility of generating high alumina basalt by separation of olivine and clinopyroxene from olivine-tholeiite has been discussed. In the North Fife Hills there exist a number of high alumina basalts with high MgO, Ni and Cr. Most prominent amongst these are OC102, with 17.5% Al_2O_3 , 183 ppm Ni and 330 ppm Cr, and OC85, which, if they represent liquid compositions, require the existence of primitive high-alumina magma. It is difficult, however, to rule out the possibility of plagioclase accumulation in either of these samples.

5.5 : NORTH MIDLAND VALLEY : CONCLUSIONS

The Old Red Sandstone volcanic rocks of the northern Midland Valley show great variety in detailed chemistry, but there are many broad petrochemical features in common between the several outcrop areas.

(a) Mineral Chemistry and Petrography

Most clinopyroxenes analysed from rocks of the northern Midland Valley are diopsidic augites low in Na, Ti and Al, very similar to those analysed from the SW Highlands. Variation between phenocrysts in a single rock is often large; while a few analysed points have Ti and Al concentrations within the alkaline field of Le Bas (1962), the vast majority are subalkaline (Fig. 5.9b). Pyroxene Ti and Na show broad correlation with their host rock chemistry (e.g. Fig. 5.9a), but it is believed that the Ti, Na, Al content of a particular pyroxene was mainly controlled by localized melt heterogeneities produced during rapid crystallisation. Fs content does not increase systematically with host rock silica (Fig. 5.9d), although there is a broad correlation with host rock $\text{FeO}/(\text{FeO}+\text{MgO})$. The small variation in Fs content of clinopyroxene, and the generally bronzitic composition of orthopyroxene (Fig. 5.9c), even in siliceous rocks, suggest that the host rocks are of calc-alkaline rather than tholeiitic affinities. The few fresh olivines are Mg-rich, with the exception of that from a small gabbroic intrusion near Glenfarg.

**Fig. 5.9 a & b : Phenocryst chemistry of North Midland Valley
O.R.S. volcanic and intrusive rocks.**

a = clinopyroxene TiO_2 as a function of host rock TiO_2

b = clinopyroxene TiO_2 and atomic tetrahedral Al

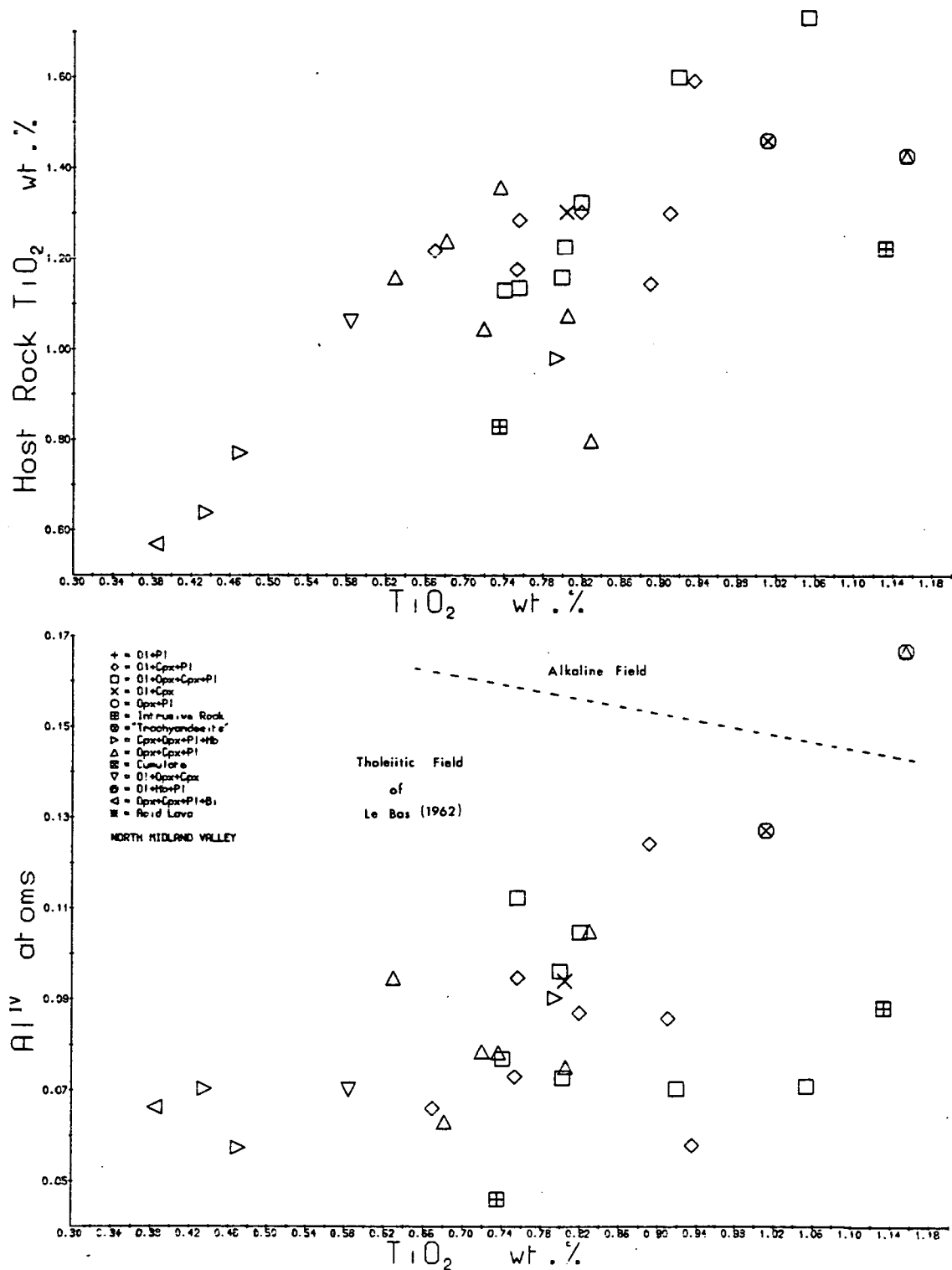


Fig. 5.9 c & d.

c = atomic Ca, Mg, Fe for pyroxenes, olivines and amphiboles

d = the composition of clinopyroxene as a function of host.

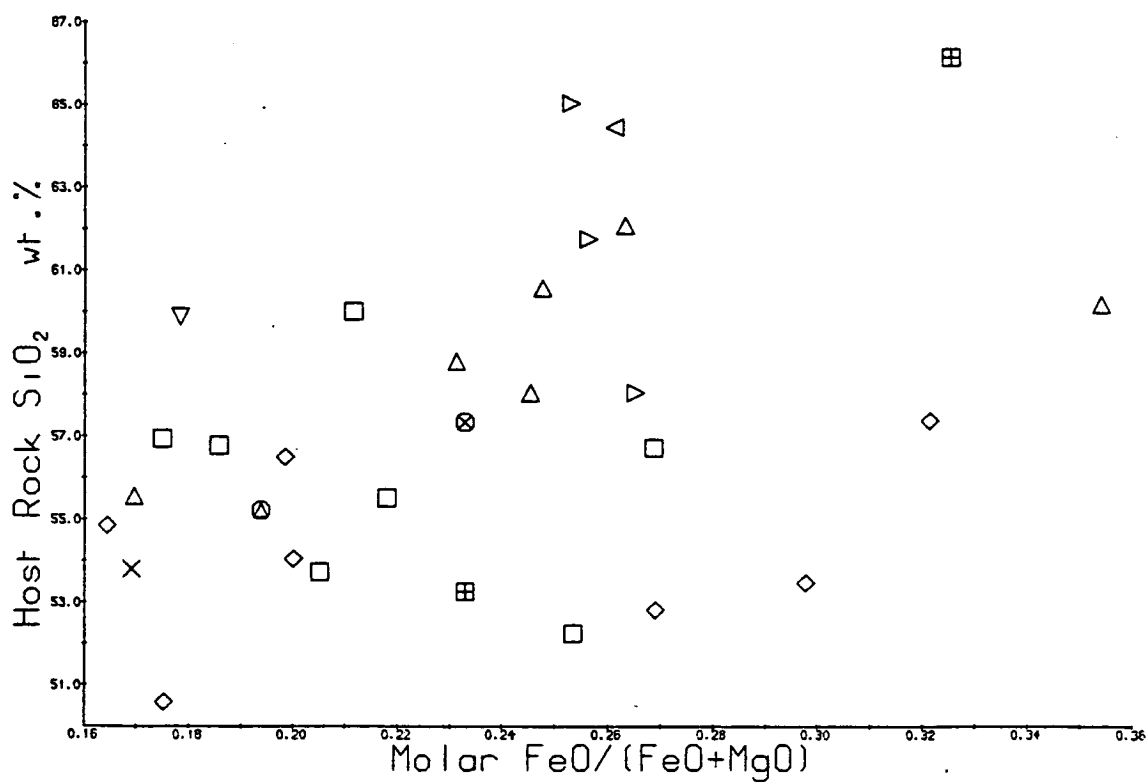
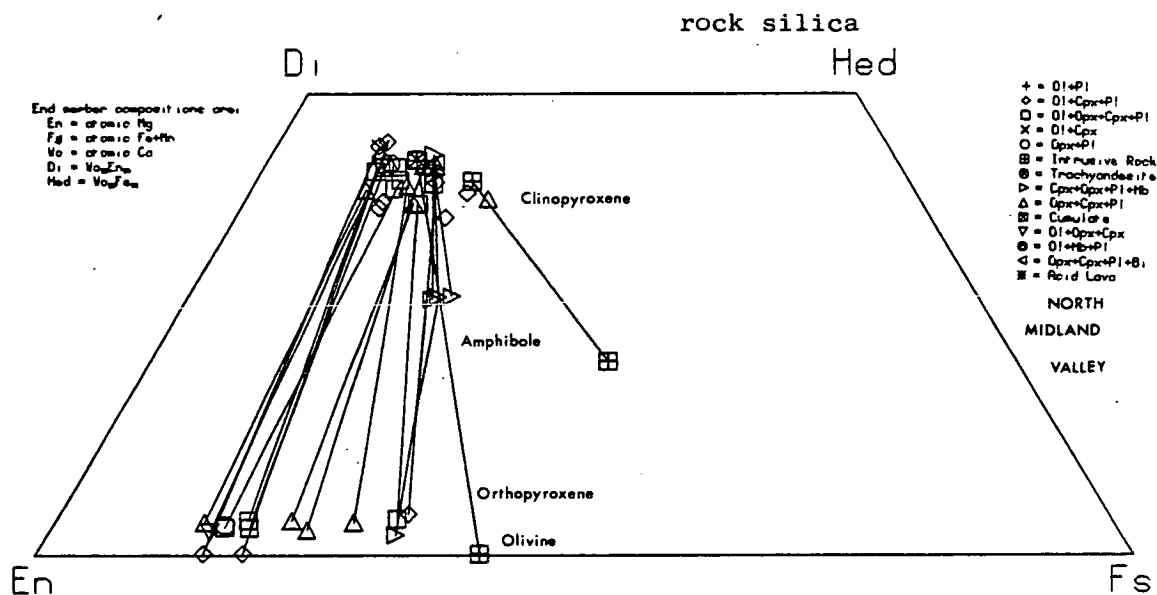
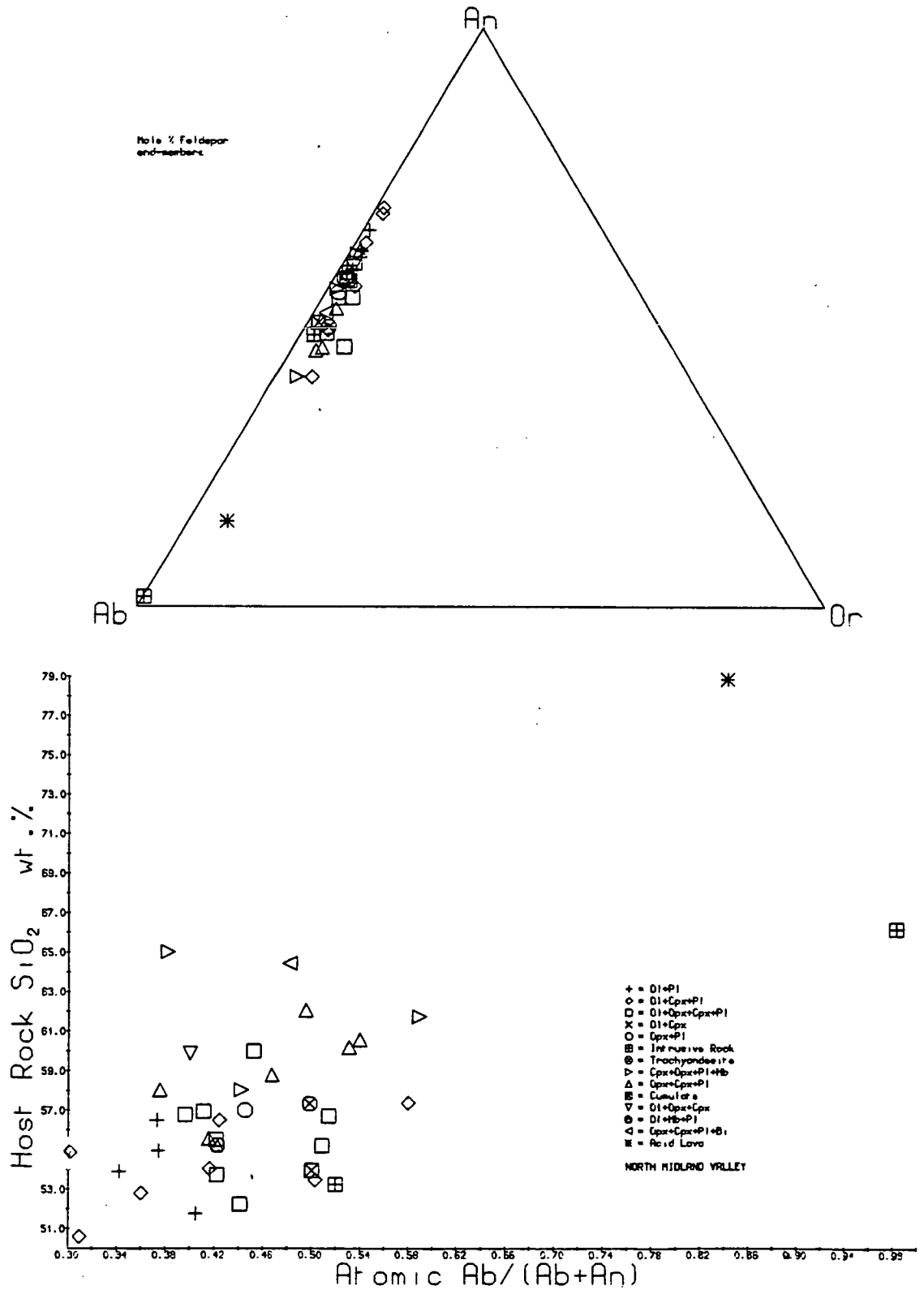


Fig. 5.9 e & f

e = plagioclase end-members

f = the composition of plagioclase as a function of host
rock silica

Most of the rocks analysed contain phenocryst plagioclase, contrasting with the rocks of the SW Highlands. This is generally labradorite-andesine, and its composition shows little correlation with host rock silica content (Fig. 5.9f). Or content of plagioclase may be related to host rock potash or to coexistence with K-rich phases, so that the plagioclase from hornblende- and biotite-bearing andesites generally has lower Or (Fig. 5.9e). Spinel is Cr-, Al-poor titanomagnetite, although those from OC152 contain up to 10% Cr_2O_3 .

(b) General Chemical Characteristics

Very few of the rocks analysed have normative nepheline, and, when they do, it is probably always due to the secondary introduction of calcite. The rocks are dominantly quartz-normative, although a few are mildly olivine-normative. Rocks with >62% silica are often peraluminous. Most rocks have low Fe/Mg, and only a very small number plot outside the calc-alkaline field of Miyashiro (1974). The inference that the lavas are calc-alkaline is further supported by the high-alumina nature of many. The lavas all have high concentrations of LIL and high field strength elements, and vary between calc-alkaline and shoshonitic on the classification of Peccerillo and Taylor (1976). Many rock analyses compare closely with average data from several continental margin calc-alkaline suites reported by Ewart (in press).

While a wide range in silica concentrations is represented in the region, most rocks have less than 60%. This is particularly true for the North Fife and Sidlaw Hills and for the Montrose area, but acid andesites are not uncommon in the Western Ochil Hills. This latter area and the Sidlaw Hills are poor in very Ni-, Cr-rich rocks relative to the other two, although such rocks do exist in all areas. These rocks can not have undergone much separation of mafic mineral phases since derivation from a mantle source region.

(c) Constraints on Petrogenetic Models

It is clear from the variation diagrams that the different rock-types can not be related by a single petrogenetic process. In particular, the great variation in relative and absolute amounts of LIL and high field strength elements shows little correlation with concentrations of elements compatible in mafic mineral phases, and can therefore not be due to multistage fractional crystallisation processes. The origin of some small groups of rocks by fractional crystallisation of a range of parental Ni-, Cr-rich magmas is however possible. For example, the siliceous, Cr-rich bronzite-andesites may have been generated by separation of plagioclase, while the Ni-, Cr-poor high-alumina samples may have been generated by separation of mafic mineral phases. For both of these however, magmas with sufficiently low concentrations of LIL elements to be parental are absent or very rare. Arguments

based on volume relations therefore suggest that many low-Ni, -Cr lavas may therefore be only slightly modified primitive melts, for large quantities of more mafic magmas not parental to these were able to reach the surface. It remains possible that all low-Ni, -Cr samples were derived by fractional crystallisation of mafic magmas essentially unrepresented at the surface.

The following hypotheses are possible:

1/ Most of the lavas seen at the surface are primary melts only slightly modified by fractional crystallisation during ascent, whose LIL and high field strength element geochemistry implies variation in source composition (Zr/Nb ratio), and probably also variation in degree of partial melting, nature of residuum etc. This requires an extremely heterogeneous mantle, and generation of the large volume of rocks very rich in LIL elements would require a very incompatible element-enriched mantle or the coalescence of melts from unreasonably large regions of mantle (section 4.4).

2/ The Ni-, Cr-, Mg-rich lavas seen at the surface are only slightly modified primary melts as before, but others are products of the fractional crystallisation at crustal levels of magmas not represented among the more mafic lavas of the area. This would imply the existence in the same area of large volumes of varied mafic magmas which fractionally crystallised and never reached the surface, and of further large volumes of varied mafic magma which reached the surface but did not undergo high level fractional

crystallisation. Those magmas which did not reach the surface must have been much poorer in LIL and high field strength elements than observed mafic lavas and therefore, since exposed mafic lavas may have high LILE content, the variation in LILE of primary melts must have been very large, and the mantle source much more heterogeneous in LILE than required by the first hypothesis. Neither of these hypotheses is therefore satisfactory.

3/ Variation in LILE and high field strength elements may have been superimposed on a small range of major element compositions by processes such as contamination or magma mixing. The major element compositions may have been generated by fractional crystallisation of a single parent magma, or may themselves represent only slightly modified primary magmas. In the latter case, equilibration with mantle can not have occurred for the more siliceous lavas, and in the former several different fractional crystallisation paths are required to generate the variety of major element-Ni-Cr compositions observed. These difficulties may be easily overcome by allowing some modification of major element chemistry by the contamination, although the most attractive feature of the hypothesis is the use of a contaminant enriched in LIL and high field strength elements to provide the high concentrations of these in the northern Midland Valley lavas.

There are strong parallels with the chemistry of the SW Highland lavas, for which three controlling processes

were inferred (section 4.4) on the basis of correlations between LIL and high field strength elements. Similar positive correlation exists in the north Midland Valley lavas (Fig. 5.10), both among Ni- and Cr- rich lavas of the whole region, and for most rocks in the individual outcrop areas. Few of these correlations are very good, and a simple binary contamination model is most unlikely. Positive correlations of note include $\text{SiO}_2\text{:La/Y}$, Zr:Nb , K:Rb , K:Ba , Sr:Ba , Sr:La/Y , Ti:Y and also Ce+La+Nd:Zr . The $\Sigma\text{LREE:Zr}$ correlation is in contrast to the lack of correlation between Ce and Zr at Lorne. There may also be negative correlation between Sr and Y.

Positive correlations between these elements can not in general be explained by fractional crystallisation of mafic mineral phases, for enrichment in LILE is unrelated to depletion in Cr. Some scatter on diagrams involving Sr may be attributed to fractional crystallisation of plagioclase, but scatter on Zr-Nb and $\Sigma\text{LREE-Zr}$ diagrams implies that the contamination process was not binary, for Zr/Nb and Ce/Zr show much variation at constant Zr. No correlation between Zr/Nb and other parameters has yet been found.

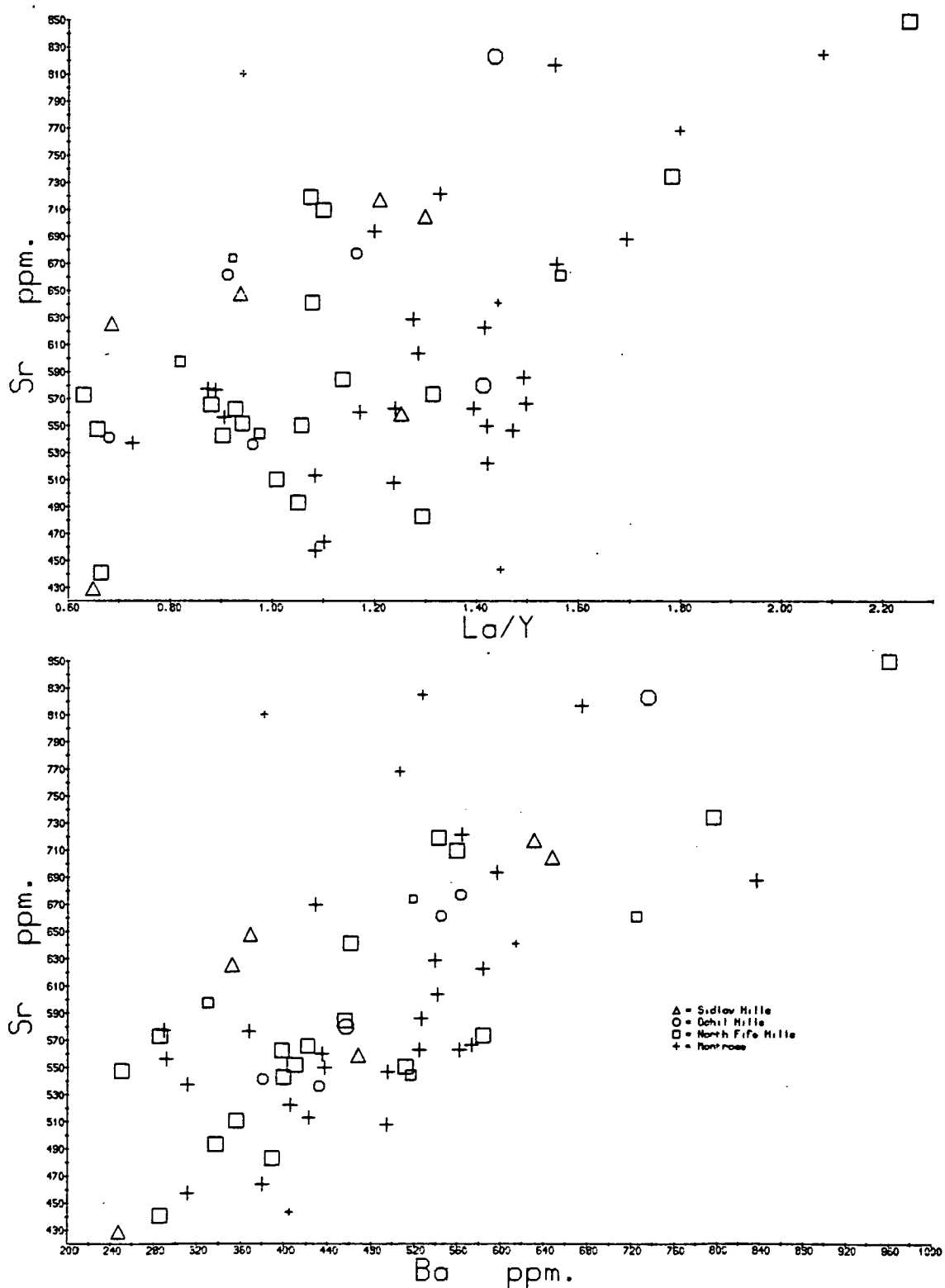
No evidence for the origin of the contaminants is yet available from isotopic work. The resemblance of the correlations between LIL elements in the north Midland Valley rocks to those in the ol- and ol-cpx-phyric rocks of Lorne strongly suggests that the same process gave rise to variation in LILE concentrations in both regions. Since the

low initial $^{87}\text{Sr}/^{86}\text{Sr}$ from Lorne implies a mantle origin for the Sr, it would be reasonable to infer that the concentrations of LILE in the northern Midland Valley rocks also have a mantle origin. It follows from this inference, and the discarding of hypothesis 2, p. 163, that a number of quite silica-rich magmas were present in the mantle prior to contamination with LILE.

The Old Red Sandstone volcanic rocks of the Northern Midland Valley are a calc-alkaline to shoshonitic suite with high concentrations of LIL and high field strength elements, and in many rocks, high Ni and Cr. The latter rocks can have undergone little fractional crystallisation of mafic minerals since separation from a mantle source, and there is evidence to suggest that many low Ni, Cr lavas may also not have suffered much fractional crystallisation. Enrichment and variation in incompatible element concentrations and ratios may best be explained by a complex contamination process, possibly involving contamination in both mantle and crust.

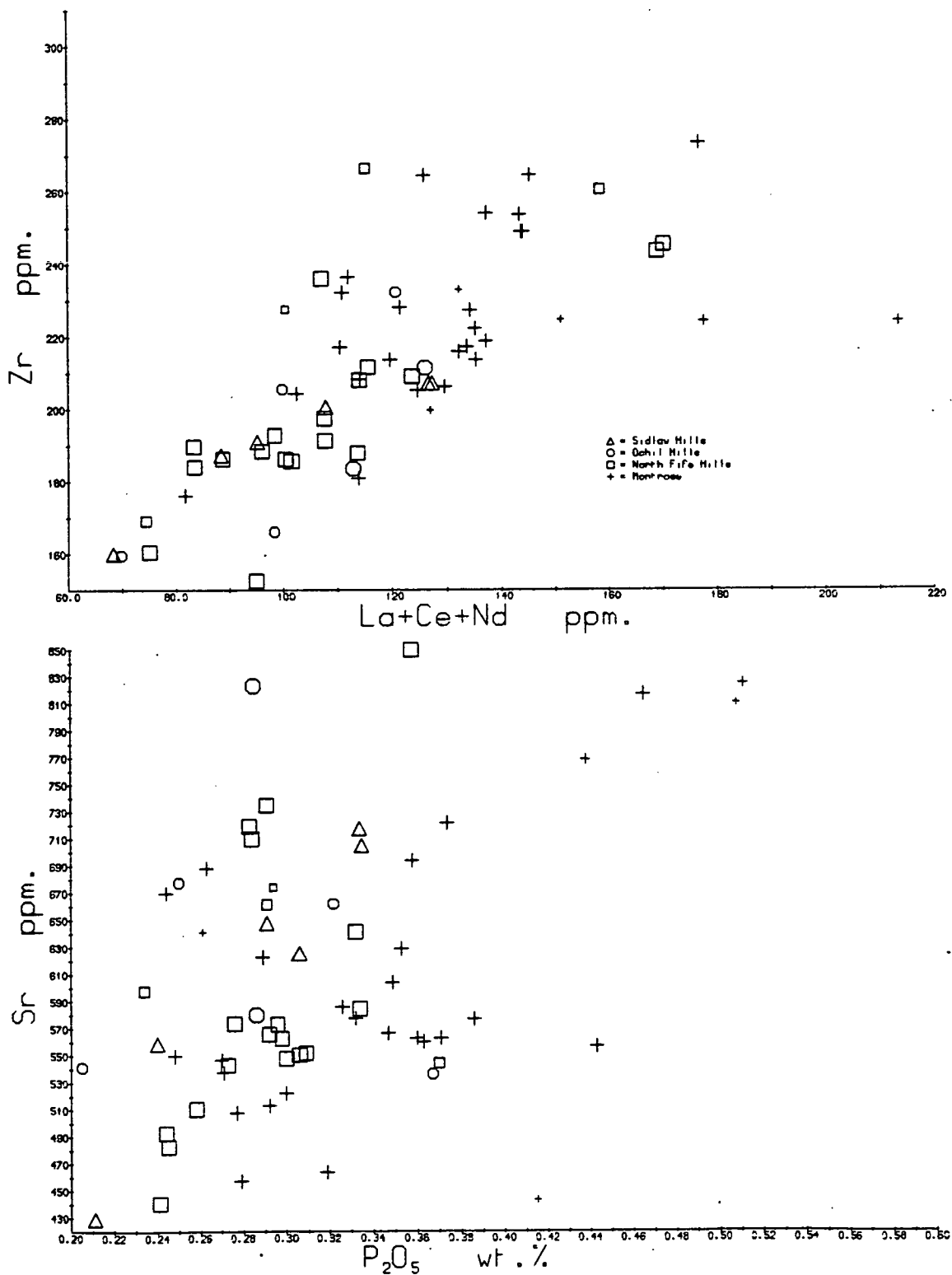
NORTH MIDLAND VALLEY

Fig. 5.10 a & b : Some relationships between LIL and high field strength elements in North Midland Valley O.R.S. igneous rocks. All samples plotted have >80 ppm. Ni and >140 ppm. Cr. Conventions as section 3.3



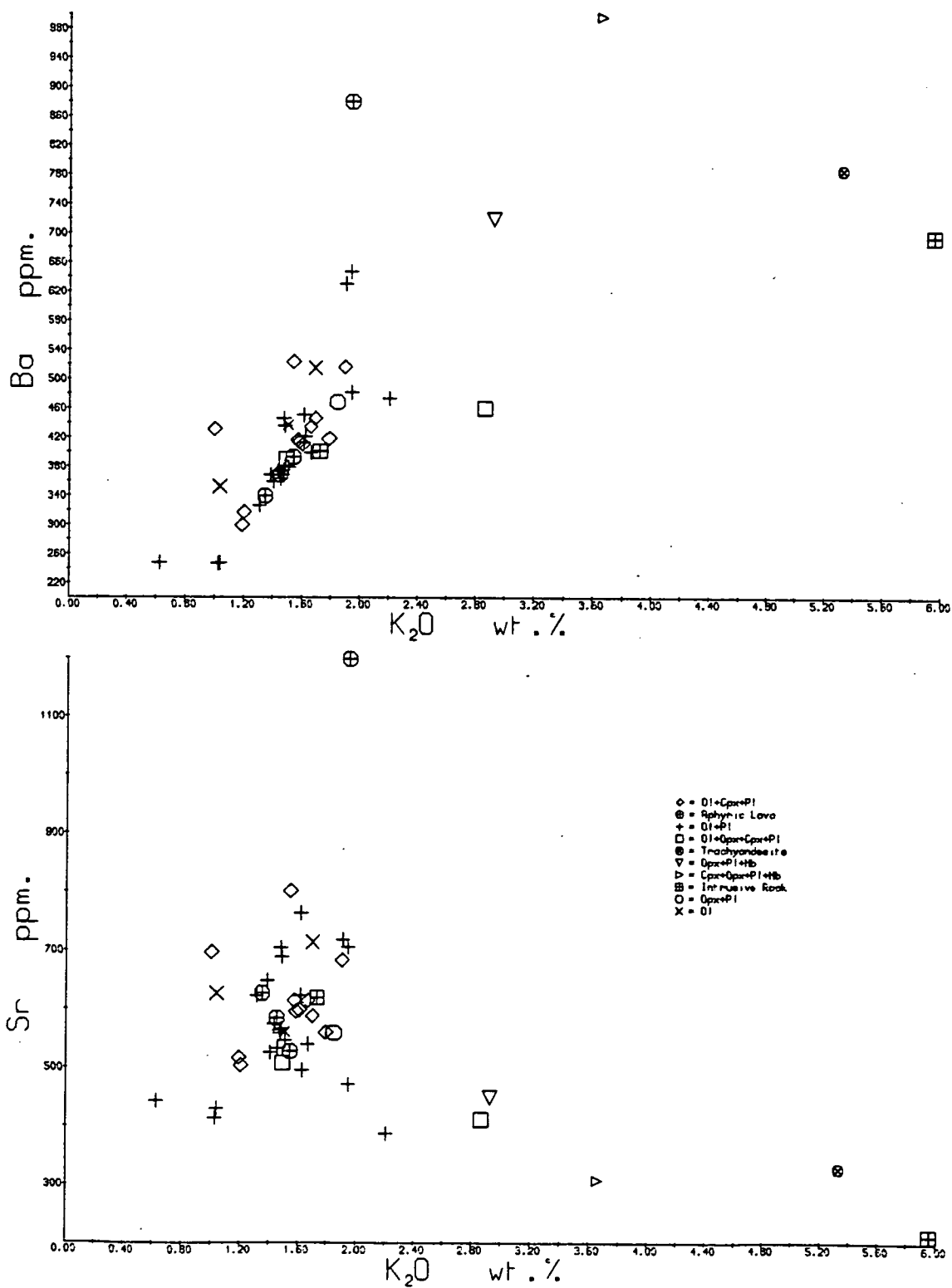
NORTH MIDLAND VALLEYFig. 5.10 c & d

All samples plotted have >80 ppm. Ni and >140 ppm. Cr.



SIDLAW HILLSFig. 5.10 e & f

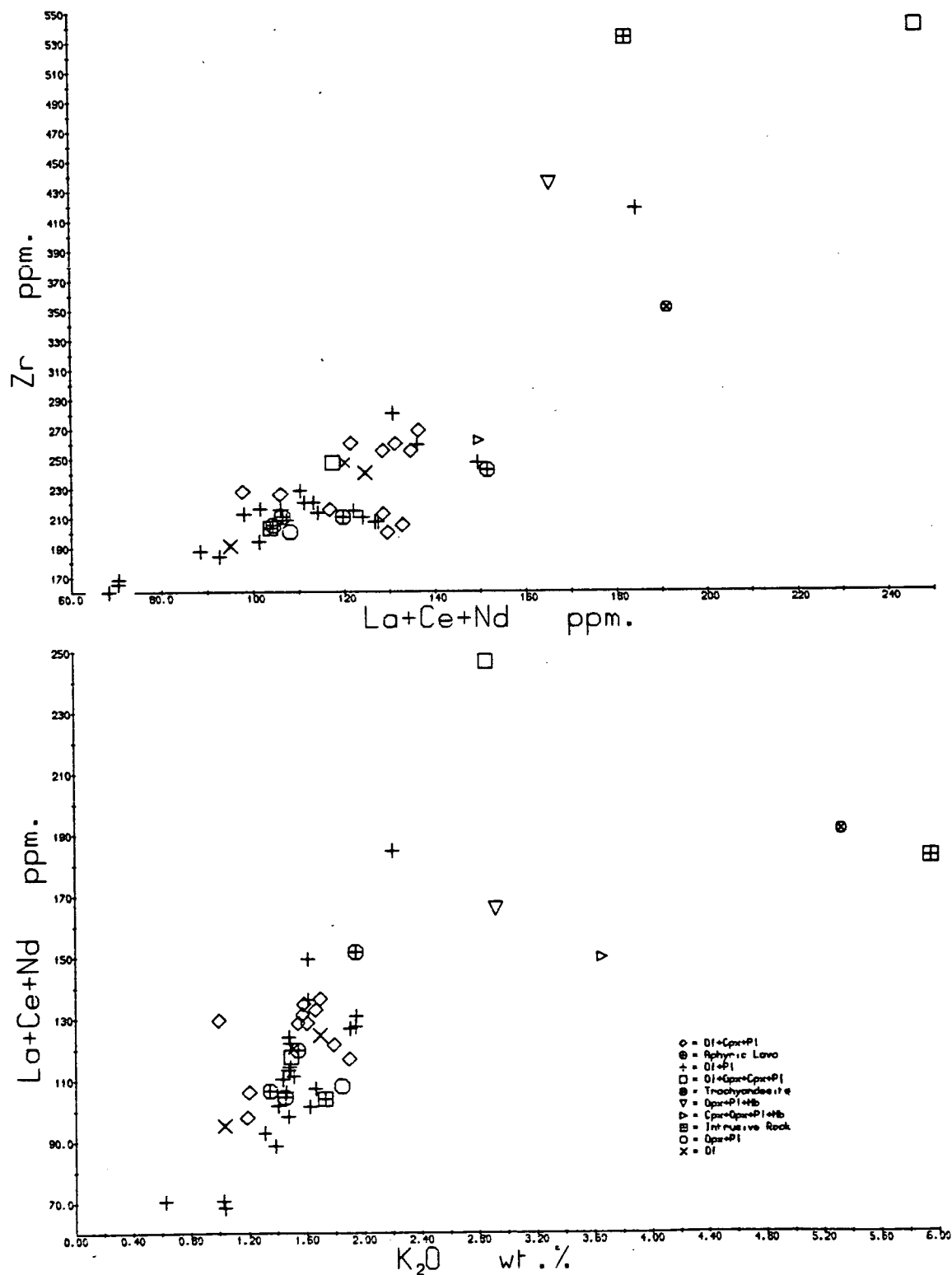
Full sample population from Sidlaw Hills is plotted.



SIDLAW HILLS

Fig. 5.10 g & h

Full sample population from Sidlaw Hills is plotted.



CHAPTER 6 : SOUTH MIDLAND VALLEY

The Lower Old Red Sandstone rocks of the southern Midland Valley outcrop discontinuously in a range of hills just north of the Southern Uplands Fault. In the NE Lower O.R.S. conglomerates rest unconformably on a sequence of sandstones and mudstones, some of continental facies, which may possibly all be of pre-Wenlock age (Mitchell and Mykura, 1962). Further SW, Lower O.R.S. rocks appear to rest conformably on the Silurian rocks of the Lesmahagow and Hagshaw Hills inliers (M. Gallagher, pers. comm., 1979), where again continental facies sediments occur higher in the Silurian sequence, and the youngest graptolite fauna recovered is upper Llandovery. Further SW in Ayrshire, the Lower O.R.S. rests unconformably on Ordovician strata. Throughout the region, Upper Old Red Sandstone and Carboniferous sediments rest unconformably on the Lower O.R.S.

The region is structurally more complex than the regions previously discussed, and the Lower O.R.S. is much folded and faulted, in particular close to the Southern Uplands Fault. The volcanic rocks of the Pentland Hills and of the Carrick Hills in Ayrshire are only gently inclined, and Mykura (1960) and Eyles et al. (1949) have described stratigraphical sequences in these areas, with total thicknesses of volcanic rocks in excess of 6000 ft (2000 m) and 1500 ft (500 m) respectively. Thicknesses of volcanic rocks in the smaller discontinuous outcrops close to the

Southern Uplands Fault or in the small region west of Distinkhorn are not known, but in some areas these must be well in excess of 1000 ft (300 m.; e.g. near Biggar). The rocks of these areas have been described by Geikie (1897) and by Richey et al. (1930). The volcanic rocks of the region can easily be divided into a number of outcrop areas, and each area could be treated separately, but unfortunately, with the exception of the Ayrshire Coast, exposure is very poor throughout the region and the rocks in many exposures are too severely altered to be suitable for detailed petrochemical study. The region has therefore been divided into the two areas of Ayrshire and the Pentland Hills; the former includes the Carrick Hills and the areas near Distinkhorn and Straiton, and is separated by some very poorly exposed ground near Dalmellington from the most southwestern of several discontinuous outcrops assigned to the Pentland Hills.

6.1 : THE PENTLAND HILLS

The stratigraphy and petrography of the volcanic rocks of the Pentland Hills (sensu stricto) have been described by Mykura (1960) and Peach et al. (1910). These authors have separated the sequence into a number of groups characterized by being dominantly basic, "trachytic", or acidic. The sequence dips gently SE and is overlain by westward-dipping Upper O.R.S. and Carboniferous sediments in the west. The top of the volcanic sequence is cut off by the Pentland Fault in the east, although rocks to the north

of the main hill-range are thought to be at a higher horizon (Mitchell and Mykura, 1962). None of the subdivisions of the Pentland sequence can be traced further SW than Carlops. The volcanic rocks and underlying Silurian are cut by a number of intrusions, of which the Lyne Water Diorite and the Tinto and Black Hill Felsites are the largest. Mykura (1960) suggested that the Black Hill Felsite could have been an extrusive dome.

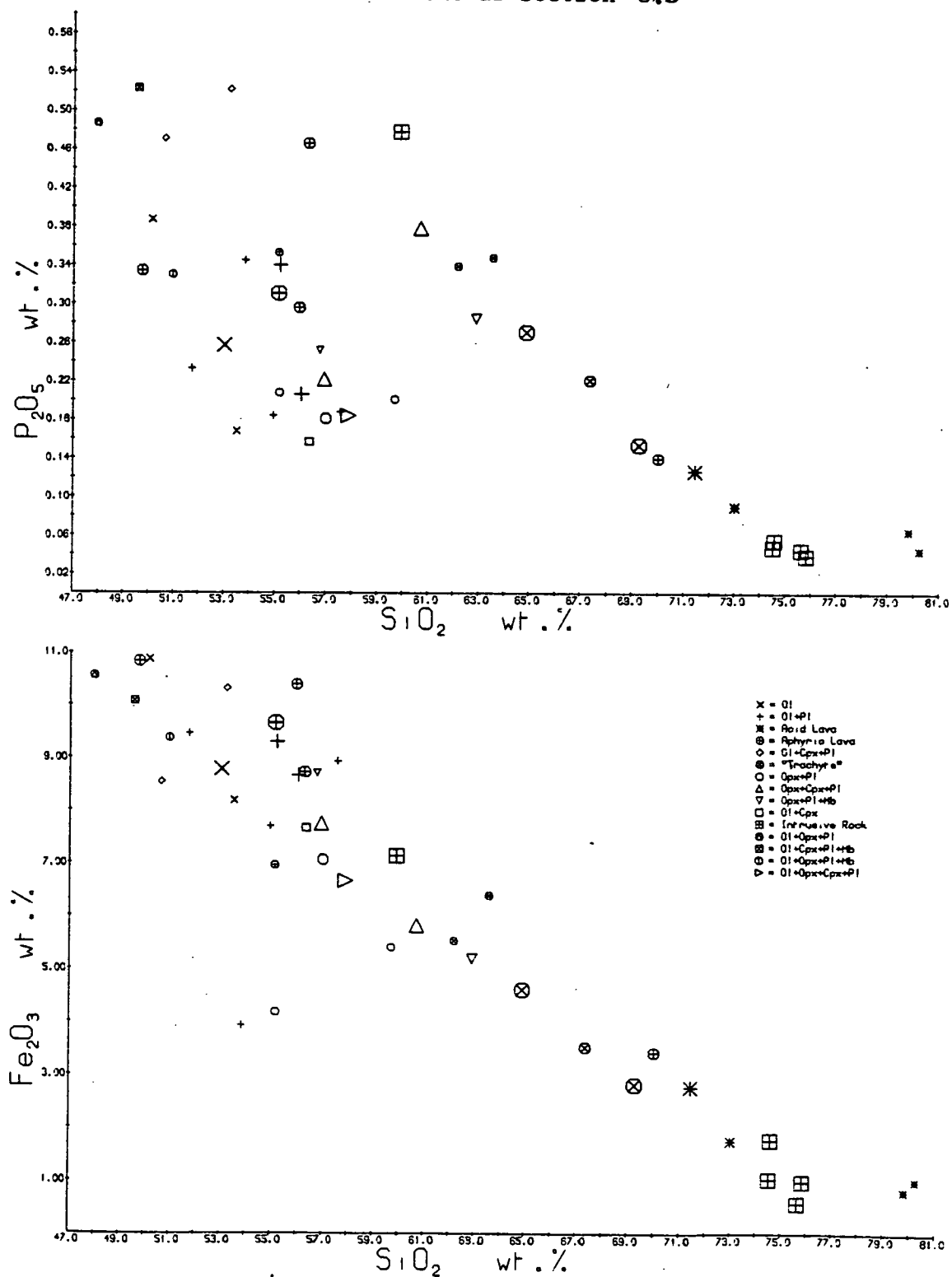
The volcanic sequence is mainly composed of lava flows, although acid pyroclastic horizons are not uncommon, particularly near West Linton. A wide range of lava lithologies has been observed among the samples collected, and, since exposure is poor and degree of alteration high, it is likely that these form only a small part of the range actually present. Most of the samples collected are closely comparable with lithologies present in the northern Midland Valley, although basic samples lacking phenocryst plagioclase are more common in the Pentland Hills, as are acid rocks, while rocks with phenocryst clinopyroxene are relatively rare. Phenocryst compositions are closely comparable to those in the north Midland Valley.

Samples from the Pentland Hills show a comparable chemical range to that described from the northern Midland Valley, with large scatter on most variation diagrams (Fig. 6.1). The occurrence of rocks with silica as low as 47% is in contrast to the 50% minimum of the north Midland Valley, while rocks with silica >60% are not uncommon. A number of

PENTLAND HILLS

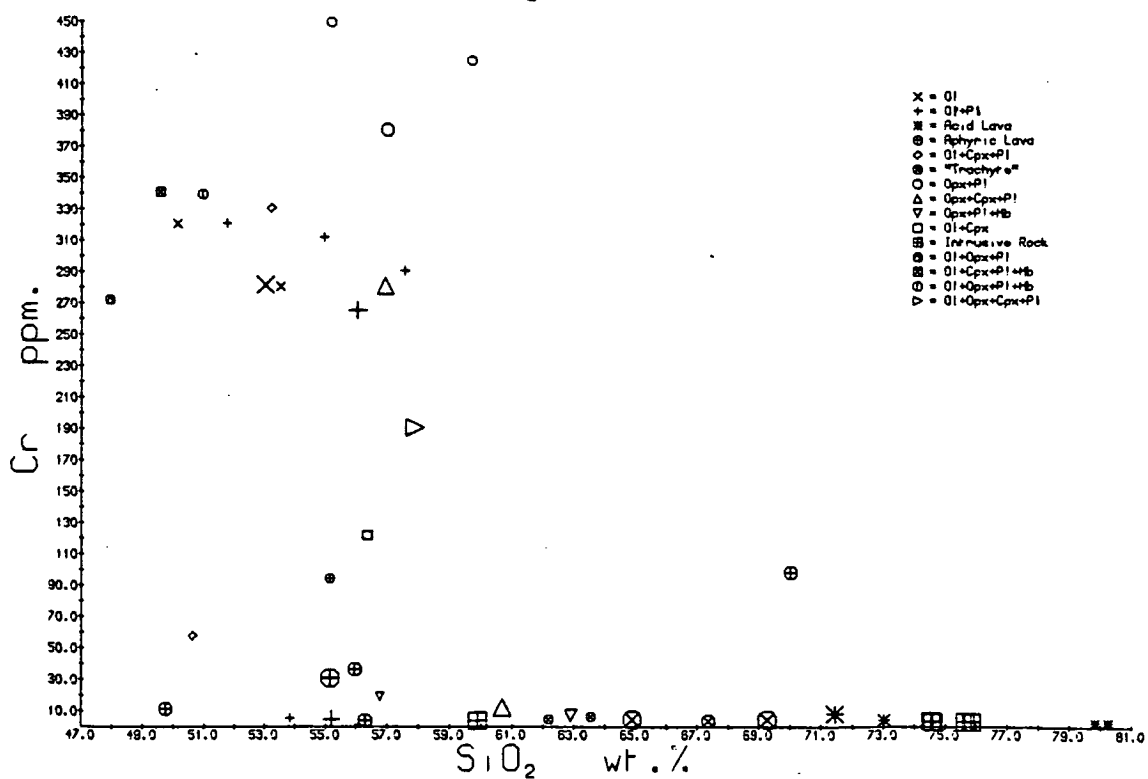
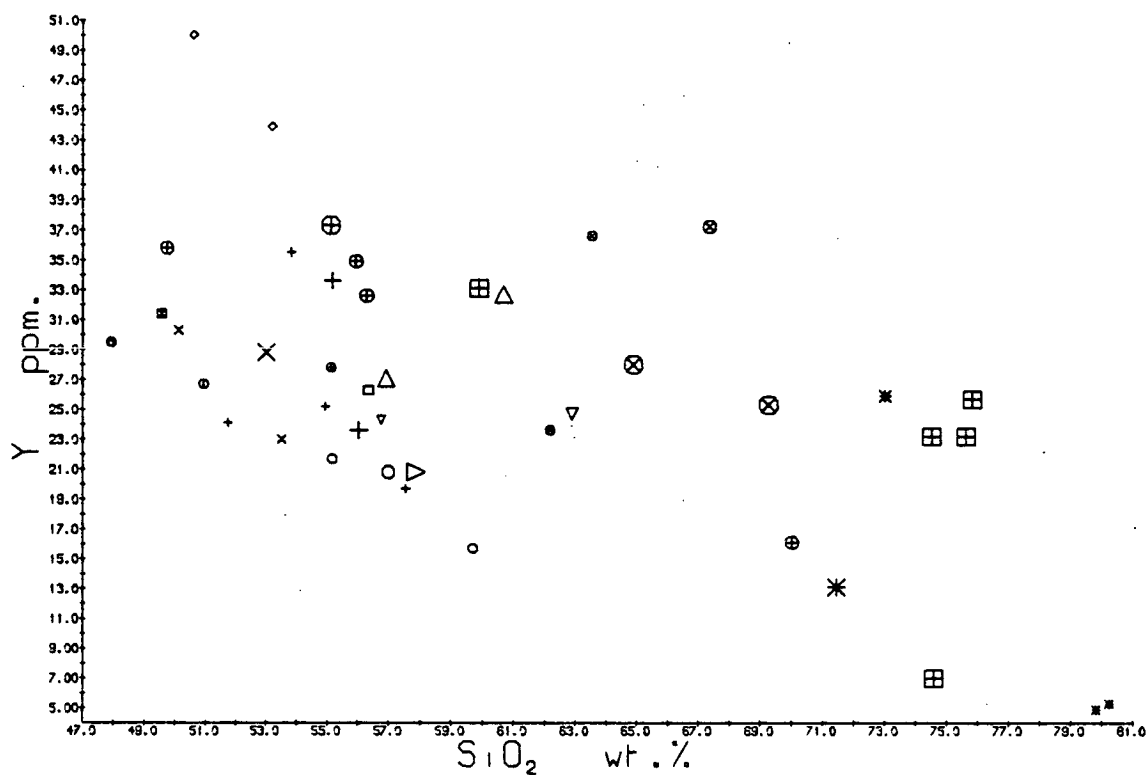
Fig. 6.1 a & b : Bulk rock variation diagrams

Conventions as section 3.3



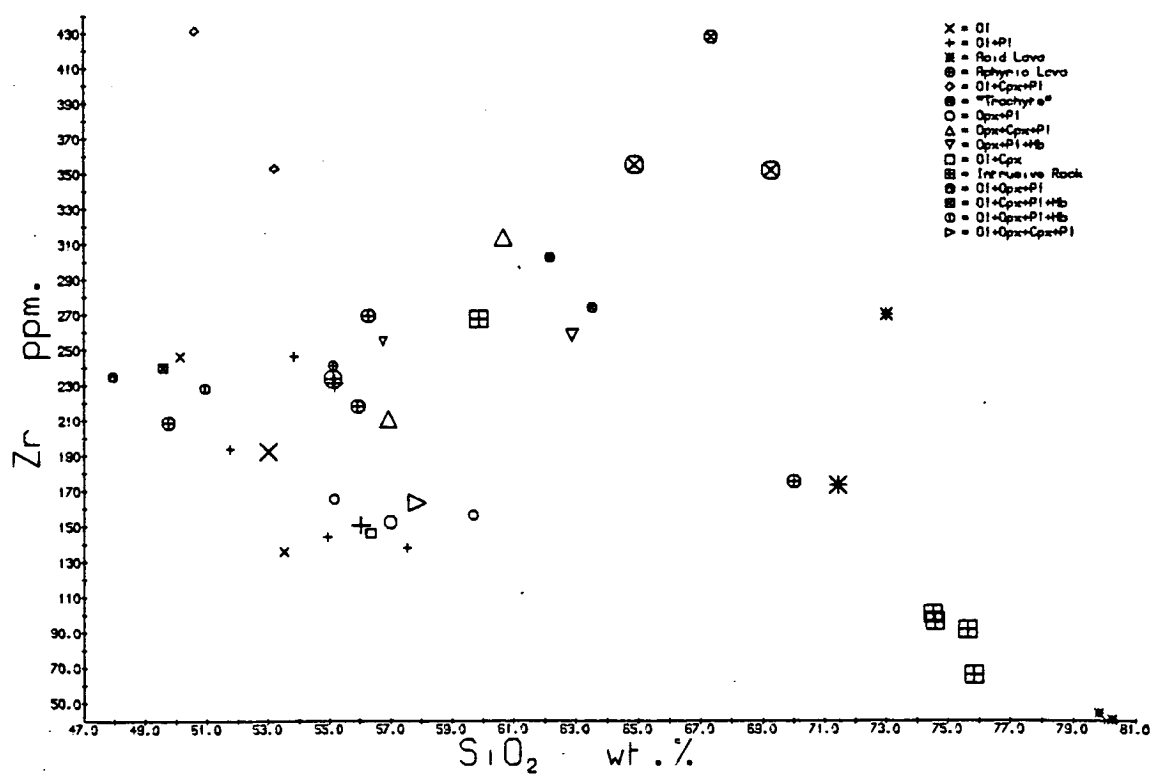
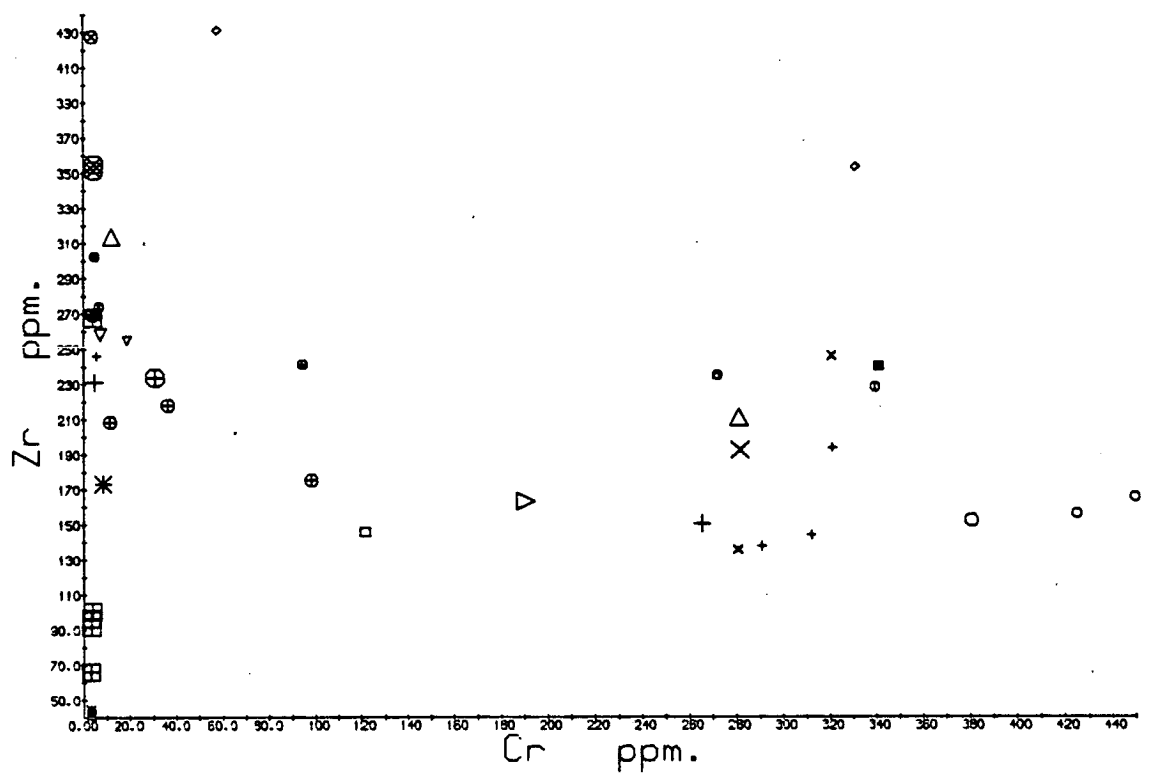
PENTLAND HILLS

Fig. 6.1 c & d



PENTLAND HILLS

Fig 6.1 e & f



rocks are strongly nepheline-normative, but these all show high LOI and CaO, and the nepheline can be attributed to introduction of calcite on alteration. Only one relatively fresh rock (PE5) has normative olivine. Basic rocks include both moderate- and high- alumina types, and Ni and Cr may be high in both. LIL and high field strength elements show much variation unrelated to SiO₂, MgO or Cr concentrations, but concentrations of LIL elements in many rocks are closer to typical calc-alkaline values (Jakeš and White, 1972) than in rocks from further north. Zr/Nb varies between 12 and 32 in basic rocks, and shows no systematic variation with Cr content. There does not appear to be any relationship between chemistry and position in the stratigraphic succession of Mykura (1960), and the data available suggests that the Allermuir Group, at least, does not have any distinctive chemical features, but itself shows great variety. The arguments discussed in sections 5.1(i) and 5.5 again apply, and suggest that no extensive liquid line of descent generated by fractional crystallisation or partial melting exists among the rocks of the Pentland Hills and areas to the SW.

The occurrence of three andesites (PE14-16, 55-60% SiO₂) comparable to the bronzite-andesites of the north Midland Valley is notable. These are the most Cr-rich rocks in the area (370-450 ppm) and are also very Ni-rich (150-250 ppm), and presumably have similar petrogeneses to the north Midland Valley bronzite-andesites. It is unlikely that these rocks could be related by fractional crystallisation,

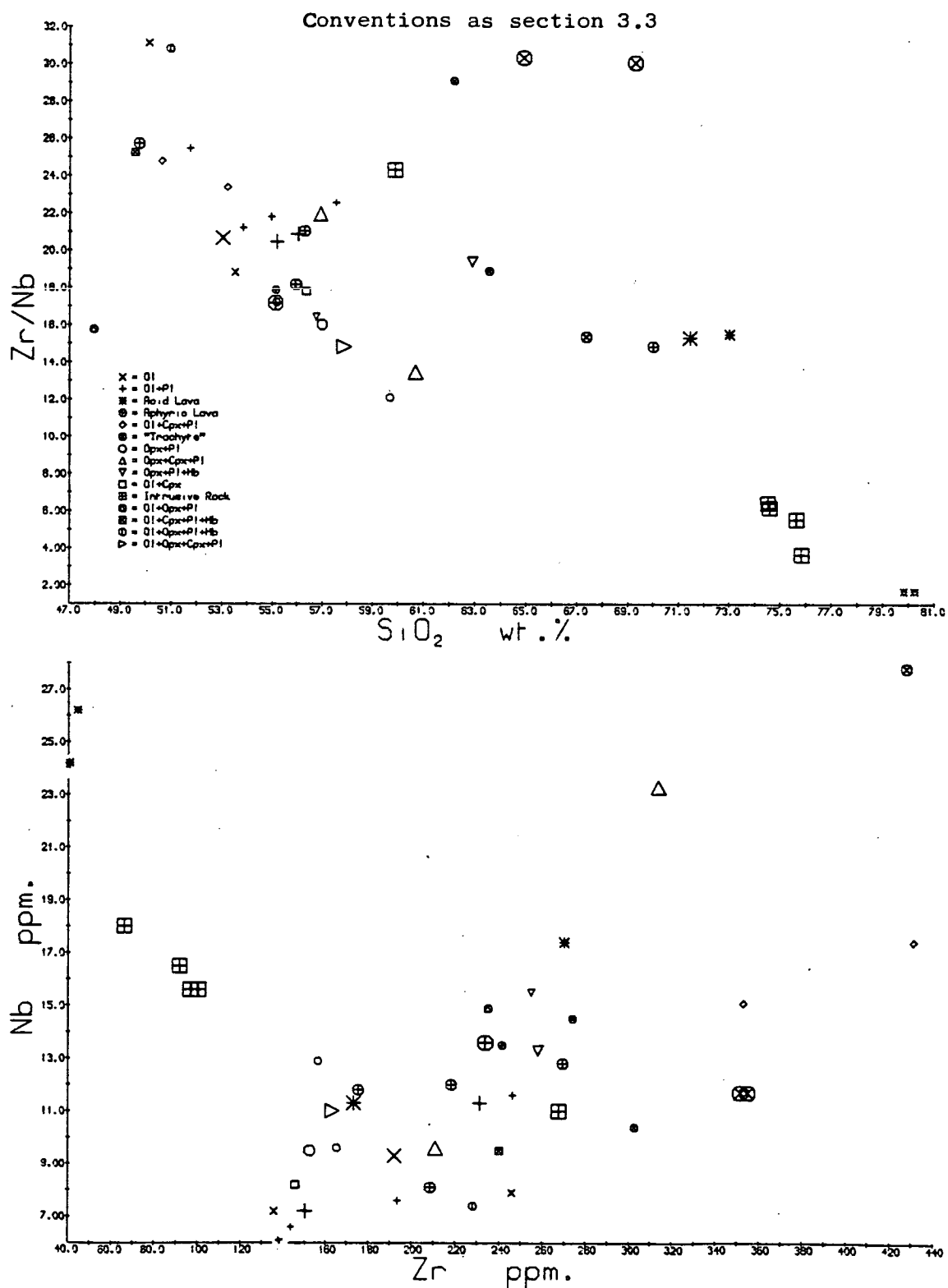
for Zr/Nb shows significant variation (12-17).

With the exception of one of the bronzite-andesites, all samples with more than 59% silica show good negative correlation with silica for P, Fe, Al and Ti, which could be taken to suggest a close genetic relationship (e.g. by fractional crystallisation). This group includes all rocks mapped as trachytes by Mykura (1960), which, as with the "trachyandesites" of the northern Midland Valley, are no more alkaline than many rocks mapped as andesites. With one exception all these rocks have low Ni and Cr. Despite the appearance of being closely related, Zr, Nb and Y do not vary systematically, and Zr/Nb again shows very low values in the most siliceous rocks (2-6). The variation in Y is particularly notable in samples from the Tinto Felsite, from which garnet has been recorded (Herriot, 1956). The one garnet-bearing sample (PE28) has much lower Y than the other three (Fig. 6.1), and also has lower Sc, elements which partition strongly into garnet (Chapter 3). This suggests that garnet separation may have occurred during ascent of the magma, a view which is supported by the observed zonation of garnet crystals (Table C3) from relatively grossular-rich to spessartine-rich compositions. Comparison with the data of Green (1977) suggests that generation of these silicic melts occurred below 20 km depth (<7% spessartine in core compositions).

As with the rocks of the northern Midland Valley there are broad correlations between concentrations of

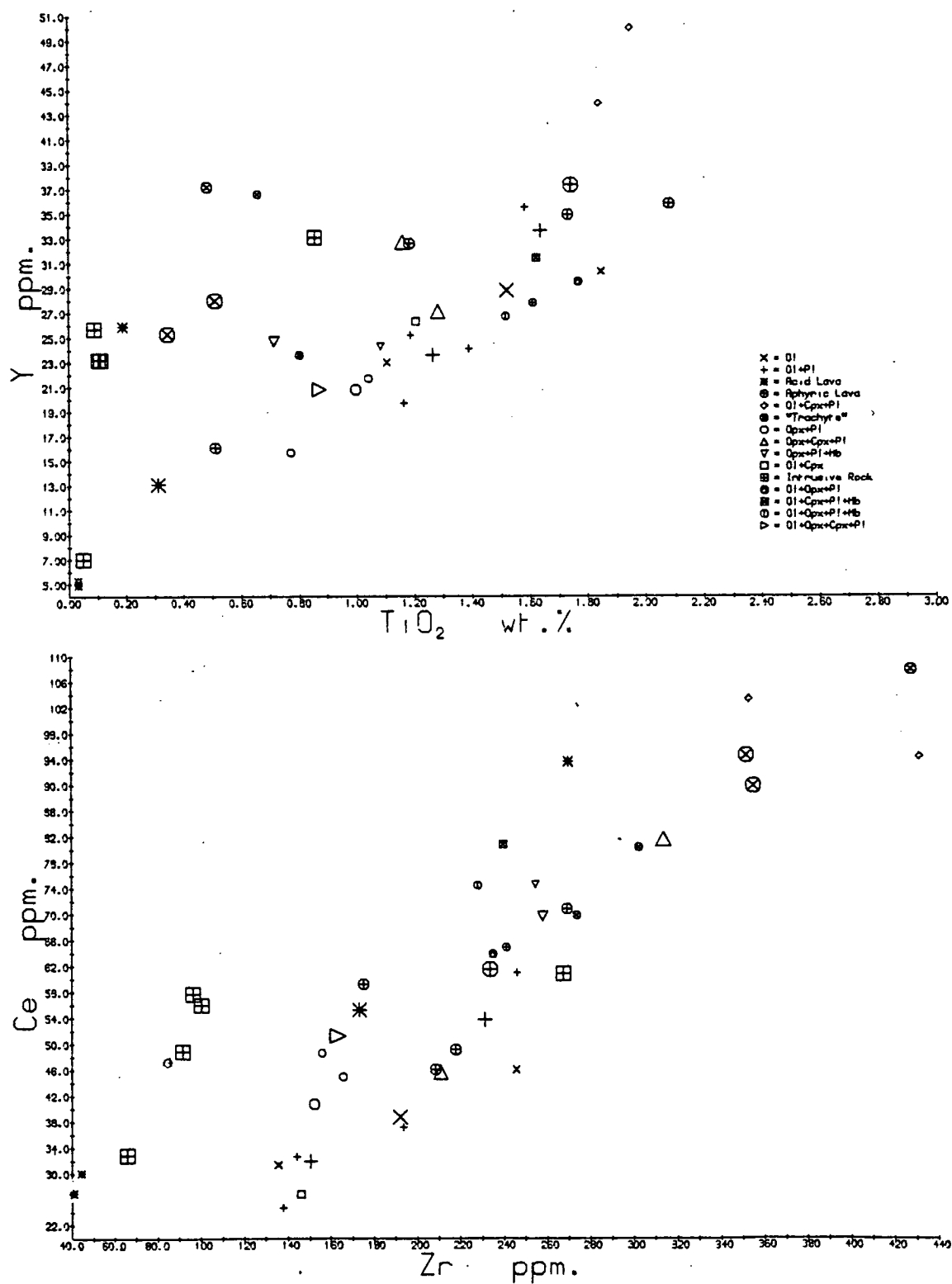
PENTLAND HILLS

Fig. 6.2 a & b : Bulk rock variation diagrams



PENTLAND HILLS

Fig. 6.2 c & d



various pairs of LIL and high field strength elements in less siliceous rocks (<58% SiO₂; Fig. 6.2). Zr-Ce and Ti-Y correlations are particularly good, but with the exception of P-ΣLREE, the poor correlations between LIL elements may be the result of the mobility of Sr, Rb, K and Ba during alteration. Despite this, the broad correlations between LIL elements include concentrations lower than many from the northern Midland Valley. Decrease in Zr/Nb appears to correlate broadly with decreasing Ti and increasing SiO₂, in contrast to the rocks from further north.

6.2 : AYRSHIRE

The volcanic rocks of the Ayrshire Lower Old Red Sandstone outcrop in three main areas: the gently northward-dipping mass of the Carrick Hills and neighbouring coast, a small synclinal area near Distinkhorn and an intensely faulted area at Straiton, close to the Southern Uplands Fault. In all areas, a considerable thickness of sandstones and conglomerates outcrop below the lavas, which in the first two areas rest unconformably on the Llandovery and Ordovician rocks of the Straiton region. In all three areas the top of the volcanic sequence is cut off by the unconformity at the base of the Upper O.R.S. A number of intrusions are present in each area, of which the most important are the large Distinkhorn granodioritic complex and the Fore Burn Complex near Straiton. The Distinkhorn Complex has some similarities with the granodiorites of the Southern Uplands (Pidgeon and Aftalion, 1978).

Pyroclastic rocks are again uncommon in the volcanic sequences of all three areas, and the range of lava lithologies described by Tyrell (1913) is smaller than in the Pentland Hills. Acid rocks are only present as intrusions or as clasts in some of the interbedded conglomerates, although some of the lavas mapped as andesites (Eyles *et al.*, 1949) may be dacitic (e.g. AY12). The bulk of the rocks collected contain phenocryst plagioclase and orthopyroxene, in association with olivine and sometimes clinopyroxene in more basic rocks, or with clinopyroxene alone in more siliceous rocks, but there is no precise relationship between phenocryst mineralogy and host rock silica. Hornblende phenocrysts are restricted to the more siliceous rocks, and biotite is absent.

Orthopyroxenes are usually bronzitic, and clinopyroxenes the typical diopsidic augites low in Ti, Al and Na, even in rocks with 65% SiO₂ (AY12), but pyroxenes analysed from two samples (AY35, 38) from the Straiton area are unusually iron-rich, although the host rocks do not have particularly high Fe/Mg. These relatively iron-rich pyroxenes zone to more normal Mg- and Cr-rich compositions, suggesting that the cores did not crystallise from their host magma. These clinopyroxenes typically show much chloritic material after exsolution lamellae parallel to (001): this is interpreted as the alteration product of exsolved pigeonite. Phenocryst plagioclase is generally Labradorite-andesine, but calcic bytownite occurs in one of the Straiton samples (AY38) and zones to andesine.

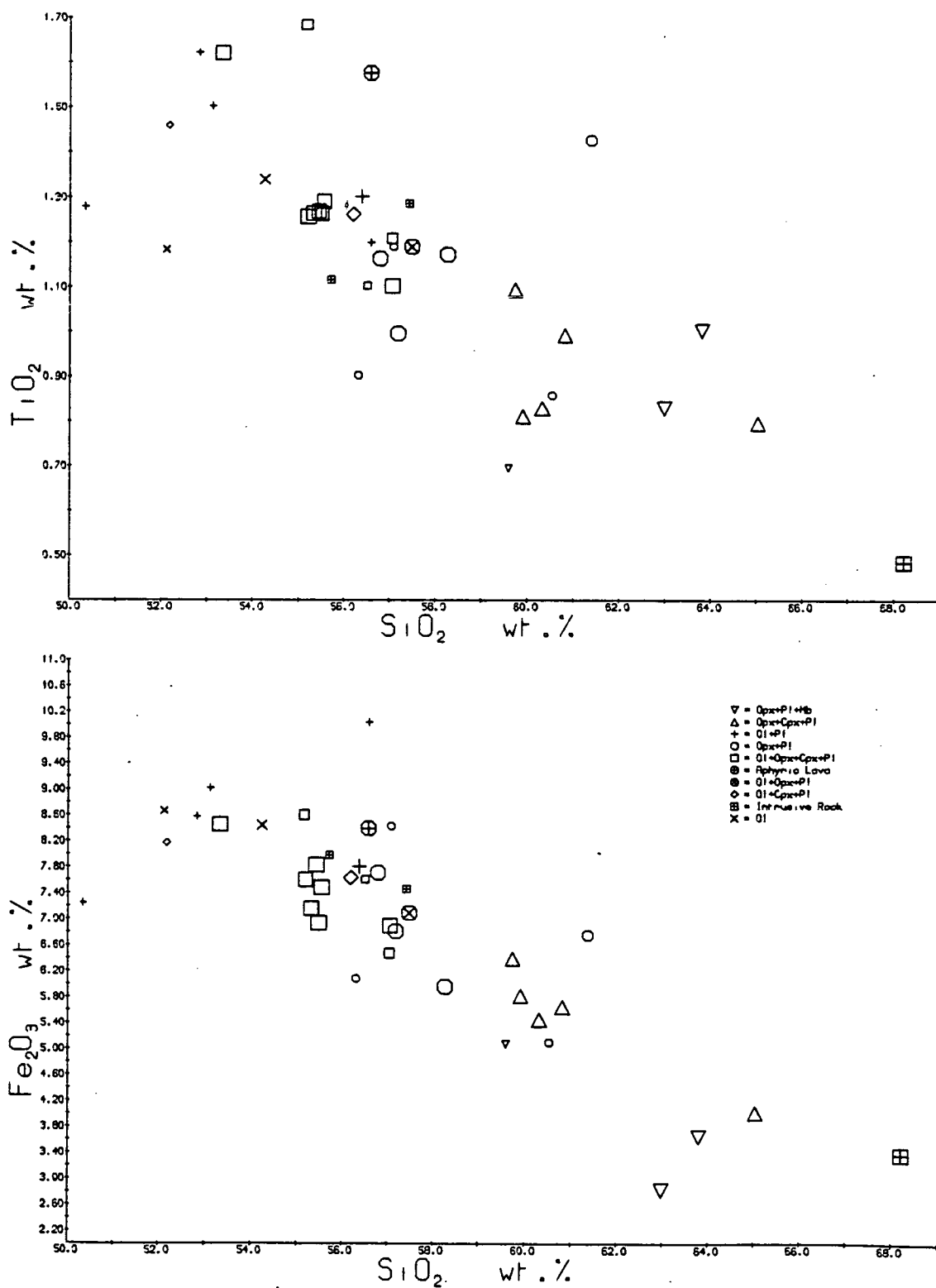
All except six altered rocks are quartz-normative, and except for an acid sill, all rocks collected have between 50 and 66% SiO_2 . No element shows good linear variation with silica (Fig. 6.3); however, K (Fig. 9.1) and Rb show a relatively unscattered enrichment with SiO_2 increase while Fe, Mg, Ca, V and Sc show a concomitant highly scattered decrease. The whole rock chemistry does not appear to be related to phenocryst association, geographic location or stratigraphical position. Use of MgO or Cr as indices of variation does not improve the scatter; Cr and Ni in particular show no systematic variation with either MgO or SiO_2 , and LIL and high field strength elements tend to show rough positive correlation with Cr.

Zr/Nb shows substantial variation (16-31) which is not correlated with Cr content, and, in contrast to the Pentland Hills, it does not appear to have negative correlation with SiO_2 or TiO_2 . However, there is again a prominent positive correlation between Ti and Y (Fig. 6.4), and between La/Y and silica. It is notable that samples from Distinkhorn tend to show higher, and those from Straiton lower than average La/Y and Sr, and hence, for more basic rocks, there is a poor Sr-La/Y correlation. Values for both of these are distinctly lower than their values in the north Midland Valley, as are concentrations of LREE and P. However, there is no Sr-P or K-Zr correlation, and Zr-Ce correlation is poor.

It is clear that there is again no extensive liquid

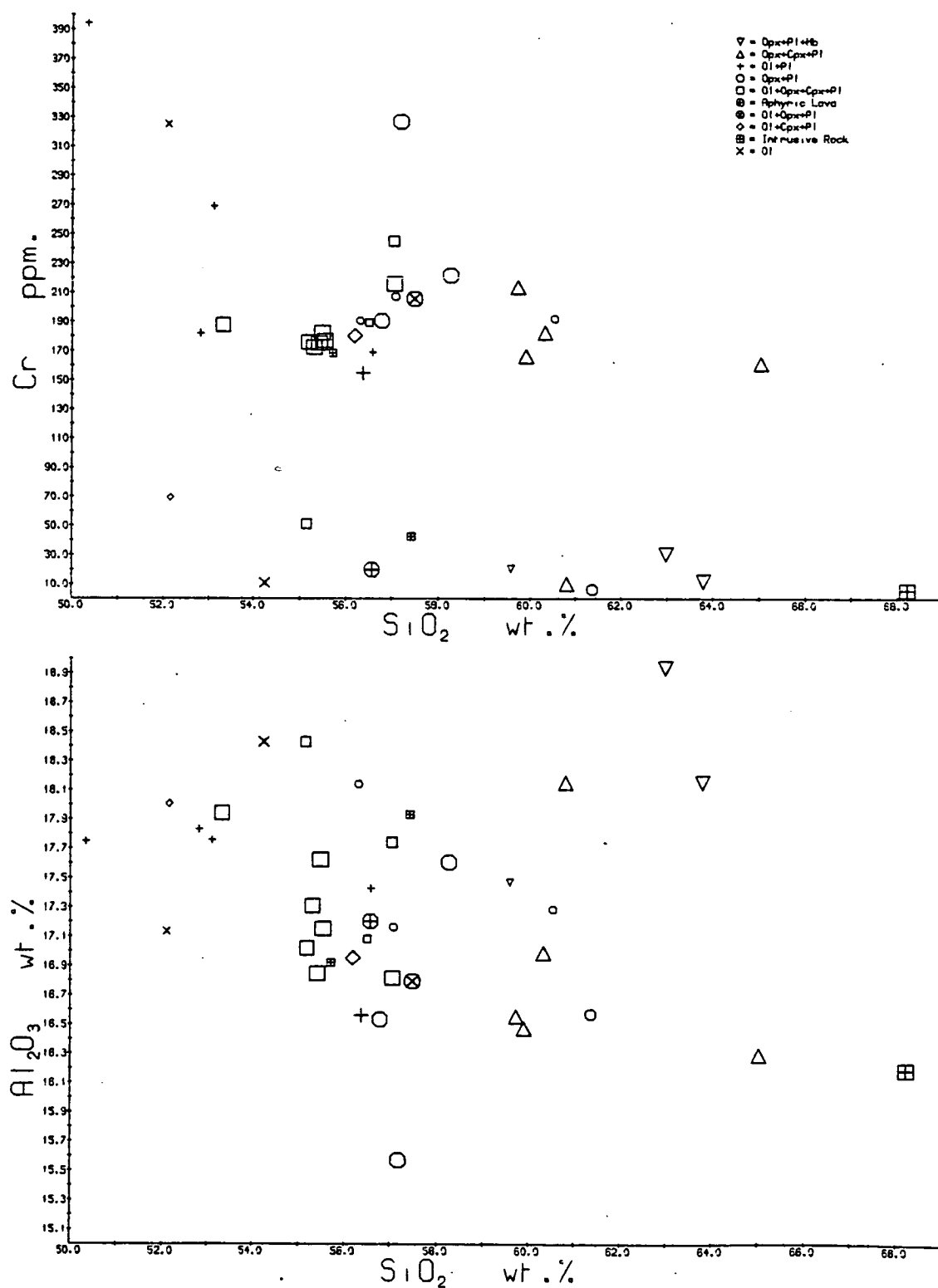
AYRSHIREFig. 6.3 a & b : Bulk rock variation diagrams

Conventions as section 3.3



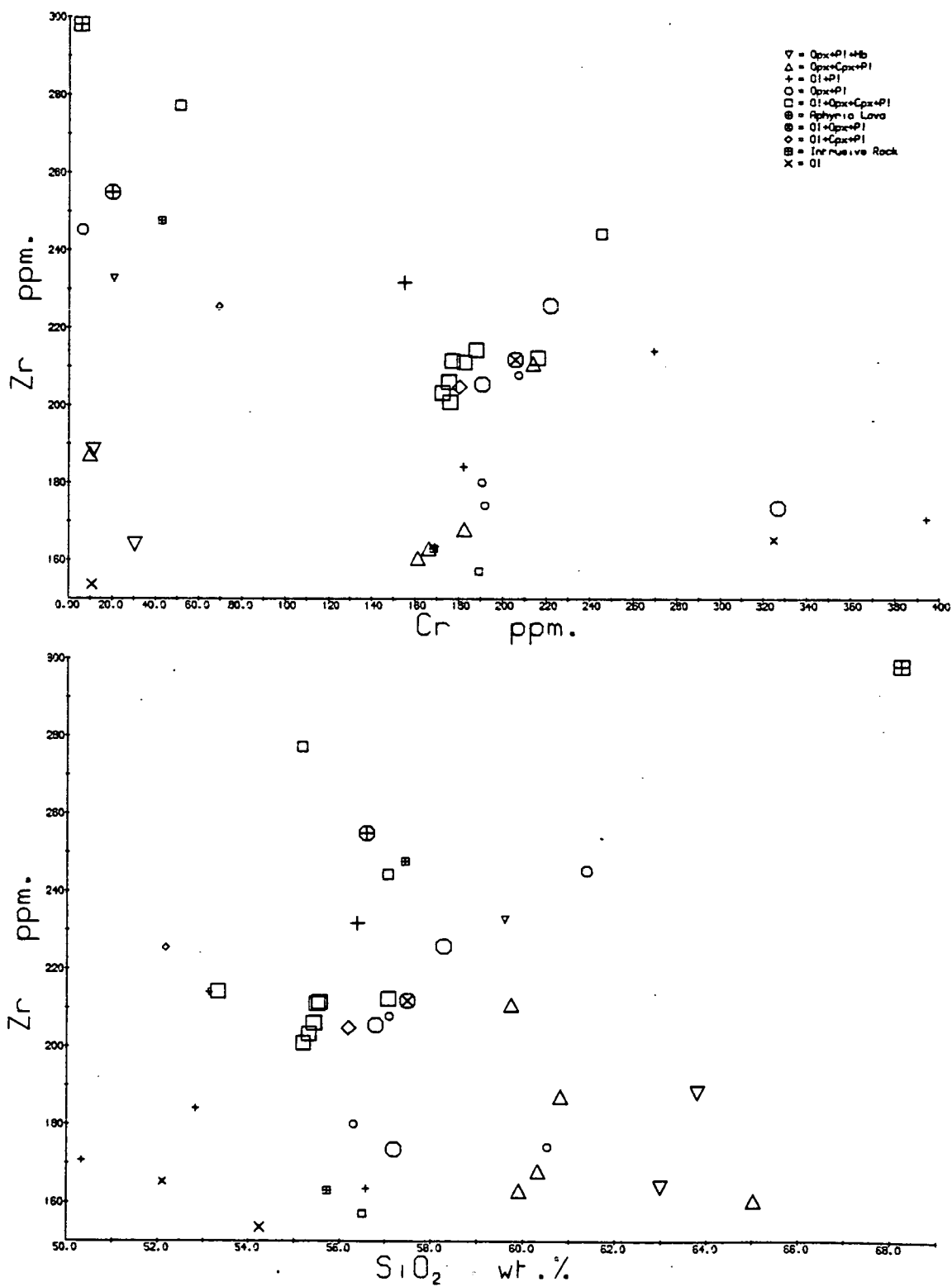
AYRSHIRE

Fig. 6.3 c & d



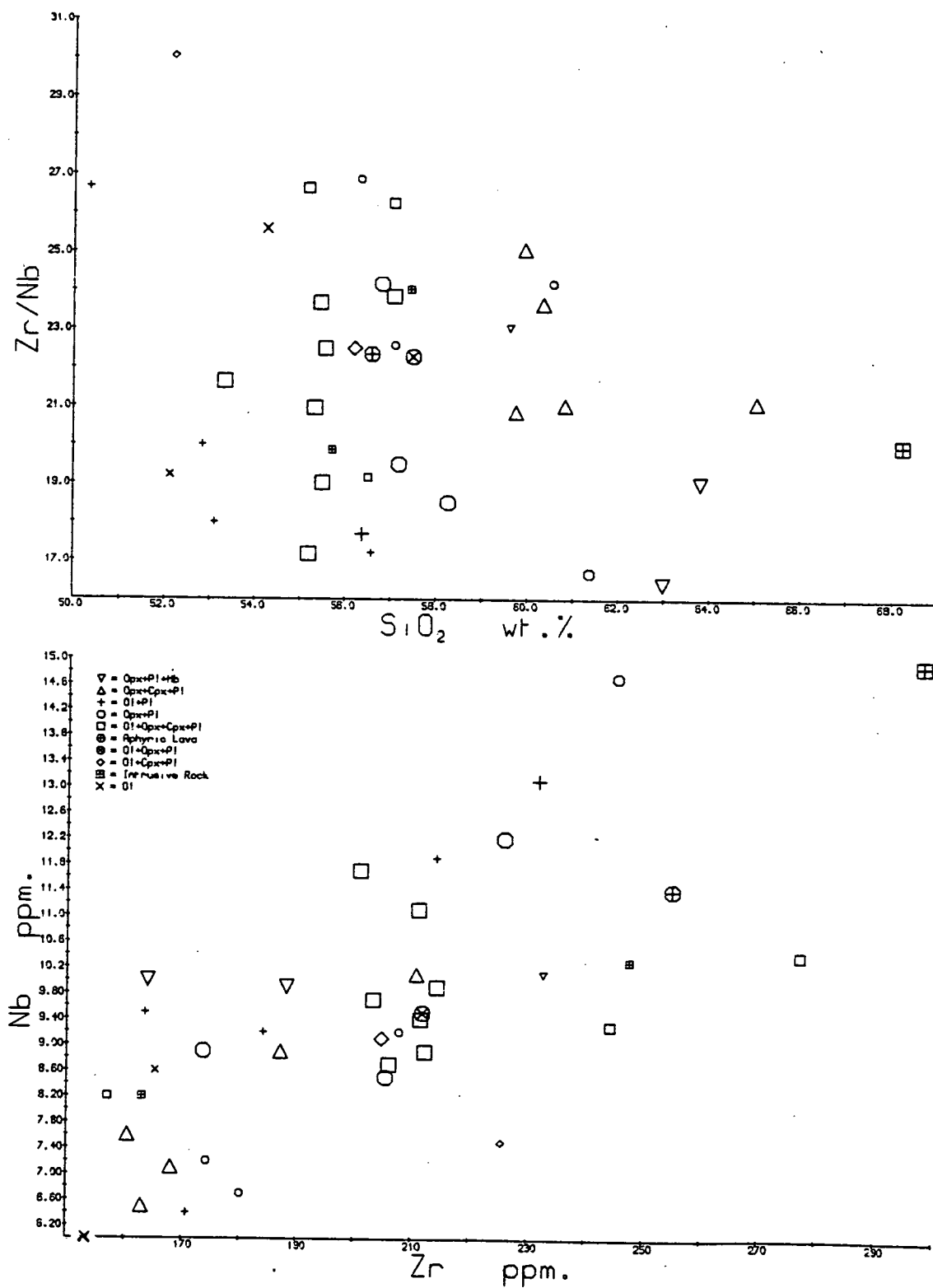
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Fig. 6.3 e & f



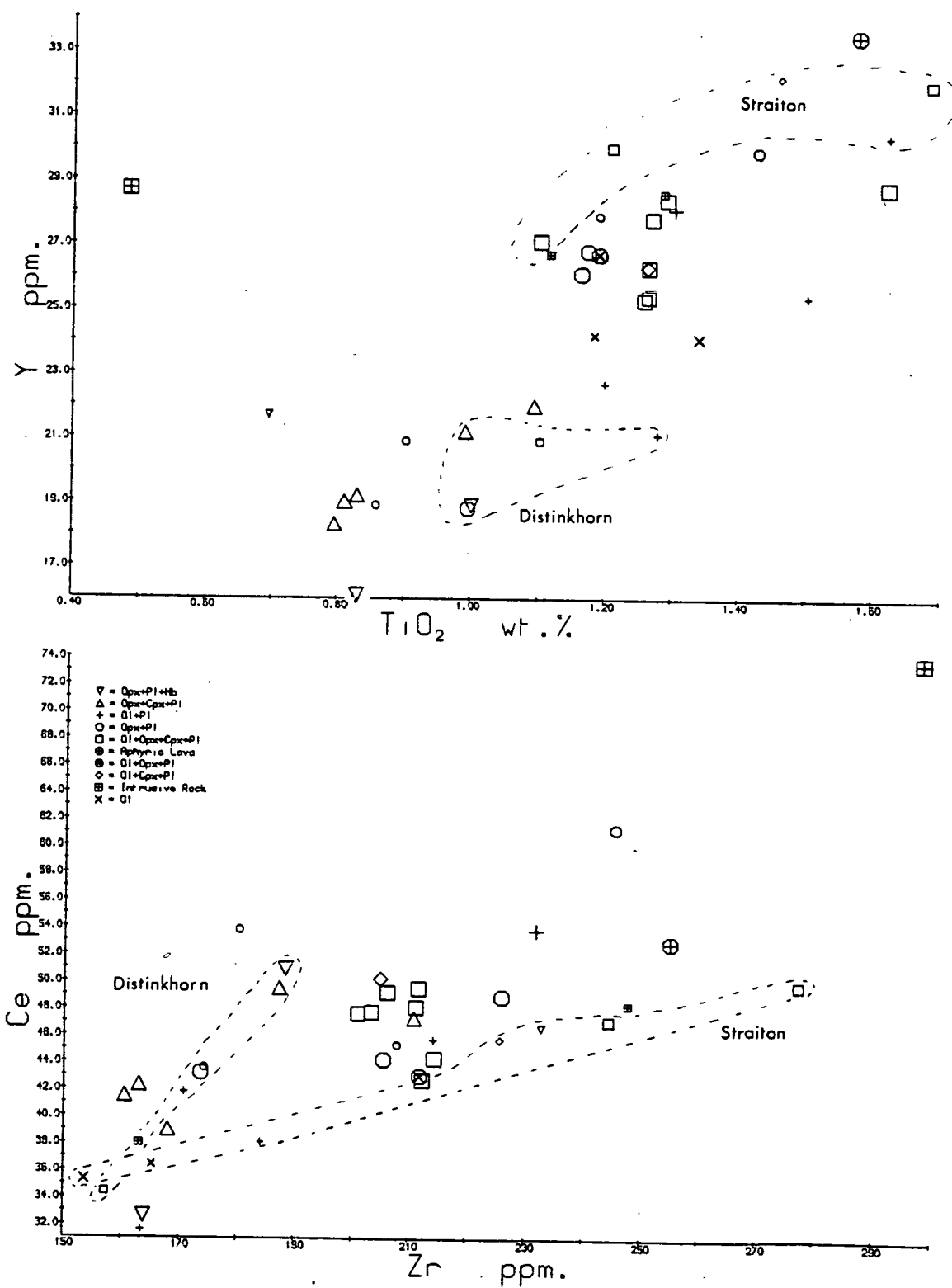
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Fig. 6.4 a & b : Bulk rock variation diagrams
Conventions as section 3.3



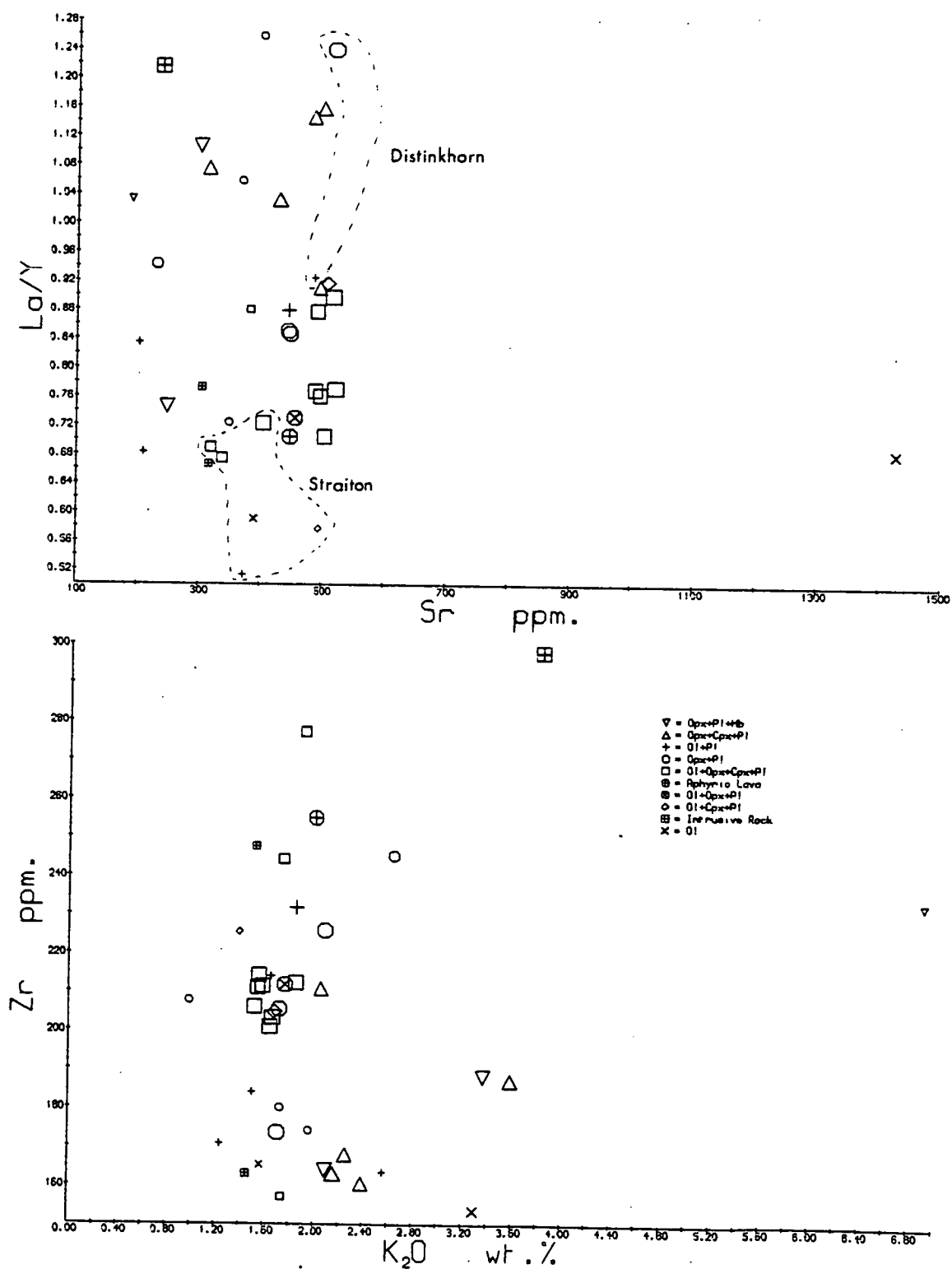
AYRSHIREFig. 6.4 c & d

Fields for samples from Straiton and Distinkhorn



AYRSHIREFig. 6.4 e & f

Fields for some Straiton and Distinkhorn samples



line of descent controlled by fractional crystallisation or partial melting in the Lower Old Red Sandstone volcanic rocks of Ayrshire.

6.3 : SOUTH MIDLAND VALLEY : CONCLUSIONS

The Lower Old Red Sandstone volcanic rocks of the south Midland Valley have considerable similarity to those of the north, particularly in the complexity of their chemical and mineralogical variation.

(a) Phenocryst chemistry (Fig. 6.5)

Clinopyroxenes are typically low Na, Ti, Al diopsidic augites, plotting within the non-alkaline field of Le Bas (1962). Orthopyroxenes are generally bronzites, even in samples with up to 65% SiO₂, suggesting that the rocks have calc-alkaline affinities. More iron-rich pyroxenes are present in the basic andesites of Straiton, and may indicate the existence of higher Fe/Mg, perhaps tholeiitic, liquids here. However, the reverse zoning of these Straiton pyroxenes suggests a complex crystallisation history. Composition of phenocryst plagioclase varies from bytownite to oligoclase and is generally unrelated to host-rock silica content.

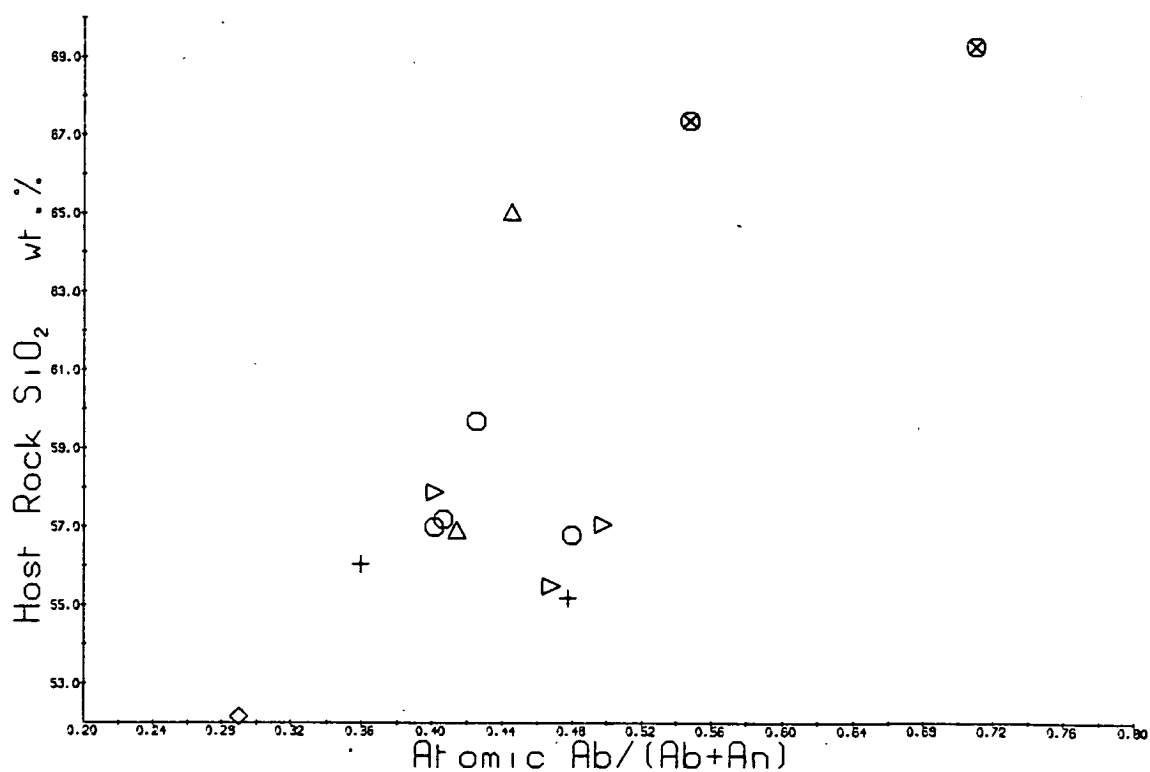
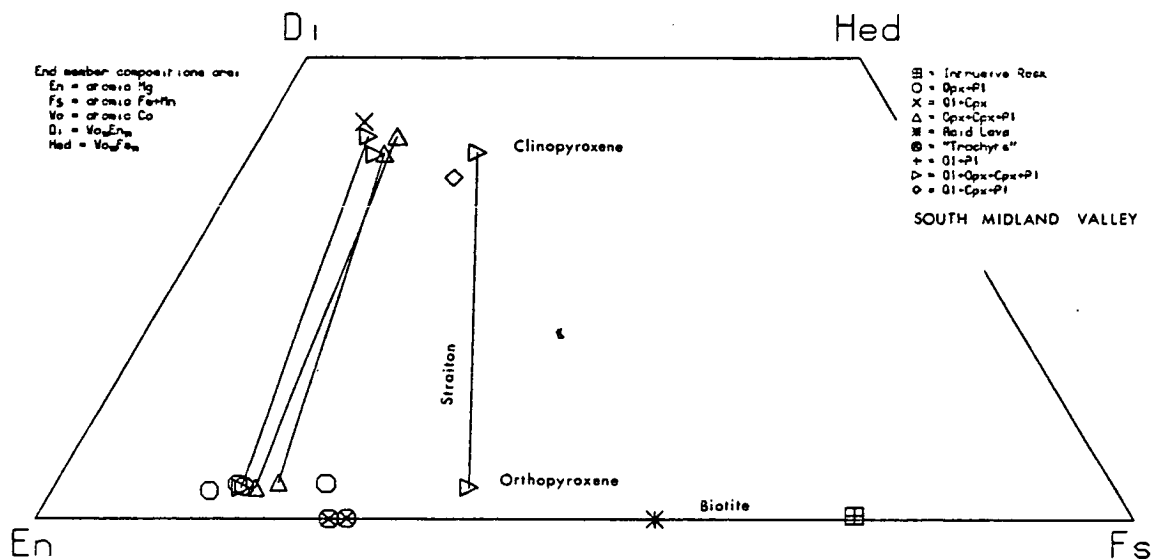
(b) Chemical affinities

Most of the samples collected are quartz-normative,

**Fig. 6.5 a & b : Phenocryst chemistry of South Midland Valley
O.R.S. lavas.**

a = atomic Ca, Mg, Fe for pyroxenes and biotites

b = the composition of plagioclase as a function of host
rock silica



and most normative olivine and nepheline in other samples can be ascribed to secondary introduction of calcite. Except for two highly altered samples from the Pentland Hills, all samples have Fe/Mg within the calc-alkaline field of Miyashiro (1974), although basaltic and andesitic rocks include both moderate and high-alumina varieties. LIL and high field strength elements again have high concentrations, and many samples show concentrations of total alkalis within the alkaline field of Kuno (1968). As with the rest of the province, however, the dominantly quartz-normative nature, the pyroxene chemistry and the low Fe/Mg strongly suggest that the rocks are best described as calc-alkaline.

Many of the samples plot outside the named fields on the Ti-Zr-Y and Ti-Zr-Sr diagrams of Pearce and Cann (1973). In common with rocks from further north, most samples plot to the Zr-rich side of the field for calc-alkaline basalts on the former diagram: this is probably due to the overall high concentrations of LIL and high field strength elements in rocks of the province.

(c) Constraints on petrogenetic hypotheses

Very few element pairs show good correlation in samples from the south Midland Valley: the best correlation is provided by TiO_2 -Y, or by Ce-Zr in the Pentland Hills. Many rocks are Ni- and Cr-rich, even samples with up to 65% SiO_2 (AY12), implying that they can not have suffered much fractional crystallisation of mafic minerals. Such

siliceous samples have Sr contents comparable to those of more basic rocks: the silica enrichment is therefore not caused by fractional crystallisation of calcic plagioclase.

Using such conclusions, the wide variability in Zr/Nb ratio, and the arguments of section 5.5, it is concluded that no extensive liquid line of descent controlled by fractional crystallisation or partial melting exists within the Lower O.R.S. volcanic rocks of the south Midland Valley. The wide variation in LIL and high field strength element concentrations in the Pentland Hills, and to a lesser extent in Ayrshire, can probably only be explained by a contamination model.

CHAPTER 7 : THE CHEVIOT HILLS

Lower Old Red Sandstone rocks south of the Southern Uplands Fault in Scotland outcrop in two areas: a small area of volcanic rocks and sediments at St. Abb's Head and Eyemouth, Berwickshire, and a much larger area of dominantly volcanic rocks forming the Cheviot Hills. The volcanic rocks of the two areas are petrochemically very different, and therefore the rocks of St. Abb's Head will be treated in the next chapter.

The Lower O.R.S. of the Cheviot Hills rests unconformably on Wenlockian greywackes and shales, and is overlain unconformably by the Upper O.R.S. of Roxburghshire and the Carboniferous sediments of Northumberland. The Lower O.R.S. occupies a very large tract of country, but because of poor exposure little is known of its detailed stratigraphy, thickness or structure. Carruthers et al. (1932) have described the field occurrence and petrography of the rocks. With the exception of an acid agglomerate at the base, the Lower O.R.S. consists almost entirely of lavas, although thin impersistent horizons of tuff and sandstone occur in several places. Carruthers et al. (1932) describe the occurrence of biotite-phyric rhyolites ("mica-felsites") above the basal agglomerate; "pitchstone-andesites" and rare horizons of "oligoclase-trachyte" at higher levels; but otherwise conclude that the volcanic series is a very monotonous accumulation of pyroxene-andesites. The lava pile is

intruded by a large number of dykes and sills and in places forms the roof to the Cheviot Granite.

Mitchell (1972) has reported the results of some K-Ar age determinations on rocks from the Cheviot Hills. The lavas were thought to have been erupted about 380-390 Ma ago.

(a) Pyroxene-andesites and "Pitchstone-andesites"

90% of rocks collected from these divisions of Carruthers et al. (1932) have the phenocryst association plagioclase-orthopyroxene-clinopyroxene-apatite-opaque oxide, and since collection has probably been biased towards less common varieties, it is likely that lavas with this phenocryst association provide more than 90% of the total volcanic sequence. Three samples from these divisions also contain rare resorption pseudomorphs after phenocryst biotite, and one sample does not appear to contain phenocryst pyroxene. This petrographic monotony is in striking contrast to rocks from elsewhere in the O.R.S. volcanic province.

In an attempt to provide a method of petrographic classification on variation diagrams comparable to that used in other areas, rocks with the phenocryst assemblage opx-cpx-pl have been subdivided according to their groundmass texture: this may be vitrophyric, hyalopilitic or a coarse or fine granular aggregate of feldspars and quartz.

Some groundmass textures are transitional, however. All rocks described as "pitchstone-andesites" by Carruthers et al. (1932) are vitrophyric with fresh glass in their groundmass and fresh mafic phenocrysts. These authors suggested (p. 14) that the "pitchstone-andesites" represented a minor magmatic type which was less susceptible to alteration through having an impermeable glassy groundmass. However, severely altered vitrophyric samples are common throughout the Cheviot Hills, and non-vitrophyric types containing fresh orthopyroxene are not uncommon (Appendix A). The distinction of a separate "pitchstone-andesite" rock type is therefore not valid.

Phenocryst orthopyroxene is bronzite-hypersthene (Table C2) and clinopyroxene is a low Ti, Al, Na augite. Fe/Mg of pyroxenes is slightly higher in the two vitrophyric samples analysed, but these are also the most silica-rich rocks. Phenocryst plagioclase is oscillatory-zoned labradorite-andesine. In sample C51, where there is additional phenocryst biotite, the phenocryst plagioclase is poorer in Or than that from other lavas (Fig. 7.3). Apatite analyses are presented in Table C2: REE contents are comparable to those predicted using the distribution coefficients of Nagasawa (1970). The opaque oxide is almost always ilmenite, in contrast to the dominance of titanomagnetite elsewhere in the province, and this may be very zirconian (Table C4).

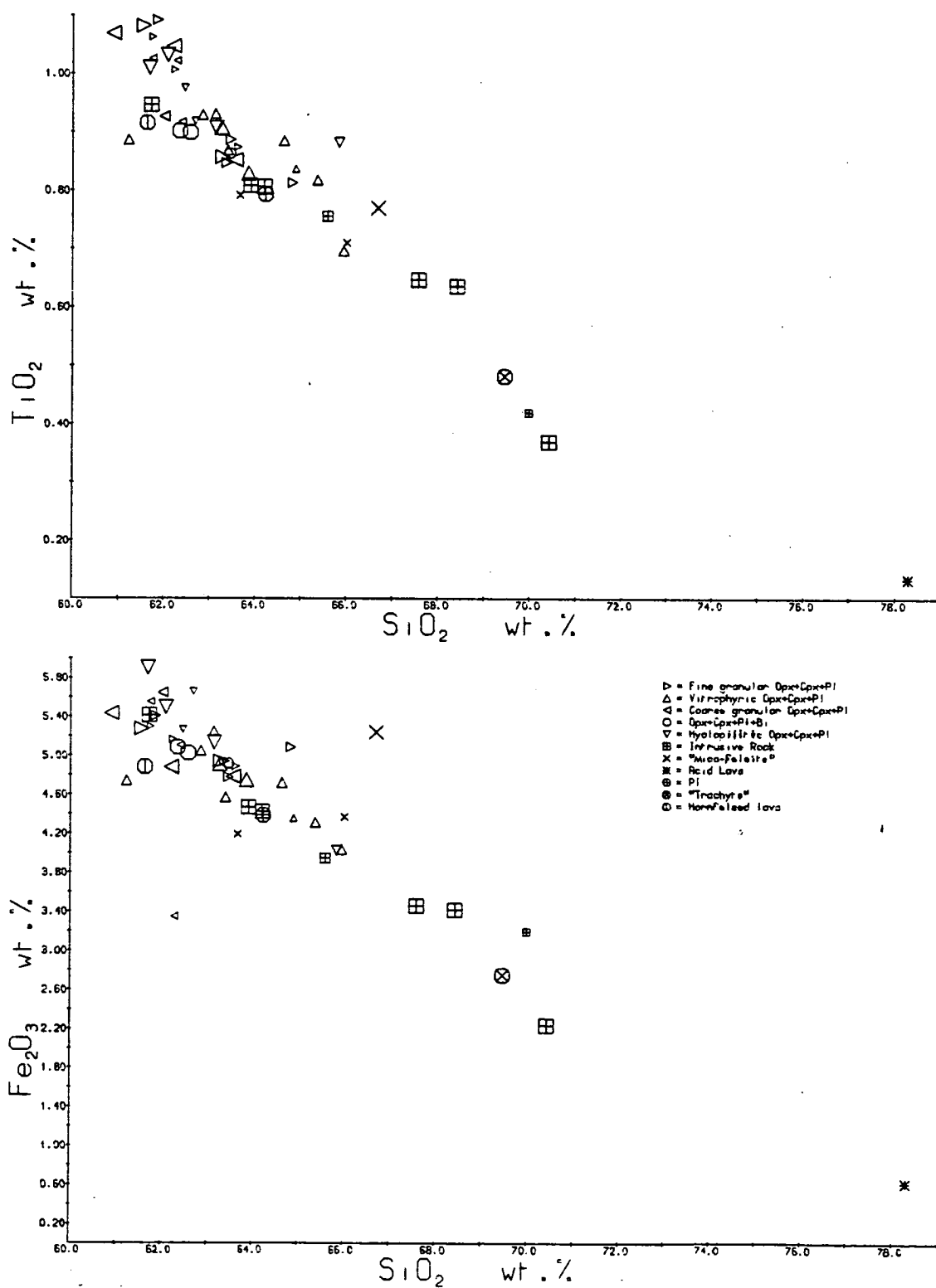
The pyroxene-andesites are all quartz-normative, and

vary between 61 and 66% SiO_2 . Fe/Mg is low, and the rocks all fall in the calc-alkaline field of Miyashiro (1974), although they only have moderate alumina (16%). They are very rich in LIL and high field strength elements, particularly in K, Rb, LREE and Th. $\text{K}_2\text{O}/\text{Na}_2\text{O}$ is close to 1, but Ba and Sr are not particularly high. They are thus comparable with some high-K andesites (e.g. Jakes and White, 1972), although Ni and Cr concentrations are much higher than the values quoted by these authors. Fe, Ti, P and less clearly, V and Sc show good negative correlation with silica (Fig. 7.1), as do Ca, Mg and Sr if allowance is made for alteration (Chapter 2). K and Rb increase with increasing silica in fresher samples, but anomalously low values are given by the "pitchstone-andesites", believed to be due to interaction with meteoric water (Chapter 2). Such interaction is also suggested by an oxygen isotope study of the Cheviot Granite (A.N. Halliday, pers. comm., 1979). Otherwise, little relationship exists between chemistry and groundmass textural types, although vitrophyric samples often have lower Y.

Over the full range of samples collected there appears to be depletion in Zr, Cr, Ni and LREE and increase in Th with increasing silica (Fig. 7.2). Within the pyroxene-andesites, however, there is very good positive correlation between Ni and Cr, and Zr and LREE increase slightly with reduction in Cr (Fig. 7.2). Zr/Nb varies between 17 and 21; while this is a narrower range than in the regions discussed in previous chapters it is

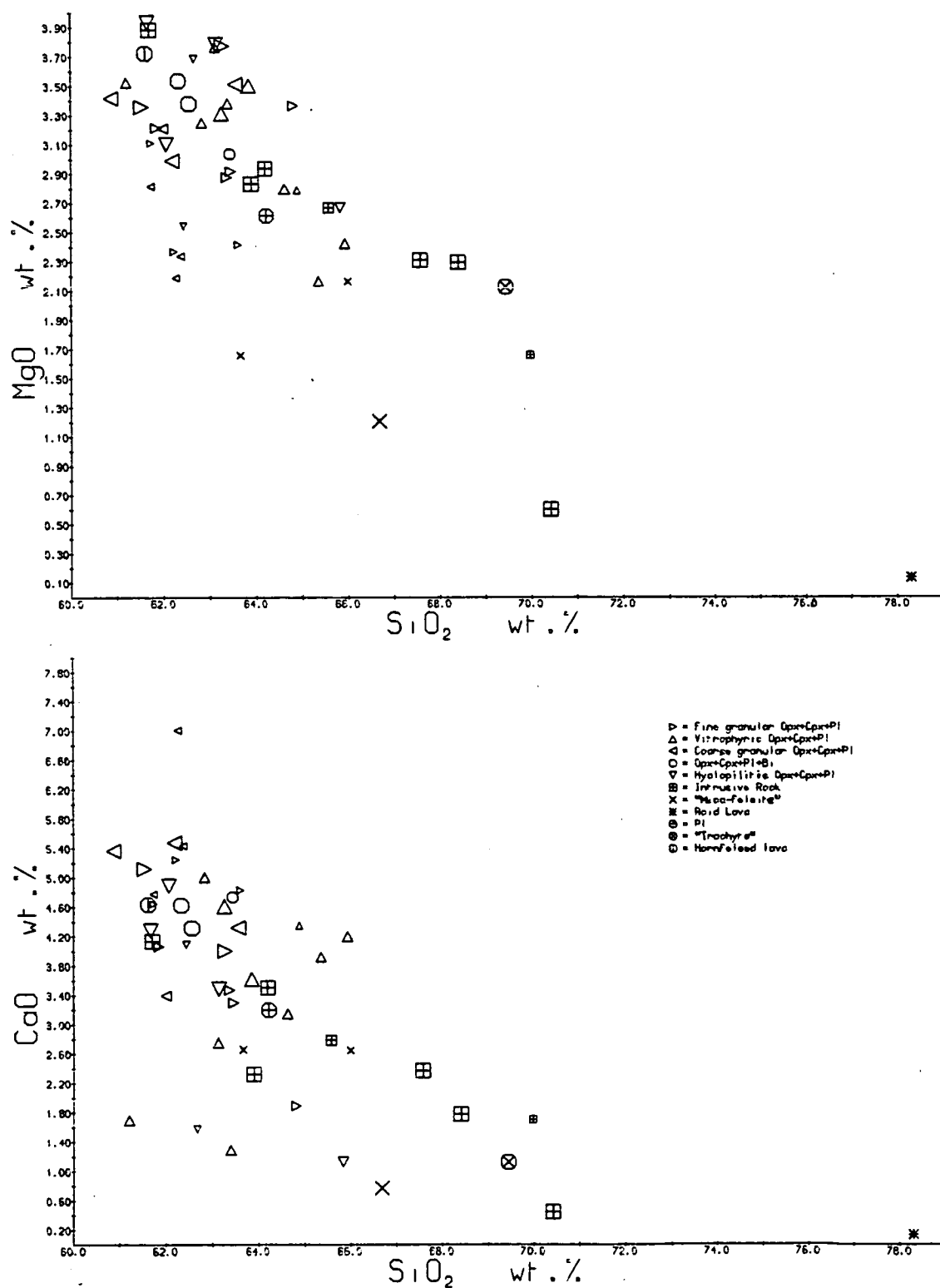
Fig. 7.1 a & b : Bulk rock variation diagrams.

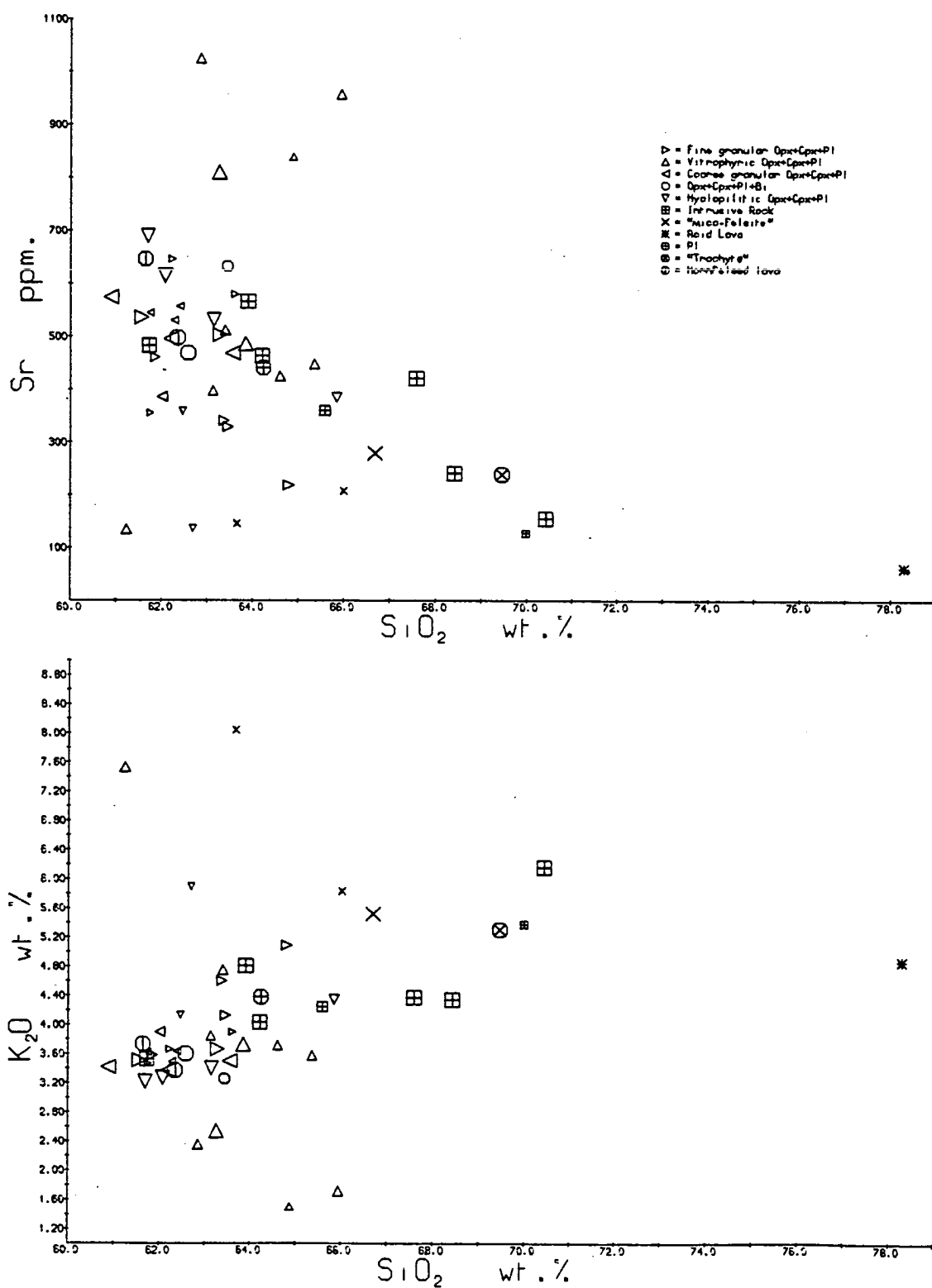
Conventions as section 3.3



CHEVIOT HILLS

Fig. 7.1 c & d

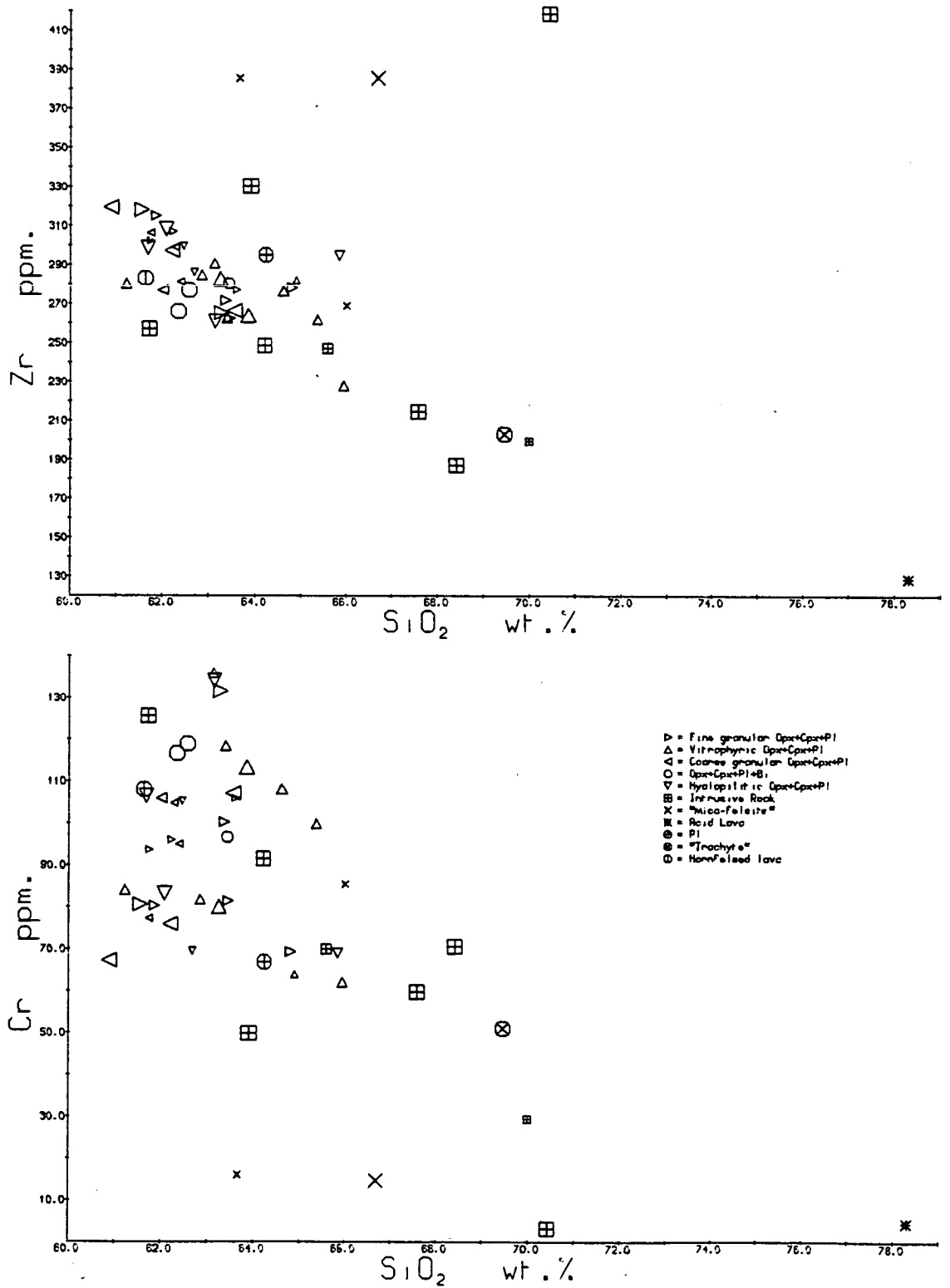


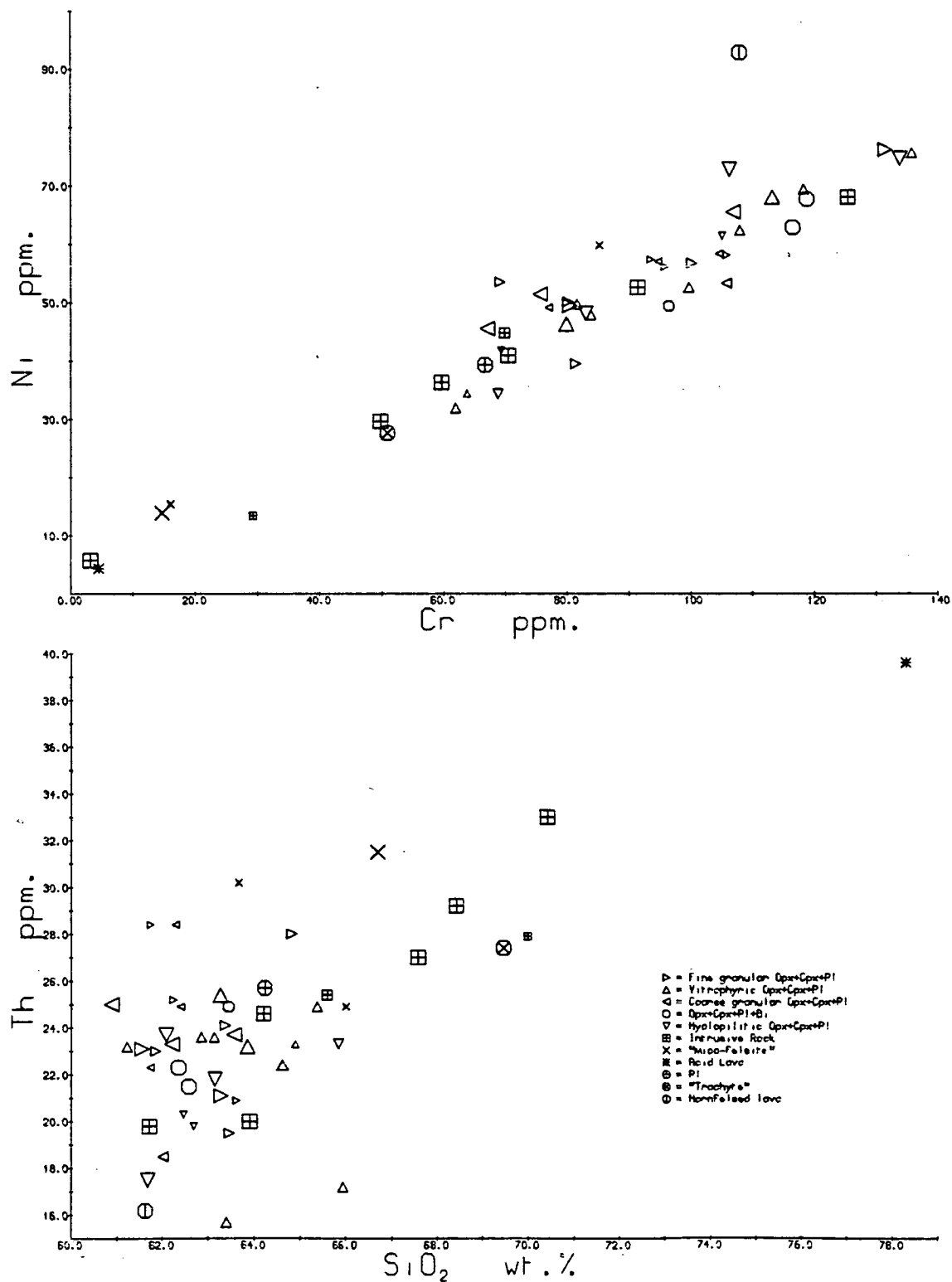
CHEVIOT HILLSFig. 7.1 e & f

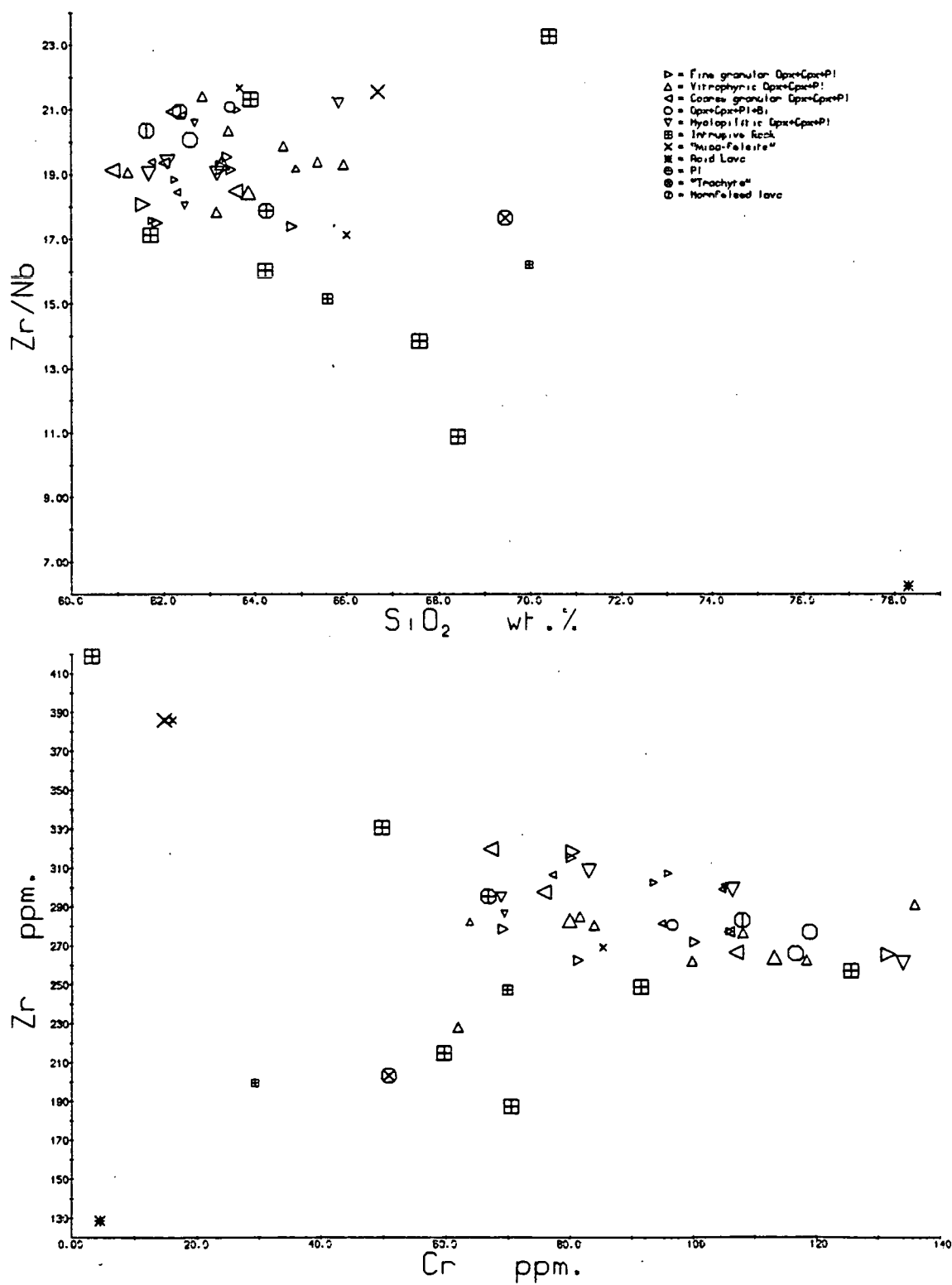
CHEVIOT HILLS

Fig. 7.2 a & b : Bulk rock variation diagrams

Conventions as section 3.3



CHEVIOT HILLSFig. 7.2 c & d

CHEVIOT HILLSFig. 7.2 e & f

nevertheless significant within analytical precision. Zr/Nb does not correlate with Cr, SiO_2 or TiO_2 , despite the presence of phenocryst ilmenite, suggesting that the pyroxene-andesites may not be derived by fractional crystallisation of a single parent magma.

The major element variation has been modelled using the least-squares computer program MODES, written by D.J. Humphries and based on that of Wright and Doeherty (1970). Initial and final compositions with 62 and 70% silica have been estimated from the variation diagrams: it is recognized that this range is wider than the variation of the pyroxene-andesites, but all elements used in the calculation show approximately linear variation with silica in this range for all rocks (Fig. 7.1). To make allowance for discrimination by the program in favour of high concentration elements, the elements used (all major elements except Mn) have been inversely weighted approximately according to their concentrations. Average phenocryst compositions have been taken from C7. The program yields a good fit (sum of squares of residuals=1.08) for fractional crystallisation of the phenocrysts in proportion 63.3% pl - 17% opx - 14.9% cpx - 3.28% ilm - 1.49% ap, which are very close to the relative proportions of the phenocrysts. The residuals for all elements are well within scatter on the variation diagrams. 43% crystallisation is required to produce silica enrichment from 62 to 70%.

Rb and Th data agree well with a model of 43% crystallisation, for both nearly double over this silica enrichment. However, Zr, Nb, Y and LREE decrease over this range, suggesting that $D(\text{bulk})$ for these elements is greater than 1. Using maximum reasonable values of $D(\text{Zr})$ for $\text{cpx}=1$, for $\text{opx}=0.1$, for $\text{pl}=0.1$, for $\text{ilm}=10$ and for $\text{ap}=0.1$, then $D(\text{Zr,bulk})=0.56$. Similarly, $D(\text{Ce,bulk})=0.77$, assuming values from Gill (1978) and $D(\text{Ce,ap})=40$, although increasing this to 50 increases $D(\text{Ce,bulk})$ to 0.91. These values are very dependant on the proportions of apatite and ilmenite in the fractionating assemblage, but P and Ti were weighted to obtain minimal residuals, and therefore the error in proportions of these phases should be trivial.

The conflict between predicted and real behaviour of these elements may perhaps be related to the the increases shown by these elements with decreasing Cr. Here, LREE appear more compatible than Zr, consistent with their relative bulk distribution coefficients calculated above, although Zr is still more compatible than predicted. This relationship, and the scattered Ni-SiO₂ and Cr-SiO₂ distributions, could be explained by a two-stage fractional crystallisation process, in which magmas parental to the first stage are not represented in the Cheviot Hills. The first stage may have led to a range of magmas with comparable major element composition, but including some slightly more evolved ones with lower Cr, Ni and higher Zr, LREE. The behaviour of Sr is reasonably consistent with the suggested amount of plagioclase extraction, although actual

depletion in Sr is larger than that predicted. The lack of Ba enrichment with silica is not satisfactorily explained by this model, nor is variation in Y and La/Y (Fig. 7.4), for Y should be less compatible in this assemblage than La (Chapter 3).

(b) "Oligoclase-trachyte"

Only one sample with this lithology has been collected, and it is severely altered. It is nearly aphyric, quartz-normative, siliceous and not significantly richer in alkalis than some of the more siliceous andesites (Fig. 7.1). It lies on the general variation trends with silica described in section (a), but its low Zr, Nb, Y and LREE can not be explained by further fractional crystallisation of the phenocryst minerals from the andesites. Biotite+zircon extraction (Pearce and Norry, 1979) can not explain the lack of K and Th depletion relative to the andesites.

(c) "Mica-felsites"

The "mica-felsites" collected in the course of this research are all feldspar-phyric, and no samples have been found of the type with biotite as the sole phenocryst phase, described by Carruthers et al. (1932). In addition to biotite, the samples contain phenocrysts of plagioclase, alkali feldspar, apatite, ilmenite and ?clinopyroxene, pseudomorphed by carbonate. They are all badly altered, and

the alkali feldspars are now near the pure K end-member.

The three samples collected have between 63 and 67% silica, and can not therefore be described as rhyolites (c.f. Carruthers *et al.*, 1932; Mitchell, 1972). Two samples, together with two intrusive rocks (C23 and C58), are enriched in Rb, K, Zr, Th, LREE and to a lesser extent Nb and Y relative to the pyroxene-andesites, and they are depleted in Cr, Ni, Mg, P and possibly Sr. This could suggest fractional crystallisation of a pyroxene-andesite magma, but it is difficult to explain the lack of silica enrichment and the incompatibility of LREE (La and Zr enrichments are comparable) when apatite must be an important part of the crystallising assemblage. The third "mica-felsite" sample (C55) is not chemically distinguishable from the pyroxene-andesites.

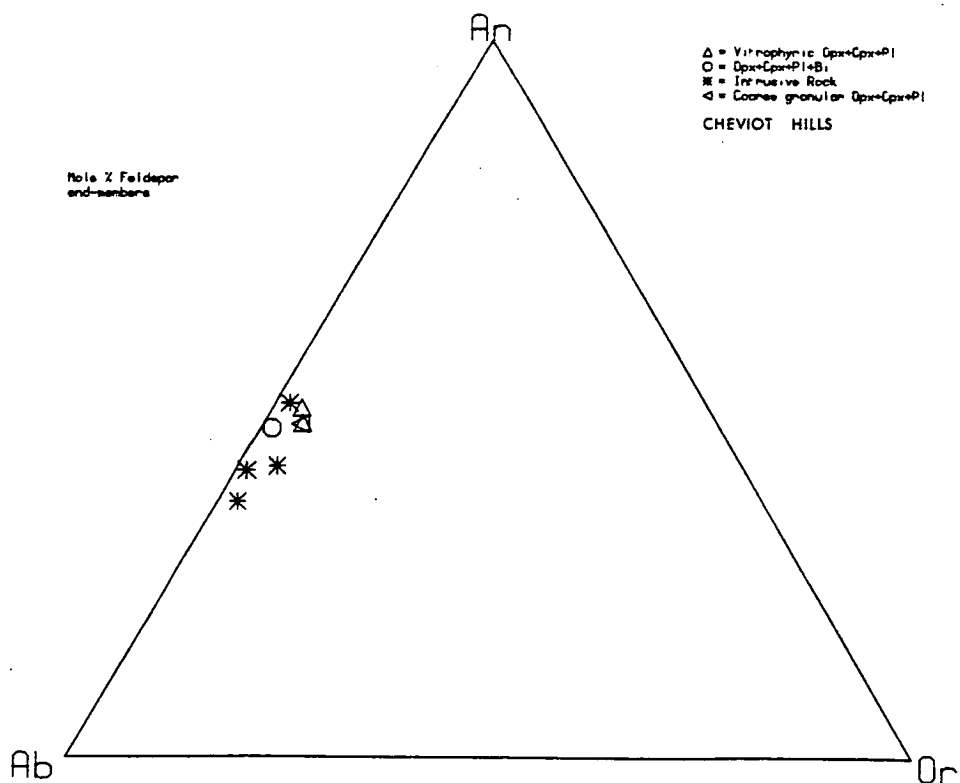
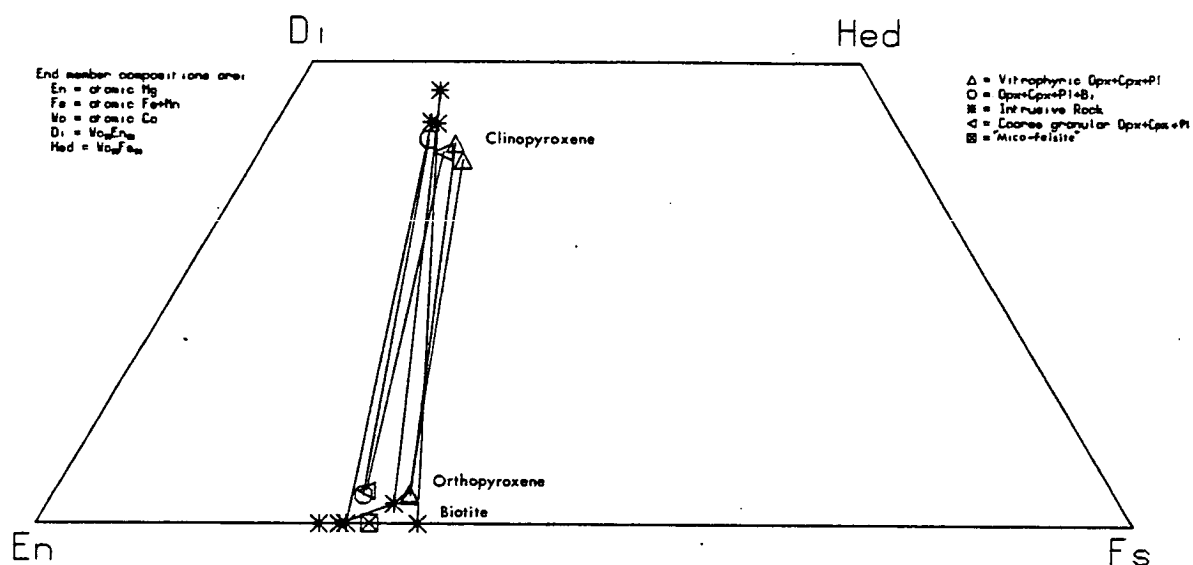
(d) Intrusive rocks

All intrusive rocks sampled have a similar mineralogy to the lavas, although phenocryst quartz appears in more siliceous varieties, and phenocryst biotite is more common. All clinopyroxenes analysed from intrusive rocks are notably more calcic than lava clinopyroxenes, and orthopyroxene is less calcic (Fig. 7.3). Ti and Al show a much more restricted compositional range than in lava pyroxenes. This suggests that the crystallisation of the intrusive rocks occurred at lower temperatures and that it was closer to equilibrium. Plagioclase is generally poorer in Or than

Fig. 7.3 a & b : Phenocryst chemistry of Cheviot igneous rocks.

a = atomic Ca, Mg and Fe for pyroxenes and biotites

b = plagioclase end-members



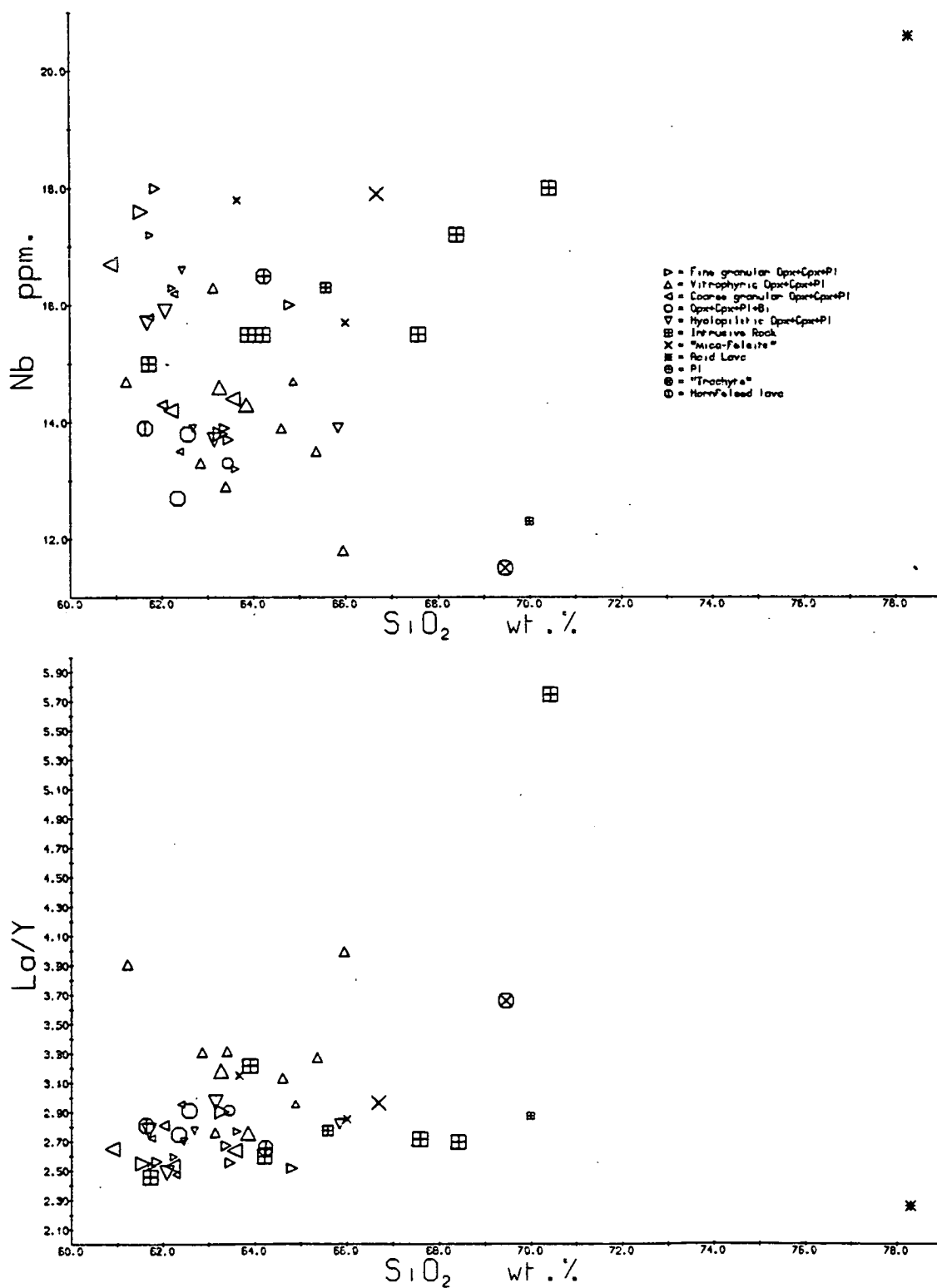
equivalent lava plagioclase.

With the exception of the two samples which appear to be related to the "mica-felsites" (section e), all the intrusive rocks fall on the general trends described in section (a) for all elements except Y and Nb, which remain constant and increase respectively, with increasing silica. The behaviour of Y gives rise to roughly constant La/Y, contrasting with the broad increase in La/Y with silica shown by the lavas (Fig. 7.4). Zr concentrations are slightly lower than those in the lavas.

C62 is an example of the marginal 2-pyroxene variety of the Cheviot Granite, interpreted by Carruthers et al. (1932) as the result of contamination of granitic magma by andesite. The lower temperature nature of the pyroxenes suggests that these are unlikely to be xenocrystal from the lavas, as suggested by Carruthers et al. (1932, p.93). Jhingran (1942) compared the analyses of a "pitchstone-andesite" and a sample of marginal 'granite', and concluded that contamination was more likely to have been the result of incorporation of sediment. The major difference between the two analyses quoted by Jhingran (1942) lies in the K₂O content, and the low K of the "pitchstone-andesite" quoted is probably the result of alteration, as suggested in Chapter 2. The marginal variety of the Cheviot Granite is chemically almost identical to the bulk of the pyroxene-andesites.

CHEVIOT HILLSFig. 7.4 a & b : Bulk rock variation diagrams

Conventions as section 3.3



C41, a severely altered clast from the basal agglomerate, is the only true rhyolite collected from the Cheviot Hills. For most elements it falls on the same variation trends as the intrusive rocks e.g. for Nb and La/Y, Fig. 7.4, but is far more siliceous than any intrusive rock collected. In common with most rhyolites of the province it has low Zr and very low Zr/Nb.

(e) Conclusions

With very few more siliceous exceptions, the volcanic rocks of the Cheviot Hills are a group of high-K calc-alkaline 2 pyroxene-plagioclase-phyric andesites, closely similar in their petrography and chemistry. This monotony is most unusual for rocks of the Old Red Sandstone Volcanic Province. Their limited major element variation may be ascribed to fractional crystallisation of the phenocryst phases: this can also generate the major element variation of all other Cheviot samples, apart from P_2O_5 in the "mica-felsites".

Trace element variation can not be accounted for by this model. Most samples are high in Ni and Cr relative to averages quoted by Jakeš and White (1972) and by Ewart (in press), and they are also very rich in LREE, Th and Rb. LREE, Th, Y, Zr and Nb do not vary systematically with silica. With the exception of the most siliceous andesite, the "trachyte", and a number of intrusive rocks, the elements Zr, Nb, Th and LREE increase with reducing Cr,

suggesting that variation in these elements could be produced by minor differences in immediately parental magmas with about 60% silica. This could suggest a two-stage fractional crystallisation process, but it is difficult to account for the high levels of Ni and Cr, unless plagioclase was a major fractionating phase in the first stage. Fractional crystallisation of the phenocrysts, the second stage, does not satisfactorily account for the Ba and Y variation.

Halliday and Stephens (in press) have noted that acid members of the Southern Uplands plutons characteristically have higher $^{87}\text{Sr}/^{86}\text{Sr}$ (0.706) than more basic ones (0.704), and suggest that the acid members could be derived by the melting of Lower Palaeozoic sediments. Such melts may have had lower concentrations of LIL and high field strength elements than the Cheviot andesites. The observed depletions in these elements with increasing silica could represent a mixing line between a lower crustal- or mantle-derived melt, very rich in incompatible elements, with a more siliceous melt derived from the lower Palaeozoic sediments. The isotopic data on the volcanic rocks, and the chemical data on the sediments needed to test this hypothesis are not yet available. It will be noted, however, that the melt derived from the sediments is required to be very Th rich, and the hypothesis can not explain the variation in Y among the pyroxene-andesites.

CHAPTER 8 : MINOR OCCURRENCES OF O.R.S. VOLCANICS8.1 : ST. ABB'S HEAD / EYEMOUTH

Old Red Sandstone volcanic rocks in Berwickshire are well exposed in the sea cliffs of St. Abb's Head where they are faulted against Llandoverly greywackes inland (Greig, 1975). To the south and west there are a few small inland outcrops where O.R.S. sediments and volcanic rocks rest unconformably on Silurian. The fairly thick (2000 ft, 600 m; Greig, 1971, p.50) southward dipping sequence at St. Abb's Head consists mainly of sparsely porphyritic lavas, often much veined by carbonate. Olivine and orthopyroxene are the only phenocrysts observed in samples from St. Abb's Head, and no biotite has been found (c.f. Greig, 1975, p.122). Where olivine occurs alone it is generally euhedral, but where orthopyroxene is present it generally mantles subhedral olivine. Phenocrysts are never common, and occur in a trachytoid or subophitic groundmass of plagioclase, clinopyroxene (rarely fresh) and opaque oxides. Both plagioclase and amphibole phenocrysts occur in the rocks near Eyemouth, but the collection is biased towards plagioclase-phyric samples, for these were specifically chosen from the collection of the Institute of Geological Sciences. No phenocryst minerals were found in sufficiently fresh condition to permit microprobe analysis.

The samples analysed range from 53 to 72% SiO_2 and are all quartz-normative. All samples from St. Abb's Head

are basic andesites with a maximum of 58% SiO_2 but samples from Eyemouth have a wider silica range. Fe/Mg is low, and all samples plot within the calc-alkaline field of Miyashiro (1974). Alumina is moderate (16%). A few elements show fairly good linear variation with silica (e.g. Fe, Cr; Fig. 8.1) despite the severe alteration, but immobile LIL and high field strength elements all show two variation trends with silica, particularly evident for P and LREE (Fig. 8.1). Each trend includes samples from both St. Abb's Head and Eyemouth.

One of these trends, the 'rapid enrichment trend', shows good positive correlation between concentrations of 'incompatible' elements and silica over the small range of silica present (53.8 to 57.5%). Nb more than doubles over this silica range (Fig. 8.1), and P, Zr and Ce show about 70% enrichment. Ti and Y show smaller increases, about 25 and 43% respectively, but Ni, Cr and V all reduce by a factor of about 30% (Fig. 8.1). If the trend were generated by fractional crystallisation, then bulk distribution coefficients for these three elements must all be close to 1.7. Comparable $D(\text{Sr}, \text{bulk})$ is suggested by the Sr concentrations of the two samples of PAS 3 (SA1 and SA20). These relationships suggest a possible origin of the trend by fractional crystallisation of an assemblage with silica close to that of the parental magma. The very small reduction in Cr and Ni over the 50% crystallisation derived from the Nb data implies that plagioclase was dominant in the fractionating mineral assemblage; the Sr data and the

Fig. 8.1 a & b : Bulk rock variation diagrams

Conventions as section 3.3

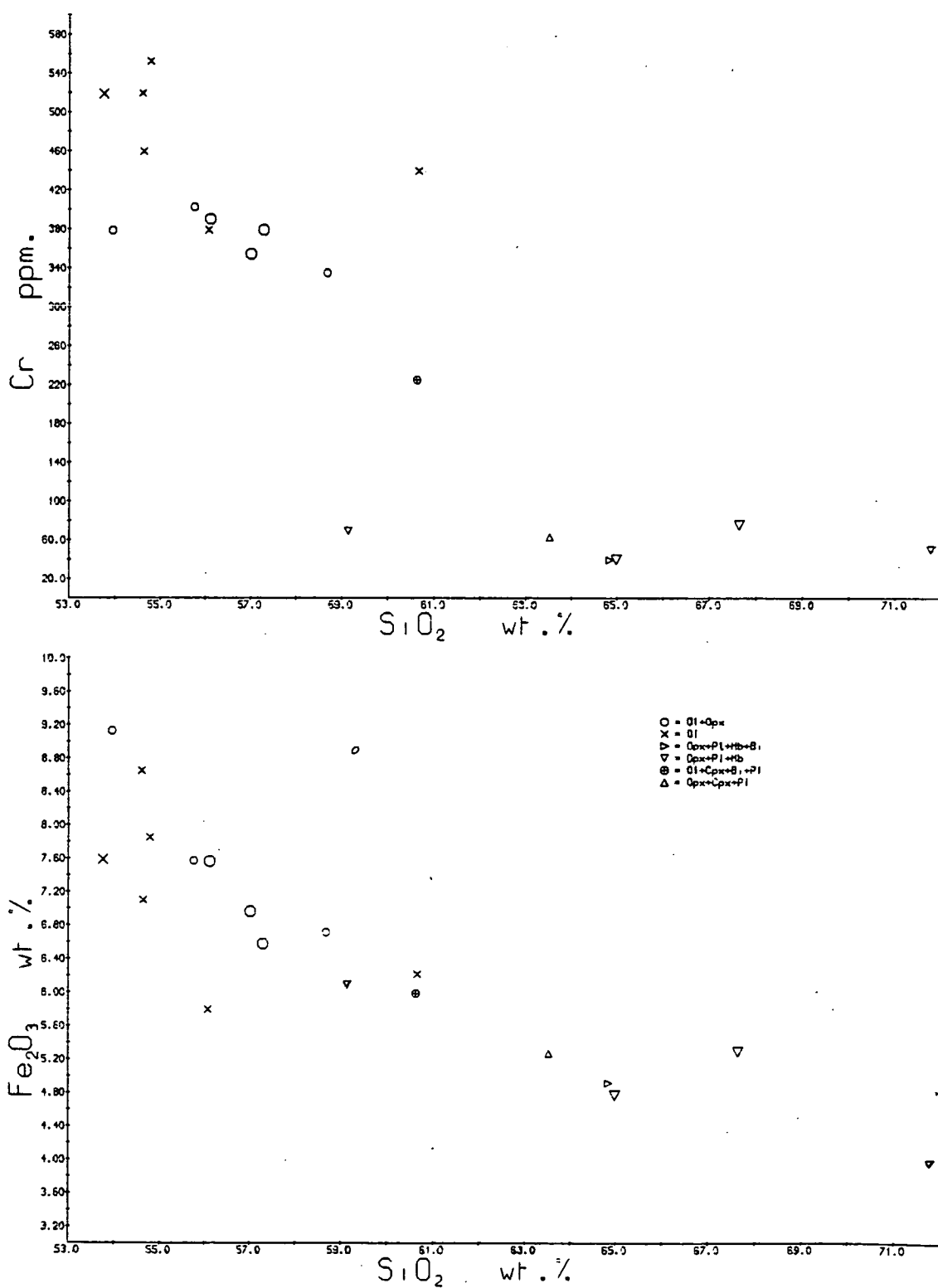
ST. ABB'S HEAD & EYEMOUTH

Fig. 8.1 c & d

ST. ABB'S HEAD & EYEMOUTH

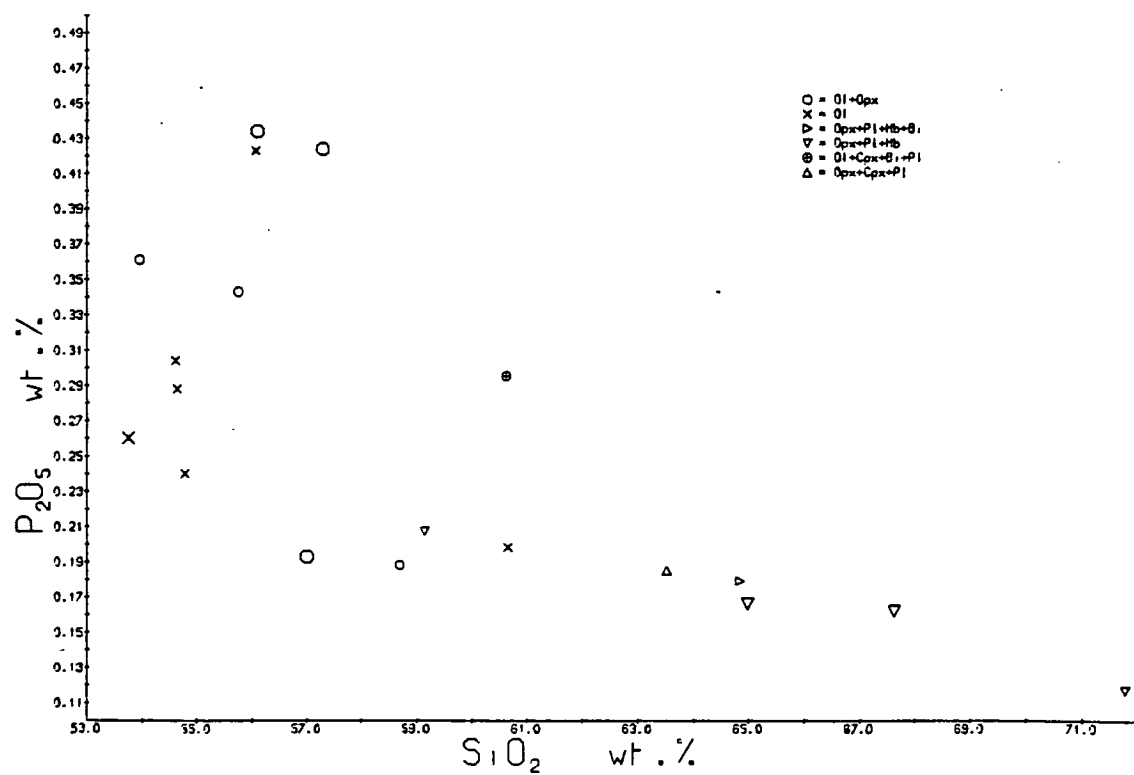
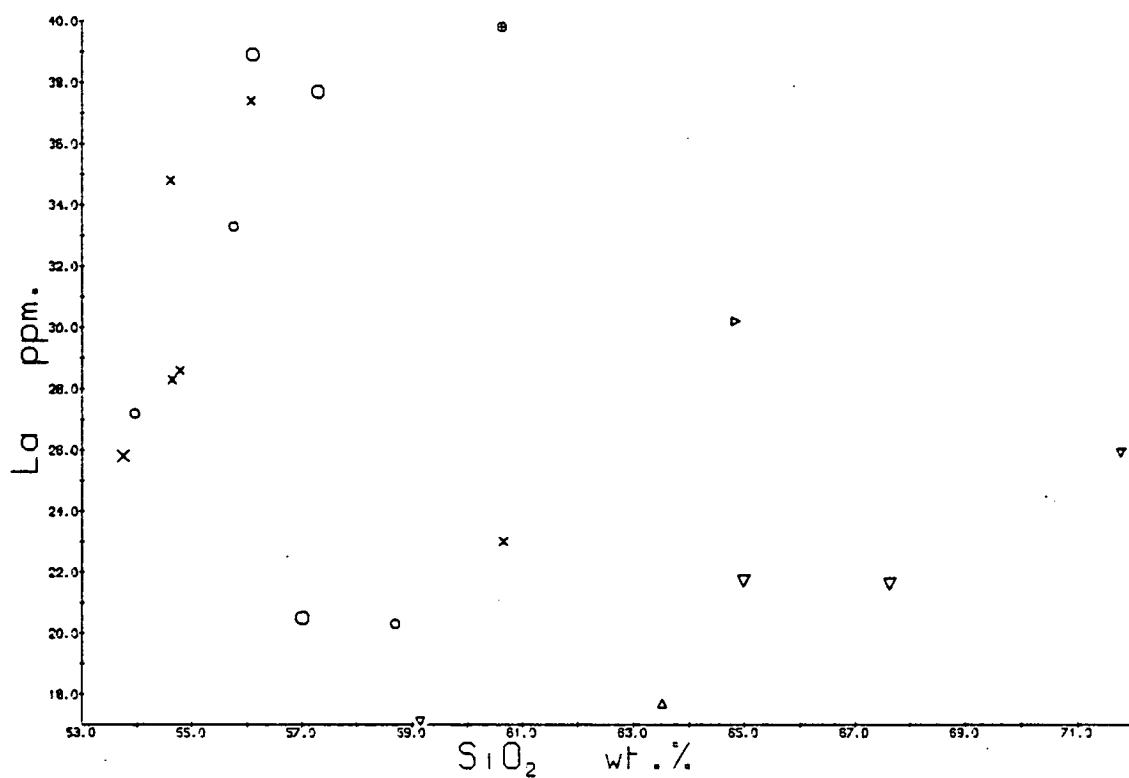


Fig. 8.1 e & f

ST. ABB'S HEAD & EYEMOUTH

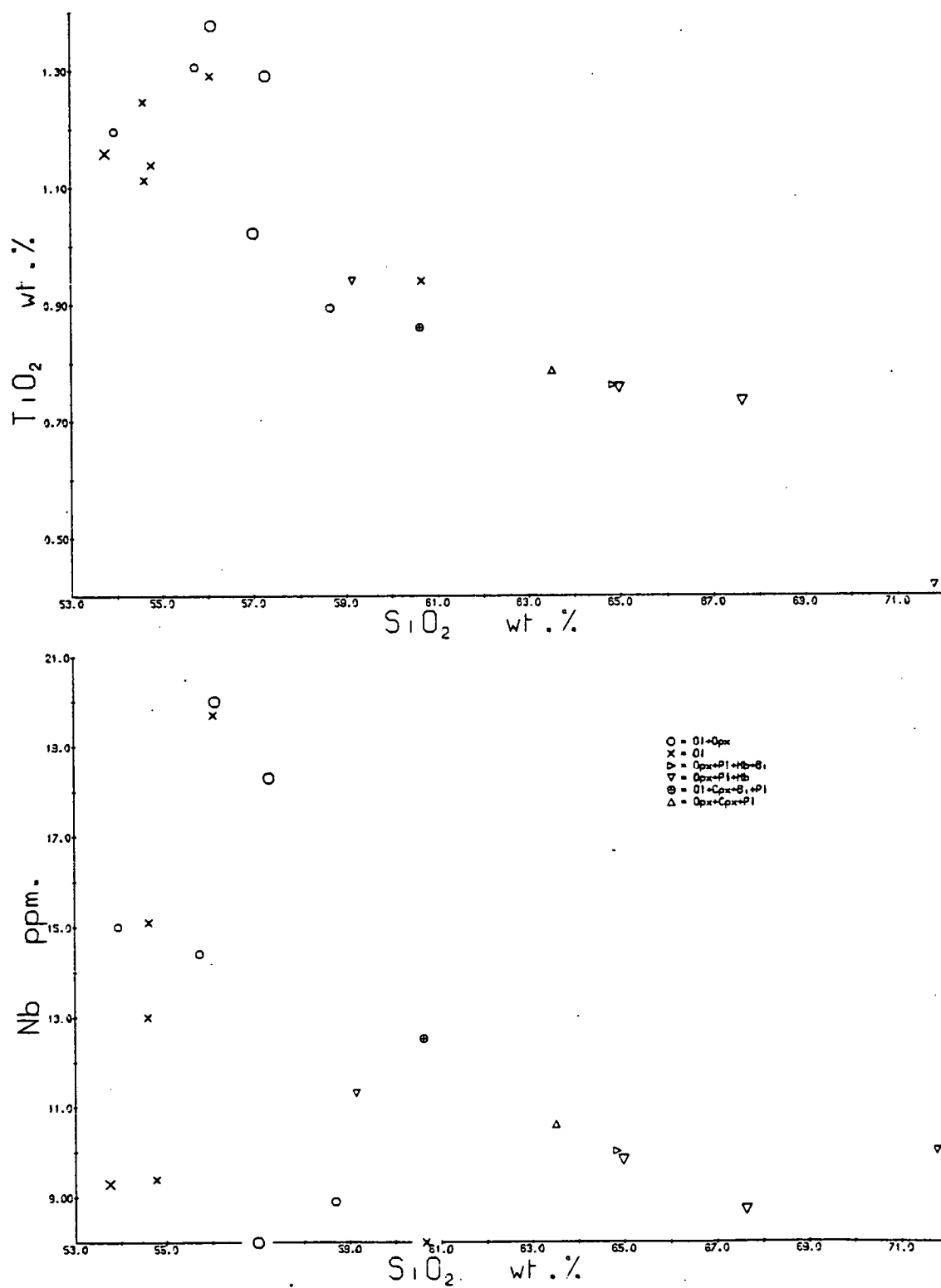
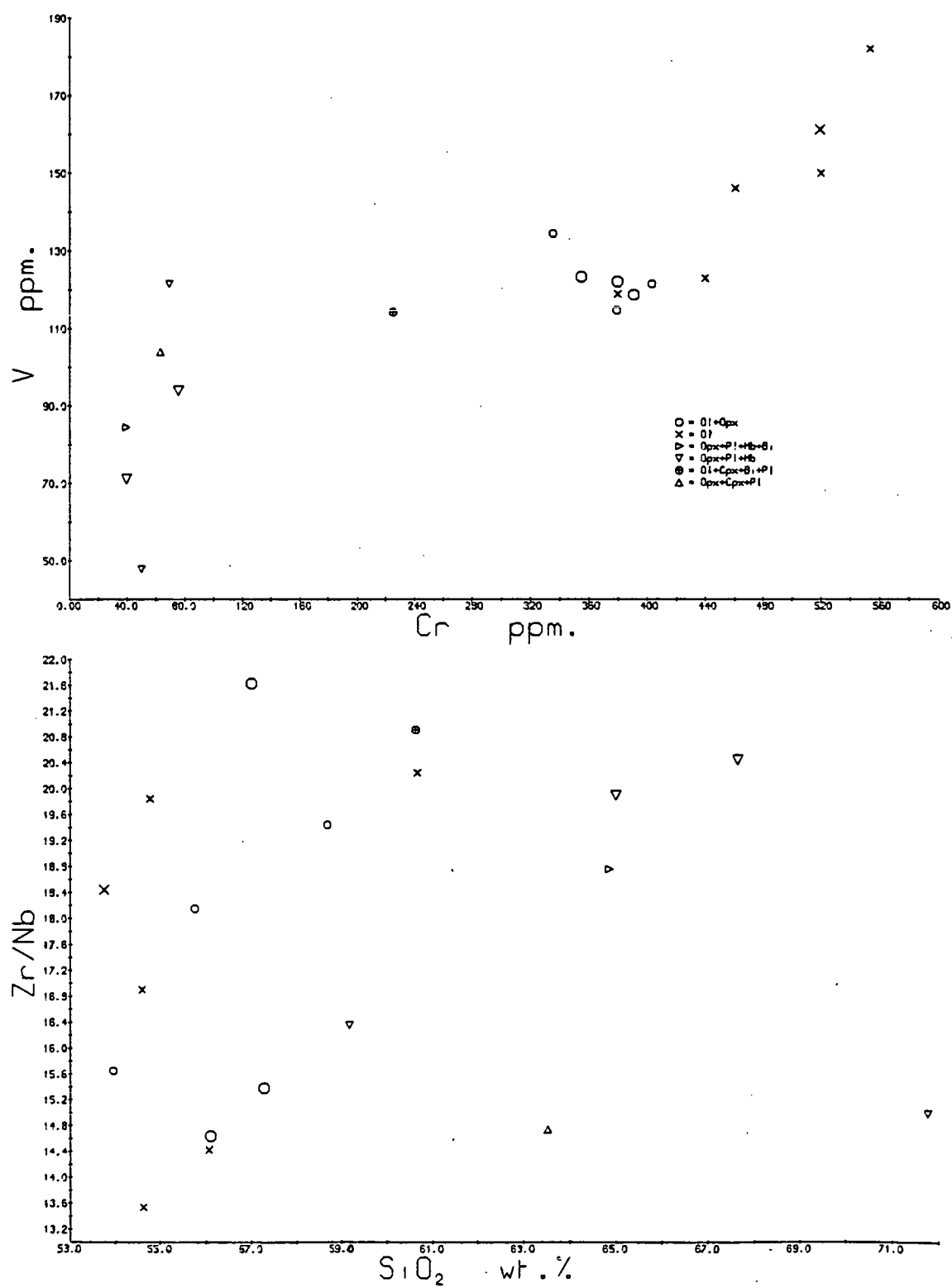


Fig. 8.1 g & h

ST. ABB'S HEAD & EYEMOUTH



small variations in Al suggest that plagioclase must constitute some 60% of this assemblage. It is clear that this variation may not be generated by fractional crystallisation of the phenocryst minerals, olivine and orthopyroxene, and it is difficult to choose a combination of 40% ferromagnesian minerals-60% plagioclase to yield $D(\text{Ni,bulk}) = D(\text{Cr,bulk}) = D(\text{V,bulk}) = 1.7$. In particular, only amphibole, magnetite and biotite have distribution coefficients in excess of 1.5 for V (Gill, 1978), but separation of these minerals would lead to greater silica enrichment than that observed. Further evidence that fractional crystallisation is unlikely to produce the variation is provided by the variability in Zr/Nb ratio (13.5-20, Fig. 8.1), which has no correlation with SiO_2 , Cr or Zr. This observation also rules out variation in the degree of partial melting of a single source, unless zircon was a residual phase.

SA17, a more siliceous sample which appears to be related to the 'rapid enrichment trend', has lower concentrations of P, Ti, Zr and Nb than the most siliceous sample of this trend. Th and LREE concentrations are, however, the highest in the area. The chemistry of this rock is not far removed from that of the least siliceous Cheviot andesites, and it is possible that they are genetically related. Since the relation of this sample to the 'rapid enrichment trend' is unclear, and also because the origin of the trend itself is debatable, further discussion of the possible relationship between the

St. Abb's and Cheviot lavas can only be speculative.

In addition to the 'rapid enrichment trend', a group of rocks showing low concentrations of 'incompatible' elements and little increase with increasing silica may be termed the 'flat' trend. Such rocks show a good negative correlation with silica for P, Fe and Ti (Fig. 8.1) but somewhat erratic scatter for most other elements. All plagioclase-phyric samples have low Ni and Cr. Considerable variation in Zr/Nb strongly suggests that rocks of the 'flat' trend may not be related to each other by fractional crystallisation or partial melting processes. One interesting feature is the occurrence of a sample (SA12) with much higher Y (44 ppm.) than any other from the area. This sample is also greatly enriched in La, Nd and Sm relative to other rocks of the 'flat' trend, but not in Ce. Possible interpretations may be based on the existence of two oxidation states for Ce, which could make it more susceptible to alteration than La, Nd, Sm and Y, or more probably this could be a magmatic negative Ce anomaly inherited from the source region.

The volcanic rocks of St. Abb's Head and Eyemouth do not closely resemble those from other areas of the province. Particularly unusual is the relatively simple phenocryst mineralogy which appears to correlate with chemistry (ol-opx-phyric samples have lower Ni, Cr and V than ol-phyric samples), and the existence for many elements of two very distinct variation trends with silica. All ol- and

ol-opx-phyric samples have high Ni and Cr (maxima 286 and 551 ppm. respectively), implying that these are mantle-derived, but the small number of samples and the high degree of alteration prevent any detailed petrochemical discussion. The rocks may be described as calc-alkaline.

8.2 : IRELAND

Old Red Sandstone strata including volcanic rocks outcrop both north and south of the Iapetus suture in Ireland, as defined by Phillips et al. (1976). Little is known about the volcanic rocks in the south, but they appear to be a few thin acid lavas and tuffs associated with very thick Upper O.R.S. in Co. Kerry (House et al., 1977, p.63), and they have not been sampled in the present study. In the north of Ireland, O.R.S. volcanic rocks are known from three areas: near Cushendall, Co. Antrim; the Fintona block, Co. Tyrone, and the Curlew Mountains inlier, near Boyle, Co. Roscommon. A welded tuff in the Upper Silurian strata of Clare Island, Co. Mayo, has yielded a K-Ar age of 412 ± 8 Ma (Cocks et al., 1971, p.119), and may be part of the O.R.S. volcanic province. At Letter Hill, Castlebar, Co. Mayo, deformed Lower O.R.S. or Silurian andesites have been reported (House et al., 1977, p.58).

(a) Cushendall

On the Antrim coast, unfossiliferous O.R.S. rocks rest unconformably on Dalradian metasediments and are

overlain unconformably by Triassic sediments. The O.R.S. contains abundant andesite boulders, and a body of quartz-andesite or dacite (the Cushendall Porphyry) near the top has been variously interpreted as lava flows (House et al., 1977, p.58) or as an intrusion (Wilson, 1972). volcanic clasts from the conglomerates (NI2, 3) are rich in phenocryst plagioclase, associated with amphibole, orthopyroxene and biotite. They are quartz-normative, siliceous (67.6-69.6% SiO_2), moderately aluminous (16%) and have high Ni and Cr (>20, >50 ppm respectively) for such siliceous rocks. They have high Ba (>1300 ppm.), Sr and La/Y, and may best be compared with some of the Ben Nevis andesites.

The sample from the Cushendall Porphyry (NI1) appears to have phenocrysts of olivine, orthopyroxene, alkali feldspar, biotite and quartz, and has a correspondingly unusual chemistry, with >10% K_2O and 63% SiO_2 . It is not certain whether the K_2O is primary or the result of alteration. Ba and Rb are also high, while P, Zr, LREE, Ni and Cr are all at least double their concentrations in the andesite clasts. Zr/Nb is also substantially higher. It is clear that these three rocks are not related by fractional crystallisation processes, but apart for the high K in NI1 they are not unusual for the O.R.S. province.

(b) Fintona

O.R.S. rocks in Counties Fermanagh and Tyrone are

faulted against Dalradian metasediments and rest unconformably on the Llandovery of the Pomeroy inlier (Wilson, 1972). The sediments are probably very thick and include several horizons of volcanic rocks, of which the most important, the Barrack Hill Member, may be 1600 ft (500 m) thick (Wilson, 1972). Apart from this member, the volcanic rocks are severely altered and badly exposed, but it appears that they are all quartz-normative, fairly siliceous (66-68%) and only sparsely porphyritic. Phenocrysts include plagioclase, both ortho- and clinopyroxene, and rare resorption pseudomorphs probably after amphibole. They are not chemically distinguishable from rocks elsewhere in the province. The sample from the Barr Church Member (NI10), although less siliceous, has lower Ni, Cr and higher 'incompatible' element concentrations than samples from Barrack Hill. The latter have substantially lower P, K, Ba and Sr than the Cushendall rocks. NI5 and 6 are fairly rich in Ni and Cr (>40, >85 ppm respectively).

(c) Curlew Mountains

The probable O.R.S. rocks of the Curlew Mountains form a small inlier lying unconformably below Carboniferous strata, and probably resting unconformably on Lower Palaeozoic rocks in the west. Charlesworth (1960) described the O.R.S. sequence and noted the occurrence of volcanic rocks at two horizons. The lower horizon was thought to be a 2000 ft (600 m) thick sequence of hornblende-andesites,

although some doubt was expressed over whether these were in fact extrusive. The upper horizon was believed to be from 50 to 100 ft (15-30 m) thick, consisting of plagioclase-pyroxene-phyric andesites and 'nodular lavas' (?autobreccias).

Exposure is minimal and there is some doubt whether the three samples collected were in situ; it is also uncertain to which volcanic horizon they belong. The samples are petrographically very different (Table A1) but are not abnormal for the province. Hornblende occurs only as very rare resorption pseudomorphs, and one sample contains fresh phenocryst orthopyroxene. All three are quartz-normative, and silica varies from 59 to 67%, the most siliceous sample having phenocryst quartz. Fe, Ti, P, V and Sr show good linear depletion with increasing silica, but the most siliceous sample is the most Cr-rich (116 ppm). Concentrations of LREE, Zr and Nb are relatively constant. K, P and particularly Ba and Sr are substantially lower than in Cushendall samples, and are closely comparable to their concentrations at Fintona.

(d) Conclusions

The O.R.S. volcanic rocks of the north of Ireland are not dissimilar to those of Scotland, and probably form part of the same volcanic province. While the rocks are generally siliceous, those from Fintona and the Curlew Mountains have significantly lower Ba, Sr and also P and K

than samples from Cushendall (Fig. 8.2).

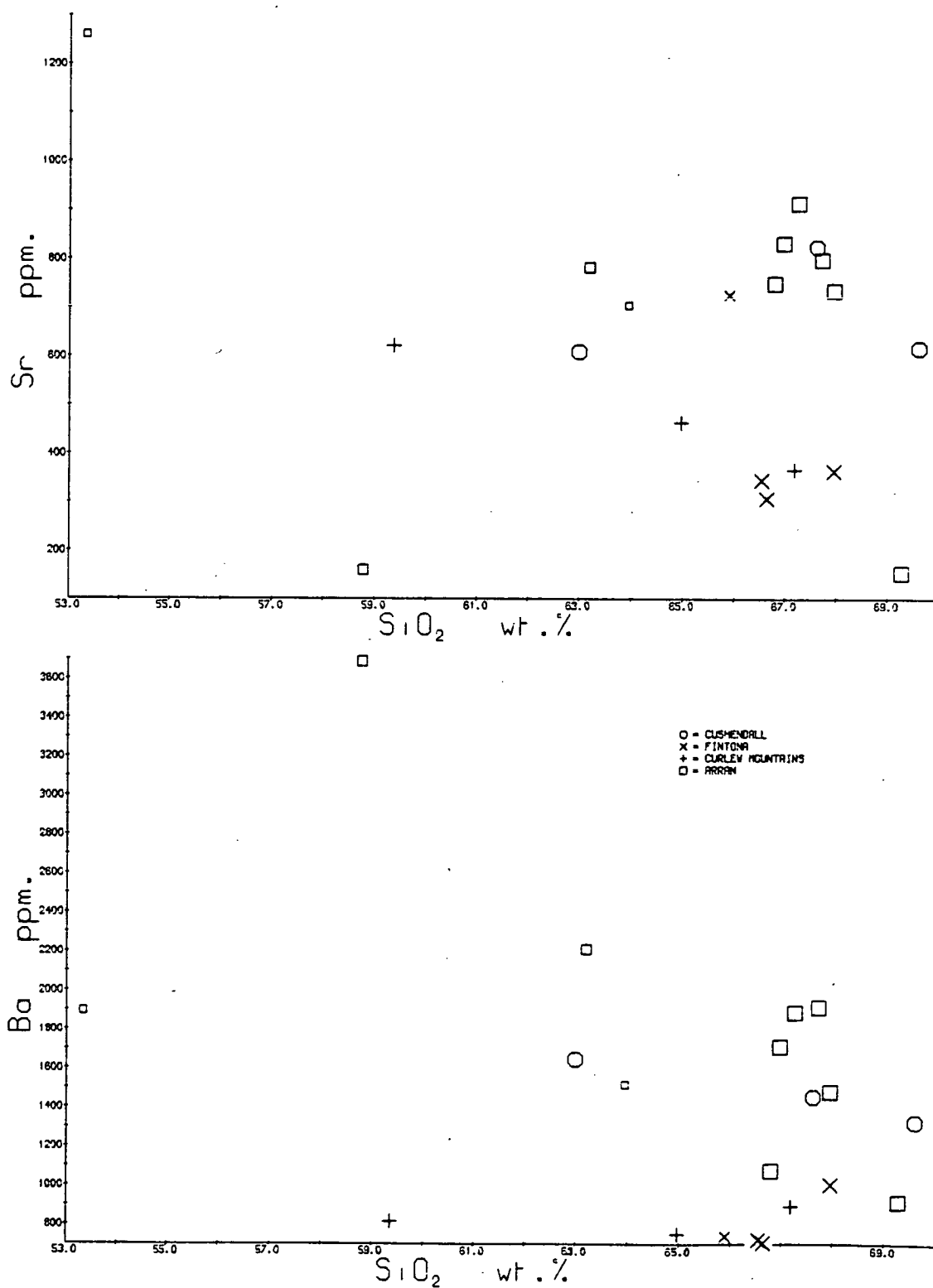
8.3 : ARRAN

Lower Old Red Sandstone conglomerates in Kintyre (Friend and Macdonald, 1968) and on Arran are rich in volcanic clasts, and on Arran Tyrell (1928) described the occurrence of a basalt lava flow at several localities. This is olivine-phyric, and is cut by numerous closely spaced carbonate veins. The sample collected in this study is olivine-normative, has 53% SiO_2 , and is rich in Ni and Cr (240, 340 ppm respectively). Zr and particularly LILE show very high concentrations, only slightly lower than in the Lorne cpx-hb-bi-phyric samples (section 4.1f).

A number of samples have been collected from clasts in the O.R.S. conglomerates of Arran. Tyrell (1928) described hornblende-feldspar-phyric andesites from these clasts; samples collected in the present study are varied and include 2 pyroxene-plagioclase-phyric types as well as amphibole- and biotite-phyric varieties. These are all siliceous (59-70% SiO_2) and all except one are quartz-normative. AR10 is slightly nepheline-normative, and has 10.8% K_2O : it is not certain whether this is primary or the result of alteration. The remaining samples are chemically comparable to the clasts of Cushendall (section 8.2a), in particular in their high concentrations of Ba and Sr (Fig. 8.2), although Y is never as low as at Cushendall, and the rocks are more varied. Many samples have fairly

Fig. 8.2 a & b : Bulk rock variation diagrams

Conventions as section 3.3

ARRAN AND IRELAND

high Ni and Cr (maxima 51 and 121 ppm respectively) despite their high silica. Hornblende-granophyre forms a further clast type (AR11): this has low Sr, Ni and Cr, and high Zr and Y. This clast was probably not derived from an O.R.S. source region.

8.4 : HUNTLY

A number of sedimentary outliers variously assigned to the Lower and Middle O.R.S. rest unconformably on the Dalradian and Moinean metasediments of the northeast Grampian Highlands. A hornblende-andesite lava and an olivine-basalt ?sill were described by Read (1923) from the Bogie outlier, a northward continuation of the Rhynie outlier. Read also noted the occurrence of a similar lava near Buckie, Banffshire (interpreted as a sill in the underlying Dalradian by Peacock et al., 1968, p.42) and an andesite sill near Cullen.

Exposure in the Bogie outlier is poor, and the only in situ sample collected (NG2) is a vesicular andesite rich in phenocryst augite and plagioclase, with rare olivine. In addition NG1, an ol-pl-phyric sample with an ophitic augite-plagioclase groundmass, was recovered from a loose block; this is closely similar to the olivine-basalt described by Read (1923). These two samples are quartz-normative and have 59 and 54% SiO₂ respectively, and for their silica contents do not have particularly high Ni and Cr. P, Zr, Nb, Th, Y and LREE are high, but are

comparable to their concentrations in the pre-Arbuthnott Group lavas of the Montrose region (Section 5.1a) and most major elements are close to their levels at Montrose.

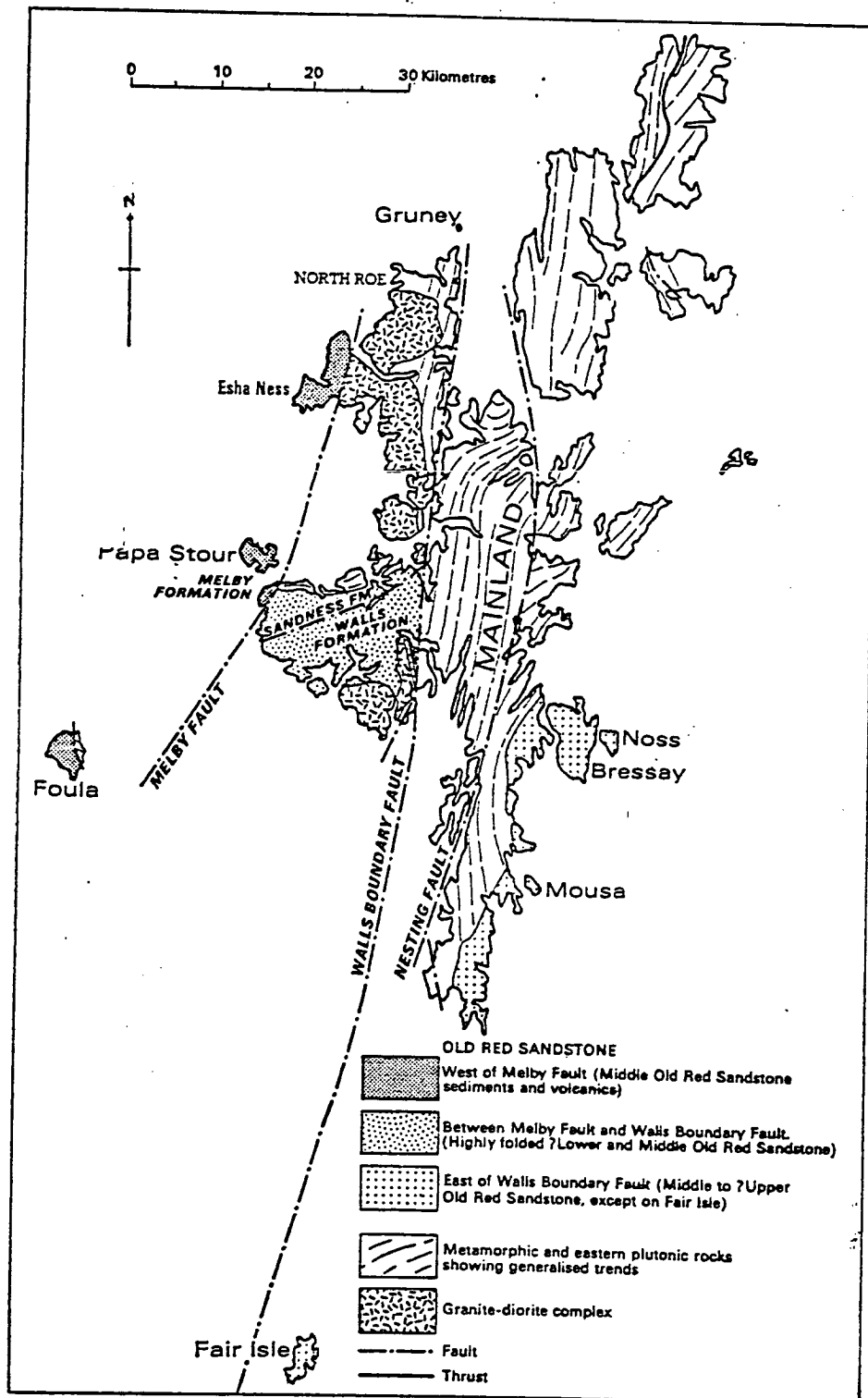
NG3 was collected from near Buckie and is a plagioclase-hornblende-phyric andesite. It is siliceous (65% SiO_2) and very rich in Rb and Th. Many elements show linear variation with silica between this and the two samples from Huntly, and Zr/Nb is almost identical for the three samples. LREE concentrations are closely comparable but Y, Zr and Nb are depleted relative to the Huntly samples.

8.5 : SHETLAND

O.R.S. strata outcrop over much of eastern Scotland north of the Great Glen Fault and its possible continuation into Shetland, the Walls Boundary Fault (Flinn, 1961). The sedimentary history of this large area was dominated by the Orcadian Lake. With the exception of Orkney and Shetland, the absence of contemporaneous volcanic rocks contrasts strongly with their abundance further south, and clasts of volcanic origin in the sediments have only been described from the Black Isle (Horne and Hinxman, 1914, p.63). Even these are very uncommon, and none was found in the present study.

The stratigraphy of the Shetland Old Red Sandstone has been reviewed by Mykura (1976) who considered that five

Fig. 8.2c



Geological sketch-map showing the outcrops of Old Red Sandstone rocks in Shetland and their structural relationships

distinct sedimentary sequences could be recognized, in the main separated by major transcurrent faults. The area to the east of the Walls Boundary Fault was believed to have been originally the most northerly, and juxtaposition was attributed to dextral post-O.R.S. transcurrent movement along the Walls Boundary Fault. Volcanic rocks are absent from this succession, although there are a few vent structures on Bressay, probably of Carboniferous age.

Between the Walls Boundary and the Melby Faults the O.R.S. may be divided into the Walls and Sandness Formations, of which the latter includes volcanic rocks. These rocks were thought to have been deposited in a position geographically intermediate between the east Shetland rocks and those of the Melby Formation, to the west of the Melby Fault. This latter has many similarities to the Orkney succession, and two rhyolitic bodies near the top have been equated with rhyolites on the island of Papa Stour (Mykura and Phemister, 1976). Flinn et al. (1968) however, have observed that there is little evidence for this correlation. The most extensive area of volcanic rocks in Shetland occurs near Esha Ness, and has been correlated with the rocks of Papa Stour by Flinn et al. (1968) and by Mykura (1976). There are a number of chemical differences, and the two areas will be discussed separately. Fair Isle and Foula also have distinct O.R.S. sedimentary sequences, although the general equivalence of the Fair Isle and Walls sequences has been suggested by Mykura and Phemister (1976, p.264). These last two areas lack volcanic rocks.

(a) Esha Ness

The O.R.S. sequence of Esha Ness is dominantly volcanic, and has been described by Finlay (1930) and summarized by Mykura (1976). The oldest beds are sandstones, which are faulted (?Melby Fault) against the Northmaven plutonic complex, but the rest of the sequence is volcanic, and rock types described include olivine-basalts, andesites, pyroxene-andesites, rhyolites and tuffs, with a mugearite and an ignimbrite. The field boundaries between these rock types (1-inch geological map, Northern Shetland) appear to be based on the presence or absence of macroscopic olivine or plagioclase. In particular, none of the four rocks collected from the area mapped as mugearite may be called a mugearite; all they have in common is their paucity of phenocrysts.

The volcanic rocks collected fall into five groups, defined by petrography and silica content. The 'basalts' (SH4, 37-39) have 51-54% SiO_2 and are sparsely porphyritic with olivine, plagioclase and in one case clinopyroxene. The 'andesites' (SH7-10) have 59 to 61% SiO_2 and SH7-9 have the phenocryst assemblage opx-cpx-pl-ap-mt, although SH10 appears to lack clinopyroxene and apatite. Clinopyroxene is a relatively iron-rich augite (anal. 89, SH9) and is rich in chlorite lamellae parallel to (001), interpreted as pseudomorphed exsolved pigeonite. In one case (SH8), these lamellae are arranged symmetrically about a twin plane, and the same herring-bone arrangement persists into an anhedral

chlorite core. This suggests the presence of early formed pigeonite, and the exsolution relationships greatly resemble those described from Straiton, Ayrshire (section 6.2).

The 'dacites' (SH1-3, 12, 13, 40, 41) have 63 to 70% silica and are rich in phenocryst feldspar, some of which is probably sanidine, although the rocks are severely altered. Mafic phenocrysts include oxide-rich pseudomorphs possibly after iron-rich pyroxene and others which may have been fayalitic olivine or hornblende. The ignimbrites have 67% SiO_2 and are rich in plagioclase and alkali feldspar crystal clasts. One severely altered rhyolitic rock has been collected, with 78% SiO_2 . It should be noted that the outcrop area is very small, and therefore the composition gaps between these rock types may have no genetic significance.

Except for three basalts, all rocks are quartz-normative. SH38 has 2% normative nepheline, but this may be attributed to alteration. Pyroxenes analysed from SH9 have low Na, Ti and Al (anal. 89), plotting within the tholeiitic field of Le Bas (1962). A number of rocks, particularly 'dacites' (Fig. 8.3b), show Fe/Mg within the tholeiitic field of Miyashiro (1974), and all rocks have low to moderate alumina (<16.5%). These criteria, and the relatively iron-rich pyroxenes, suggest that the rocks are best classified as transitional between calc-alkaline and tholeiitic, despite the high levels of K_2O (Fig. 8.3).

Fig. 8.3 a & b : Bulk rock variation diagrams

Conventions as section 3.3

ORKNEY AND SHETLAND (field for Esha Ness ignimbrites)

a : boundaries from Peccerilo and Taylor (1976)

b : boundary from Miyashiro (1974)

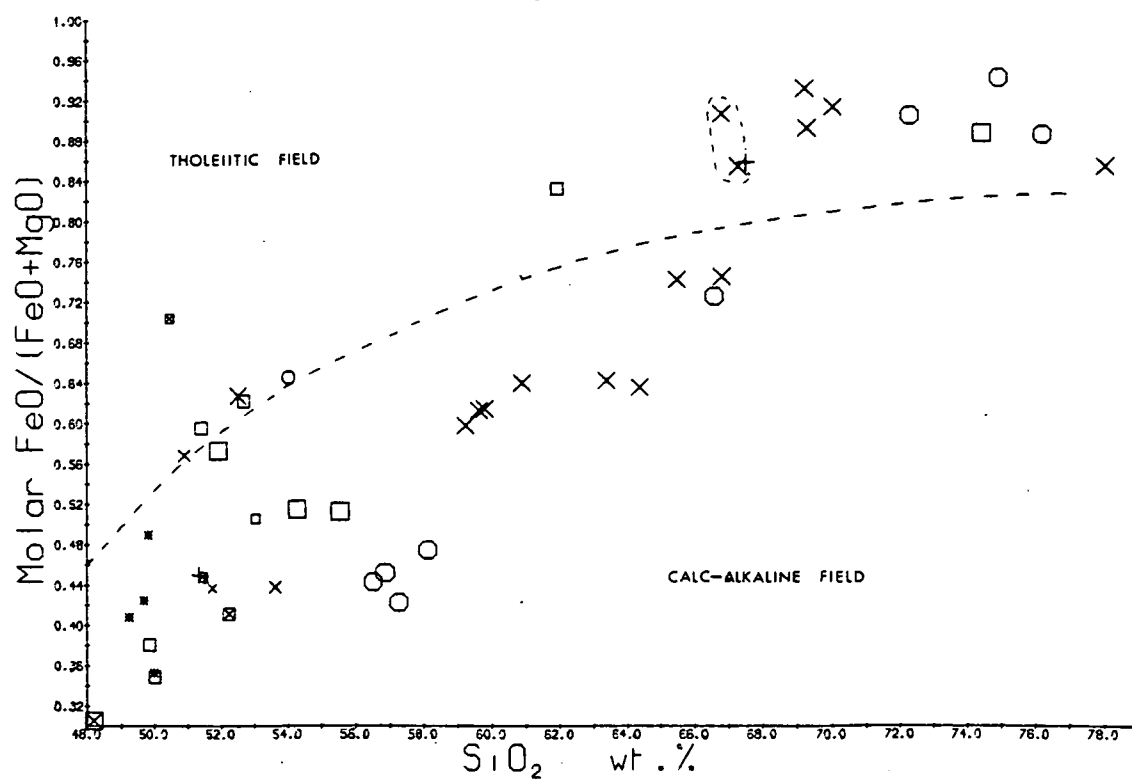
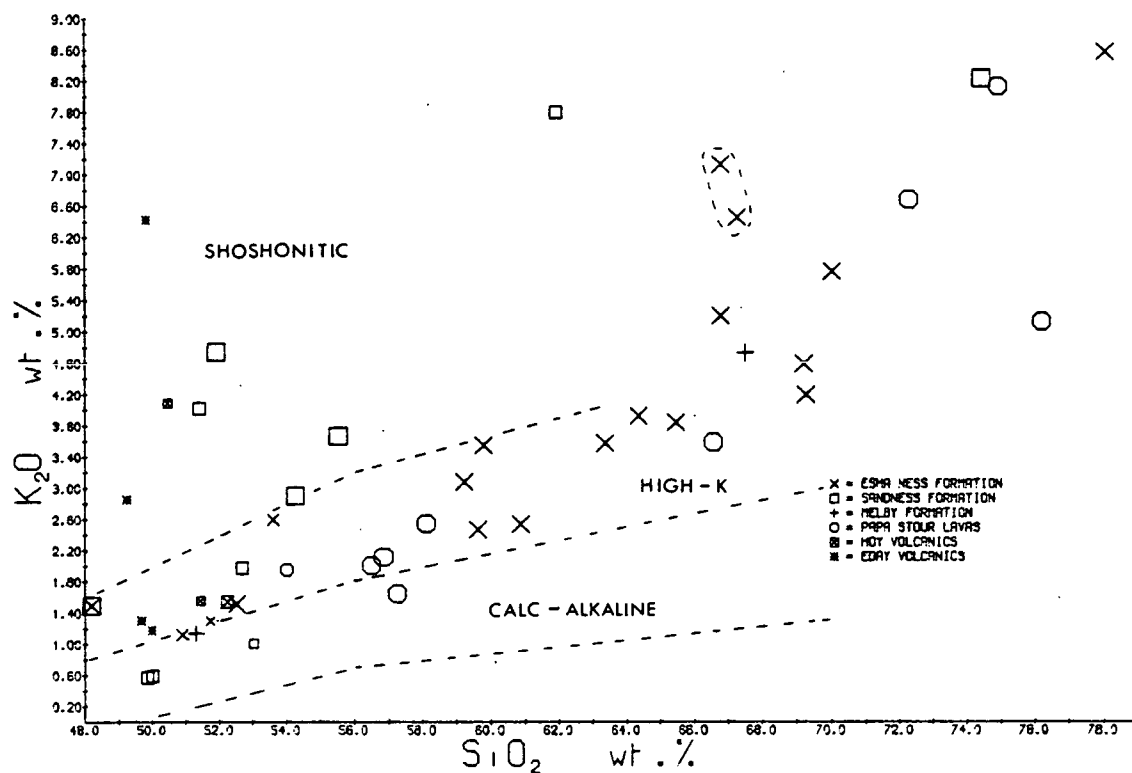


Fig. 8.3 c & d

ORKNEY AND SHETLAND

Field for Esha Ness ignimbrites.

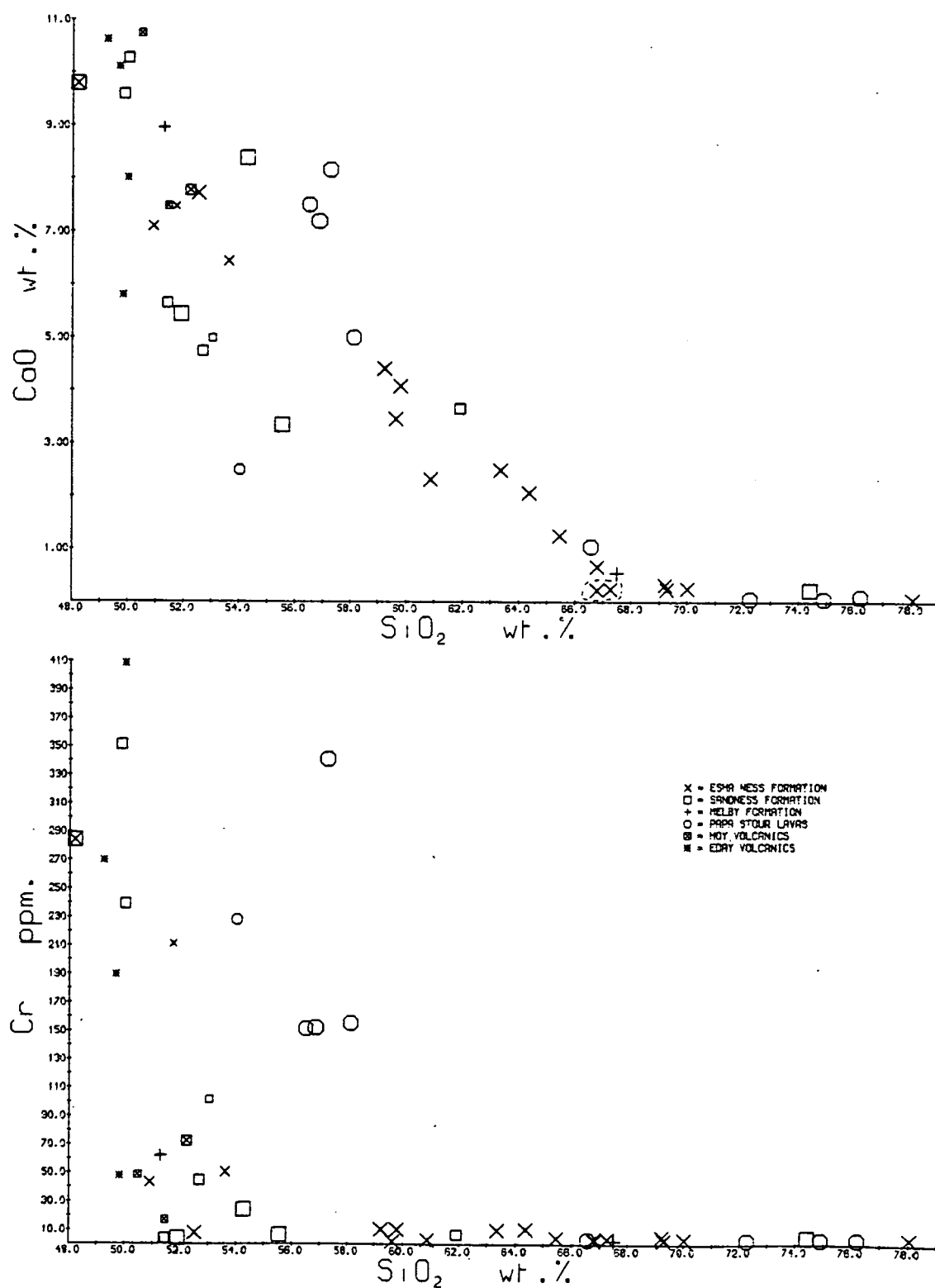


Fig. 8.3 e & f

ORKNEY AND SHETLAND

Field for Esha Ness ignimbrites

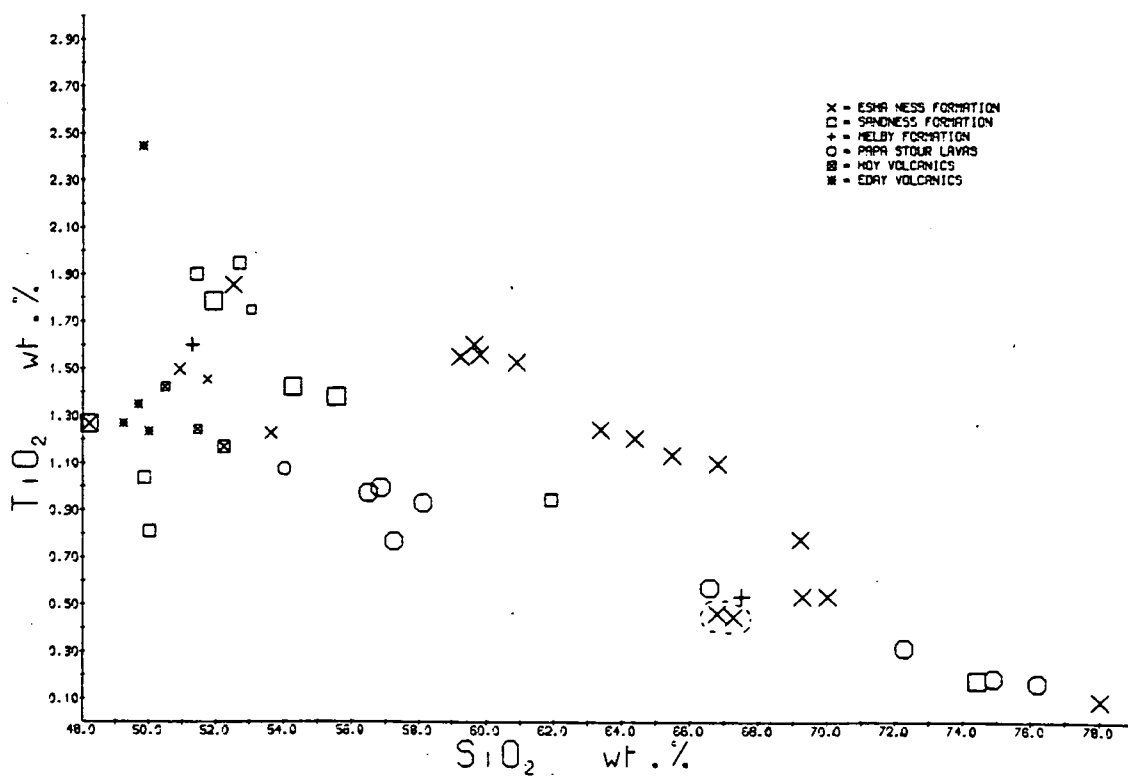
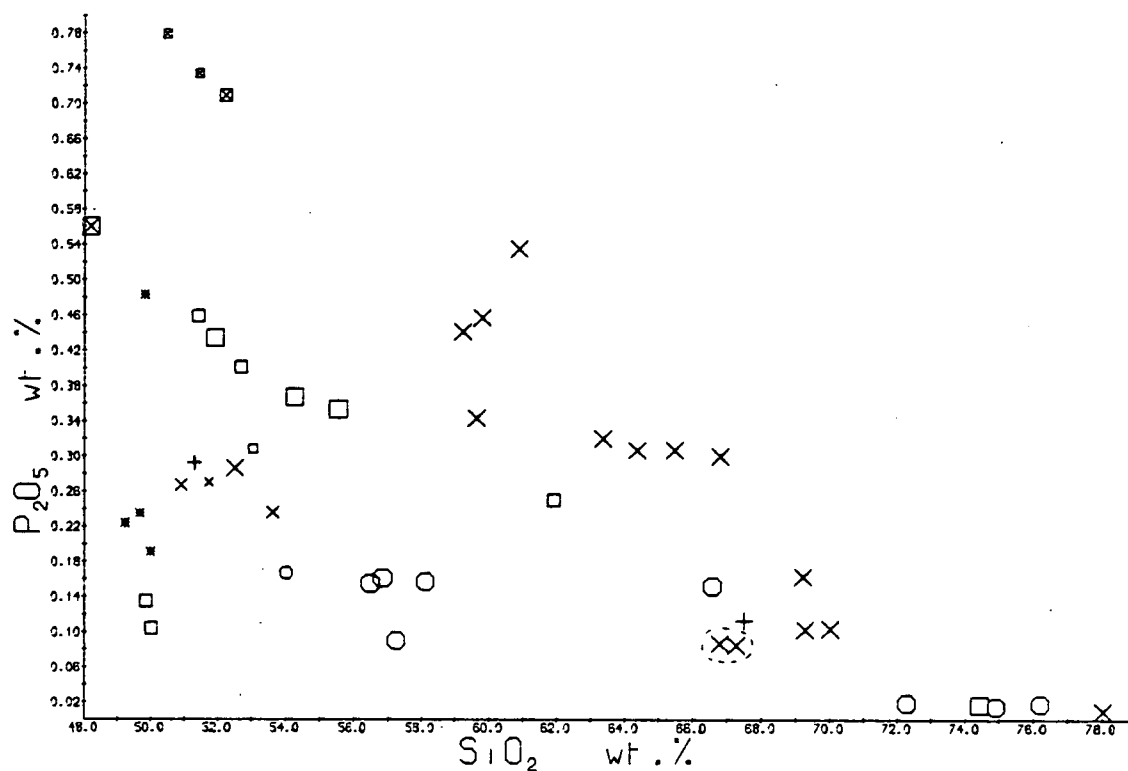


Fig. 8.3 g & h

ORKNEY AND SHETLAND

Field for Esha Ness ignimbrites

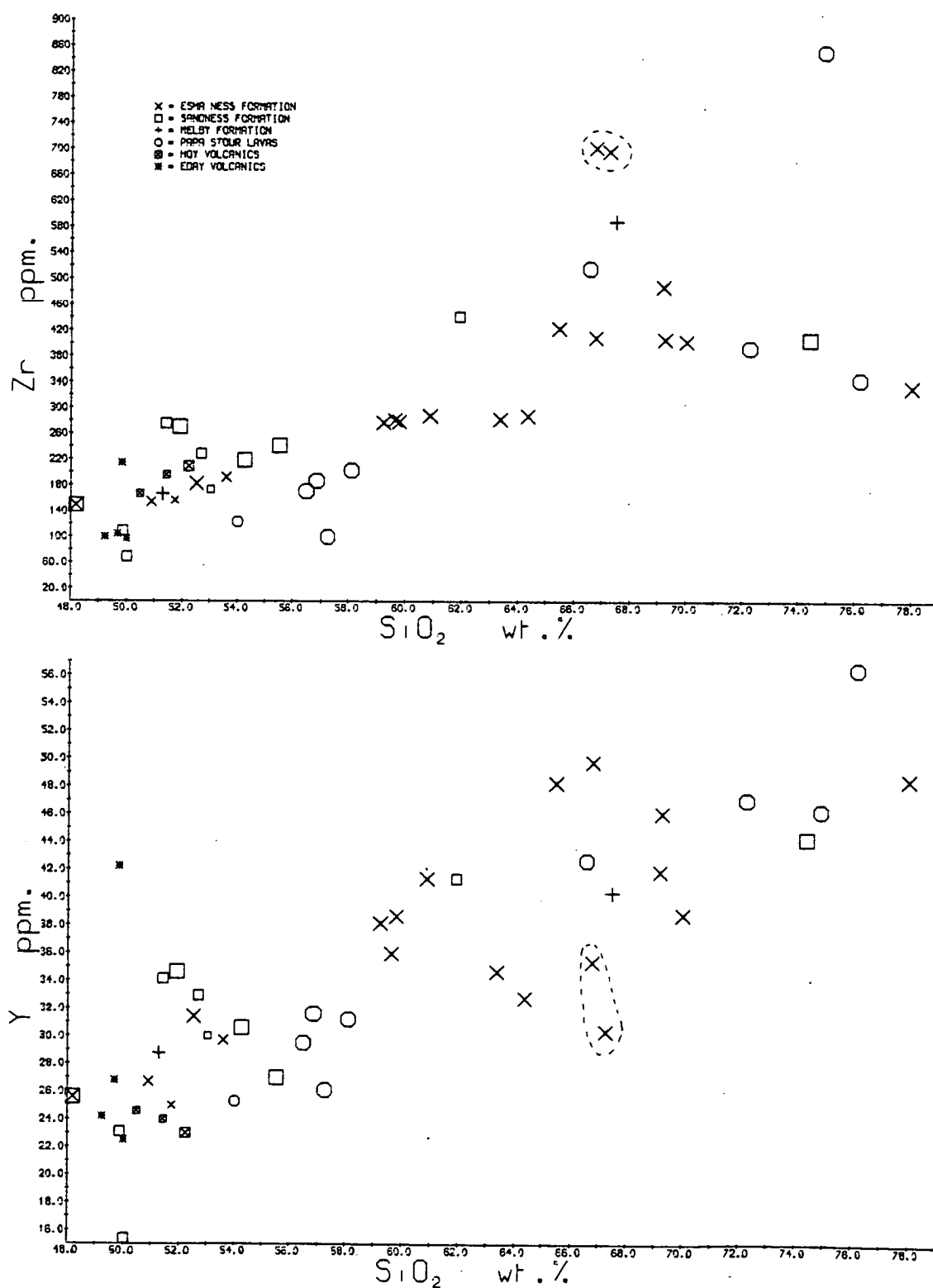
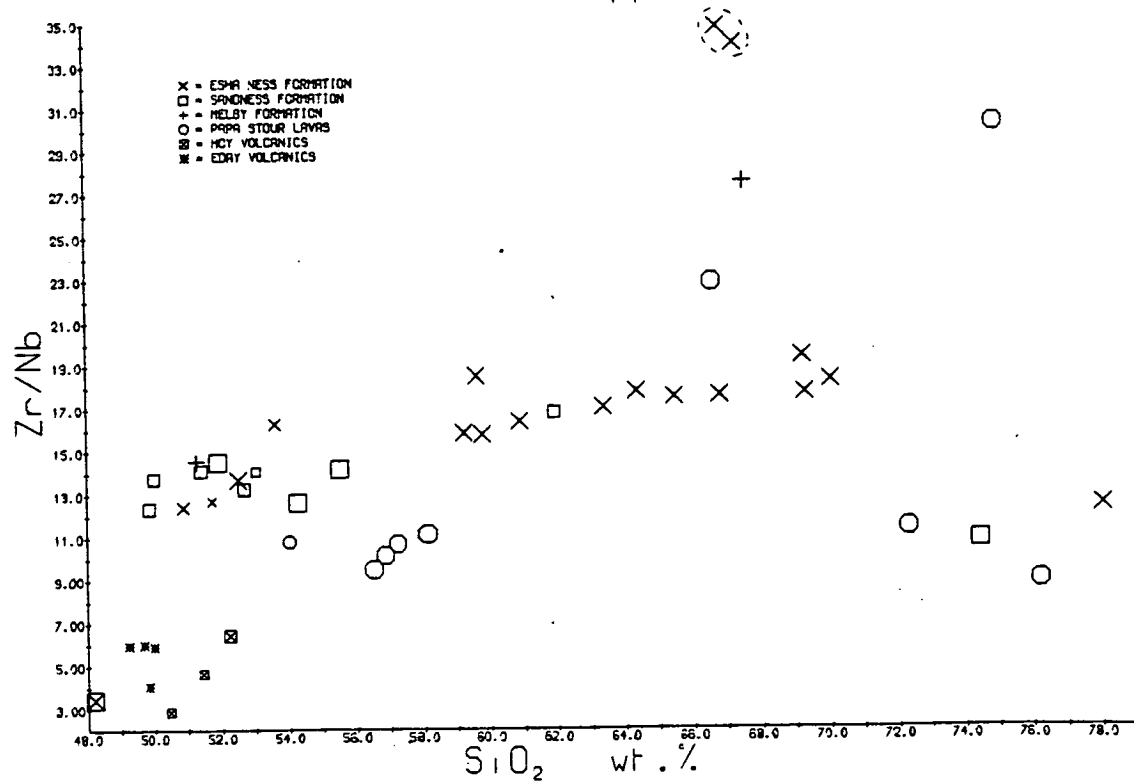
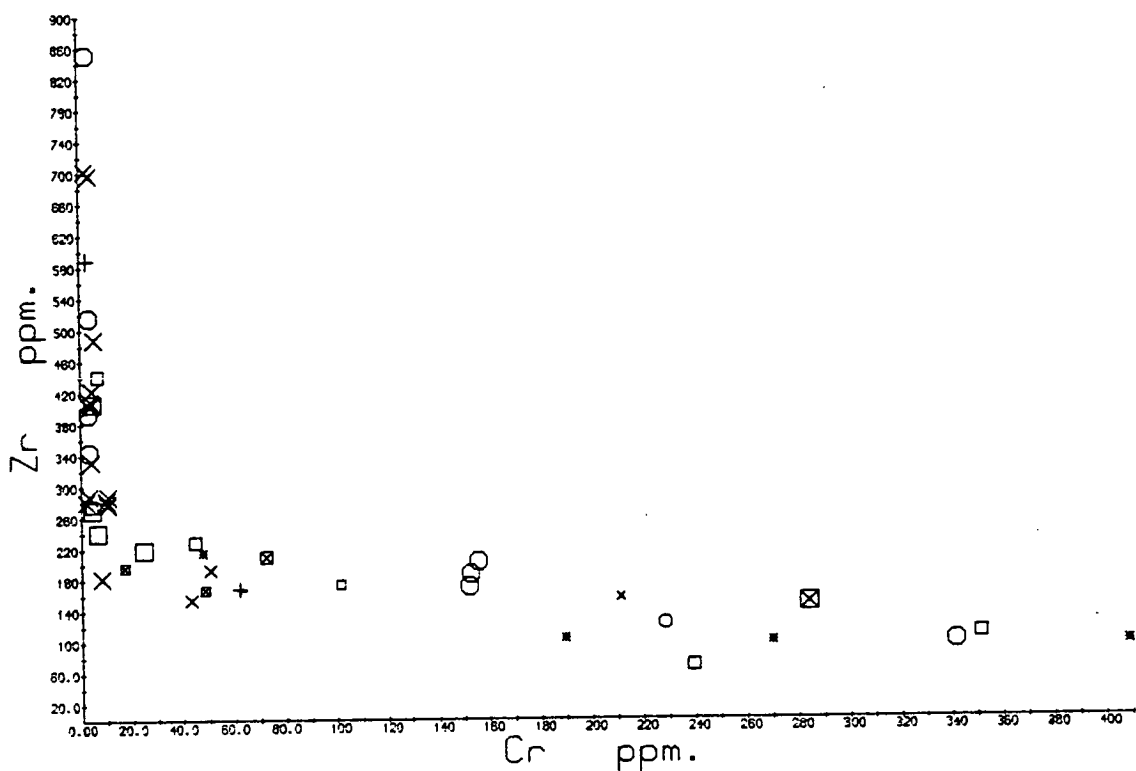


Fig. 8.3 i & j

ORKNEY AND SHETLAND

Field for Esha Ness ignimbrites



With the exceptions of the ignimbrites and the rhyolite, all samples show excellent negative correlation with silica for Al and Ca (Fig. 8.3c). Close negative correlation with silica also exists for Fe, Ti and Mg, and to a lesser extent for V and Sc, in the andesite-dacite range. Ni and Cr are always lower than 18 and 11 ppm respectively in rocks with more than 54% SiO_2 , contrasting strongly with the situation elsewhere in the O.R.S. volcanic province, although the lack of compositions between 54 and 59% SiO_2 should be noted. One of the 'basalts' (SH4) also has very low Ni and Cr, and has the highest concentrations of Fe, Ti, V and also Ca and Sc. P concentrations are at a maximum in the andesites (Fig. 8.3e). Zr, Nb, Y and LREE all show fairly good positive correlation with silica, and La/Y and Zr/Nb show slight increases with increasing silica (Fig. 8.3f). These relationships suggest that the suite could be genetically related by fractional crystallisation. The variation in Zr/Nb from 12 to 19 correlates well with increasing SiO_2 and Zr: the three-fold increase in Zr suggests a high degree of crystallisation, and the increase in Zr/Nb may be well explained by an implication of Pearce and Norry (1979) that $D(\text{Zr/Nb}) < 1$ for most plausible fractionating minerals (Chapter 3).

The variation described above for the basalts may probably be accounted for by fractional crystallisation of the phenocryst minerals olivine and plagioclase, associated with minor chrome-spinel. However, the enrichment in Ti and V in SH4 is not associated with enrichment in Zr or Nb, and

the highly altered state of the basalts leads to difficulty in the development of a quantitative model.

The change from basalt to andesite is marked by 1.5X enrichment in Zr and Nb, 1.8X enrichment in LREE, and substantial depletion in Ca, Mg, Sc, V, Fe, Al and Ti (in order, with greatest depletion in Ca). This suggests the incoming of at least one extra liquidus phase; for example plagioclase, clinopyroxene, orthopyroxene or titanomagnetite. Major element variation from SH4 to SH9 (an andesite) and from SH9 to SH12, a dacite, has been modelled using the computer program MODES, using the weighting facility as in Chapter 7. Mineral analyses were taken from SH9, together with an estimated titanomagnetite and the orthopyroxene from AY35 (cpx analyses of SH9 and AY35 compare closely). A very good fit (sum of squares of residuals $\sum r^2 = 0.03$) is given for fractional crystallisation of 7.3% mt, 3.3% opx, 0.3% ap, 15% cpx and 32.8% pl from SH4 to form SH9. This model is supported by the nearly constant Sr, and the c. 1.5X enrichments in Zr and LREE, which will be partially retained by titanomagnetite and apatite. These elements, together with Sc, V and Ni, have been modelled using the Rayleigh equation for perfect fractional crystallisation and the distribution coefficients of Gill (1978) and Pearce and Norry (1979). Reasonable agreement is provided by Zr, LREE, Sr and Sc, but in the latter case only if $D(\text{Sc}, \text{cpx})$ is taken as 4. V content of SH9 is too high for the required amount of magnetite separation (assuming $D(\text{V}, \text{mt}) = 24$) and Ni and Cr are higher in SH9 than SH4, even

though $D(\text{Ni}, \text{bulk}) = 2.5$. It is clear that SH9 may not be derived by fractional crystallisation of a liquid of composition SH4, but it is believed that it could be derived from a liquid immediately parental to SH4 with higher concentrations of Ni and Cr.

Chemical variation among the four andesites is substantial for P, V, LREE and Fe (Fig. 8.3), and this variation is correlated with smaller changes in Mg, Sc and Y. SH10, the apatite-free andesite, has highest P, LREE and lowest Fe, Mg, V, Sc: it is suggested that this variation could result from minor variation in the relative proportions of phases crystallised from a basaltic parent.

The variation between SH9 and the dacites (e.g. SH12) is not well modelled by fractional crystallisation of the phenocrysts of SH9 ($\xi r^2 = 5$) although a better fit is provided for generation of a less siliceous dacite, SH40 ($\xi r^2 = 1.2$). Both of these models have large residuals for Ti, suggesting that a Ti-rich phase should be incorporated into the model. Recognition of the mafic phenocrysts in the dacites is difficult, and it is possible that one of them may have been a Ti-rich amphibole.

The ignimbrites show much higher Zr/Nb than other rocks, mainly due to their very high Zr content, while the rhyolite has slightly lower Zr/Nb. It is possible that the rhyolite represents the final stage in the fractional crystallisation sequence, but this is difficult to model

because of the severe alteration.

Despite the small area of rocks exposed at Esha Ness, there is good evidence that the suite may be derived by multistage low pressure fractional crystallisation. The first stage involved separation of an olivine-dominated assemblage from a magma close in composition to an olivine-tholeiite, and was followed by crystallisation of orthopyroxene (or pigeonite), clinopyroxene, plagioclase, titanomagnetite and apatite, and later by a Ti-rich phase. Major iron enrichment in andesites and dacites is prevented by crystallisation of titanomagnetite, but the rocks are transitional between calc-alkaline and tholeiitic. The area is thus distinguished from the rest of the province, where fractional crystallisation processes have been inferred to be of minor importance. The principal petrochemical differences are as follows:

- 1/ Gently increasing Zr/Nb with increasing SiO_2 and Zr.
- 2/ Positive correlation between SiO_2 and Zr, Nb, Y and LREE, despite the later crystallisation of apatite and Ti-rich phases.
- 3/ Good correlation between phenocryst mineralogy and host rock SiO_2 .
- 4/ Very low Ni and Cr in rocks with $>54\% \text{SiO}_2$, and the absence of rocks with low Ni and low 'incompatible' elements, and of rocks with high Ni and high 'incompatible' elements.

It is possible that variation in Zr/Nb in the basalts

is significant, and that the petrogenesis is not quite as simple as presented above. Because of the high degree of crystallisation implied above within the basalt range, and from basalt to andesite, andesite to dacite, incompatible element concentrations increase rapidly with SiO_2 : the most mafic rocks have low K_2O (<1.4%), low LREE (<30 ppm La) and low Ba (?500 ppm) relative to many rocks in the rest of the province.

(b) Melby - Papa Stour

The two rhyolites of Melby are severely altered, and the one analysed (SH20) compares well with the Esha Ness ignimbrites, although similarity between two such acid rocks is not necessarily significant. A sparsely ol-pl-phyric lava is exposed on the Holm of Melby, an island in the Sound of Papa; this is basaltic (SH36), and compares very closely with the moderate-Ni, -Cr basalts of Esha Ness (SH38, 39), except for the more mobile elements Ba, Rb, K and Na. It is suspected that the high and variable Zn concentrations are also due to alteration.

The rocks of the island of Papa Stour have been described by Mykura and Phemister (1976). They were assigned to the Middle O.R.S. on the basis of correlation with the Melby rhyolites, which overlie sediments with a rich fish fauna. The sequence consists of at least four 'basalt' flows, overlain by tuffs, sandstones and two thick rhyolite lavas. The samples collected from the basic flows

have olivine and plagioclase phenocrysts, with olivine common in SH32, but SH27, 29 and 30 are all sparsely porphyritic. SH31 is an altered coarse-grained variant. SH30 contains rare phenocrysts of relatively iron-rich augite, low in Ti, Al and Na (anal. 90), and augite-rimmed orthopyroxene in addition. With the exception of the altered sample, they are all quartz-normative. They are not basalts (54-58% SiO_2), but have much higher Ni and Cr than most Esha Ness samples (Fig. 8.3d), suggesting that the rocks of these two areas can not be related by fractional crystallisation. In addition, Zr/Nb is much lower at Papa Stour, and is constant for all mafic samples. Fe/Mg is low, and the rocks are best described as calc-alkaline. SH32 has the highest concentrations of Mg, Ni, Cr, Ca, Sc and V, and the three other fresh samples are enriched in P, LREE, Rb, Ba, Zr and Nb by an amount which could be attributed to about 40% crystallisation of a liquid of composition SH32. Ti, Y and Sr are slightly enriched in the evolved samples (Fig. 8.3). It is suggested that these four samples are likely to be related by fractional crystallisation, not of the phenocryst phases, but possibly of an assemblage rich in clinopyroxene at higher pressure. The small number of samples available does not permit quantitative modelling by extract calculations. The most mafic sample has very low concentrations of many incompatible elements compared with rocks elsewhere in the province e.g. 0.09% P_2O_5 , 220 ppm Sr and 34 ppm Ce.

The rhyolites contain phenocrysts of sanidine and

sometimes plagioclase, with some pseudomorphs possibly after hornblende. Two have Zr/Nb similar to that of the mafic rocks, but the other two have high Zr/Nb comparable to the Esha Ness ignimbrites (Fig. 8.3). All four have moderate to low Ba, perhaps attributable to fractional crystallisation of sanidine, but the four are very variable for most elements, and the small number of samples does not permit the suggestion of petrogenetic hypotheses.

The new chemical data suggests a review of the correlation proposed by Finlay (1930), Flinn et al. (1968) and Mykura (1976) between the Esha Ness, Papa Stour and Melby volcanic rocks. It is considered unwise to use probably impersistent rhyolites as a basis for correlation, and more emphasis should be placed on basic lavas and ignimbrites. The mafic lavas of Papa Stour are very different from those of Esha Ness, particularly in Zr/Nb, P_2O_5 , Ni and Cr, but that of the Holm of Melby is very similar to the Esha Ness basalts. Ignimbrites have not been recorded from Papa Stour, but are known from Melby (Mykura and Phemister, 1976, p.151). It is therefore suggested that Esha Ness - Holm of Melby - ?Melby formed a single volcanic region, from which Papa Stour was distinct. These differences may be explained by postulating a transcurrent fault in the Sound of Papa, or by invoking an age difference between the two areas.

(c) Sandness Formation

The Sandness and Walls Formations lie between the Melby and the Walls Boundary Faults, and are separated from each other by the Sulma Water Fault. The Walls Formation is wholly sedimentary, but the Sandness Formation contains a number of thin lava flows and pyroclastic horizons described as the Clousta Volcanic Rocks. The occurrence and petrography of these have been described by Mykura and Phemister (1976). The rocks have suffered polyphase deformation, and sometimes low-amphibolite facies metamorphism. The effects of the deformation may often be seen in thin section; for example, the dislocation of phenocryst plagioclase in SH23.

Mykura and Phemister (1976) have described pyroxene-andesites, basalts and ignimbrites from the Clousta Volcanic Rocks. Most rocks collected in the course of this research are sparsely porphyritic with olivine and plagioclase, although SH23 has abundant calcic labradorite (anal. 78) and diopsidic augite phenocrysts. A few of the latter are rich in Ti and tetrahedral Al, but the average (anal. 88) plots within the tholeiitic field of Le Bas (1962). A severely altered ignimbrite sample and an apparently acid clast rich in sanidine from the Clousta Tuff have also been collected.

The mafic rocks include two slightly nepheline-normative samples (0.5% ne), but this can be

attributed to alteration. Three further samples are olivine-hypersthene normative. Silica varies from 50 to 55%, and SH23, the 'pyroxene-andesite' with abundant phenocryst plagioclase from Burga Water (Mykura and Phemister, 1976, p.92), has 50% SiO_2 and is Ni- and Cr-rich. Several rocks have Fe/Mg within the tholeiitic field of Miyashiro (1974), and they may be described as transitional between calc-alkaline and tholeiitic. Zr/Nb is identical within analytical error (12-14.5) and the rocks can not be distinguished from those of Esha Ness on the basis of Zr/Nb (Fig. 8.3). SH23 has the lowest concentrations of most incompatible elements (e.g. 69 ppm Zr), but does not have the highest Ni or Cr. The high alumina of SH23 suggests that the low incompatible element concentrations may be due to plagioclase accumulation, for in general samples with higher incompatible elements have lower Ni and Cr.

The chemical variation may be due to fractional crystallisation of olivine, clinopyroxene and plagioclase, with additional spinel for the two more siliceous rocks (SH15, 16). This is suggested by enrichment in V, Ti and Fe and depletion in Mg, Ni, Cr, Ca and Sc between SH23, 25 and SH18, 19, 22 and 24. Over this same range, Sr, Y and V increase by a factor of about 1.8; Ti by about 2.4; Zr, Nb and P by about 3.5; Ba and LREE by about 6 and K, Rb and Th by about 7. It should be noted that the lack of silica enrichment over the large degree of crystallisation necessary will occur if $D(\text{SiO}_2, \text{bulk})=1$, which may be the case during separation of the assemblage ol-cpx-pl, although

it is surprising that the phase assemblage seems not to have changed over such a large degree of crystallisation.

Separation of titanomagnetite can generate the higher silica and lower Fe, Ti and V of SH15 and 16.

While the more evolved rocks show significantly higher incompatible element concentrations and lower Sc and V than the Esha Ness basalts, there is broad similarity between the two areas (Fig. 8.3), and the most mafic Esha Ness rocks generally fall on the variation trends for Sandness rocks. This suggests the possibility that the parental magmas of each were in many ways similar, although Esha Ness rocks all have lower Al.

The apparently acid clast from the Clousta Tuff has only 62% SiO_2 , but 7.8% K_2O . Zr/Nb is close to that of basic Sandness rocks and it is conceivable that this could be derived by further fractional crystallisation of the basic Sandness magmas. The ignimbrite has lower Zr/Nb, comparable with the Papa Stour rocks (Fig. 8.3), but it is greatly altered and little can be concluded concerning its petrogenesis.

(d) Shetland : Conclusions

The three volcanic sequences of Shetland form three petrochemically distinct groups. The basic and intermediate rocks of each sequence can be related by fractional crystallisation processes. This is in strong contrast to

rocks from elsewhere in the province, where Ni- and Cr-rich rocks frequently have high concentrations of incompatible elements. The compositions of Shetland lavas often imply a large degree of crystallisation of parental magmas deficient in incompatible elements. These parental magmas, while not primary magmas, are represented in Shetland by a few rocks with 100-200 ppm Ni, and have lower concentrations of incompatible elements than observed from elsewhere in the province.

8.6 : ORKNEY

Most of the rocks exposed in Orkney have been assigned to the Old Red Sandstone (Wilson et al., 1935) on the basis of abundant fish faunas. Volcanic rocks are present at two horizons in the O.R.S. sequence: near the base of the Eday Flags (Middle O.R.S.) and at the base of the Hoy Sandstone (?Upper O.R.S.). The rocks associated with the Eday Flags on Shapinsay and at Deerness comprise lavas and associated intrusions (Kellock, 1969). The lavas are sparsely ol-pl-phyric with a groundmass of plagioclase, augite, analcite and other zeolites, and the intrusive rocks are coarse-grained with the same mineralogy. Kellock (1969) compared the rocks with the Carboniferous teschenites and alkali basalts of the Midland Valley, although the analcite may be secondary. Two of the samples have normative nepheline, but this can be attributed to the introduction of carbonate on alteration. All four rocks have 49-50% SiO₂, but a significant range in Ni and Cr concentrations exists.

The three samples with higher Ni (OR5, 7, 8) show increases in Zr, Nb, Y, P, Ti and LREE with decreasing Cr, while Zr/Nb is constant at about 6. (Fig. 8.3j). $Y/Nb > 1$ for these three samples, suggesting that they are not alkaline (Pearce and Cann, 1973), and most immobile incompatible elements have low concentrations similar to those at Esha Ness, although Nb is slightly higher. OR6, however, has 52 ppm Nb and $Y/Nb < 1$. Such high Nb is not known from elsewhere in the O.R.S. province. Ti in OR6 is closely comparable to its concentrations in Carboniferous alkali basalts (Macdonald 1975) but in the other three Ti is much lower. It is believed that OR5, 7 and 8 are olivine-tholeiites similar to the Shetland rocks, and that the intrusive rock OR6 is probably younger, and Carboniferous.

The volcanic rocks of Hoy are thought to be of Upper Devonian age (House *et al.*, 1977) because of the occurrence of Holoptychius, an Upper O.R.S. fish, in the Caithness equivalents of the immediately overlying Hoy Sandstone (Mykura, 1976, p.89). A K-Ar stepwise degassing age of 368 ± 8 Ma has been reported by Halliday *et al.* (1977). Tuffaceous sediments are overlain by the Hoy lava(s) which were described as ol-pl-phyric by Mykura (1976). Olivine is fresh in two samples and has composition Fo83 (anal. 4, OR3). Plagioclase is generally bytownite (anal. 77, OR3), and there are also frequent phenocrysts of augite. This is often rich in Ti and tetrahedral Al (anal. 87, OR3) and most analysed points plot in the alkaline field of Le Bas (1962). An isotropic groundmass mineral is probably analcite.

All four samples have normative nepheline (3-5% ne), and since two samples have fresh olivine the nepheline is believed to be primary. Silica varies from 48 to 52% and OR3 is rich in Ni and Cr. Nb is very high (32-58 ppm) and Zr/Nb very low (3-6). There is no correlation between Zr and Nb, or between these and depletion in Cr or Ni: the rocks can not therefore be related by fractional crystallisation. Y/Nb is less than 1 and La/Y, P_2O_5 and Sr are much higher than any other rock from Shetland and Orkney (Fig. 8.3). They may therefore be described as alkali basalt and hawaiite, but their low Ti distinguishes them from the younger Carboniferous alkali basalts. Whitford (1975) noted that alkali basalts erupted in subduction-related magmatic arcs characteristically have low Ti.

CHAPTER 9 : SPATIAL VARIATION, DISCUSSION AND CONCLUSIONS

9.1 : CHARACTERISTICS OF THE O.R.S. VOLCANIC SUITE

The volcanic rocks associated with the Old Red Sandstone in Britain have a number of features in common. The most important are:

(a) Most rocks are quartz-normative. Basic rocks are sometimes olivine-hypersthene normative, but apart from the Hoy lavas, significant normative nepheline is never present in rocks free from secondary carbonate.

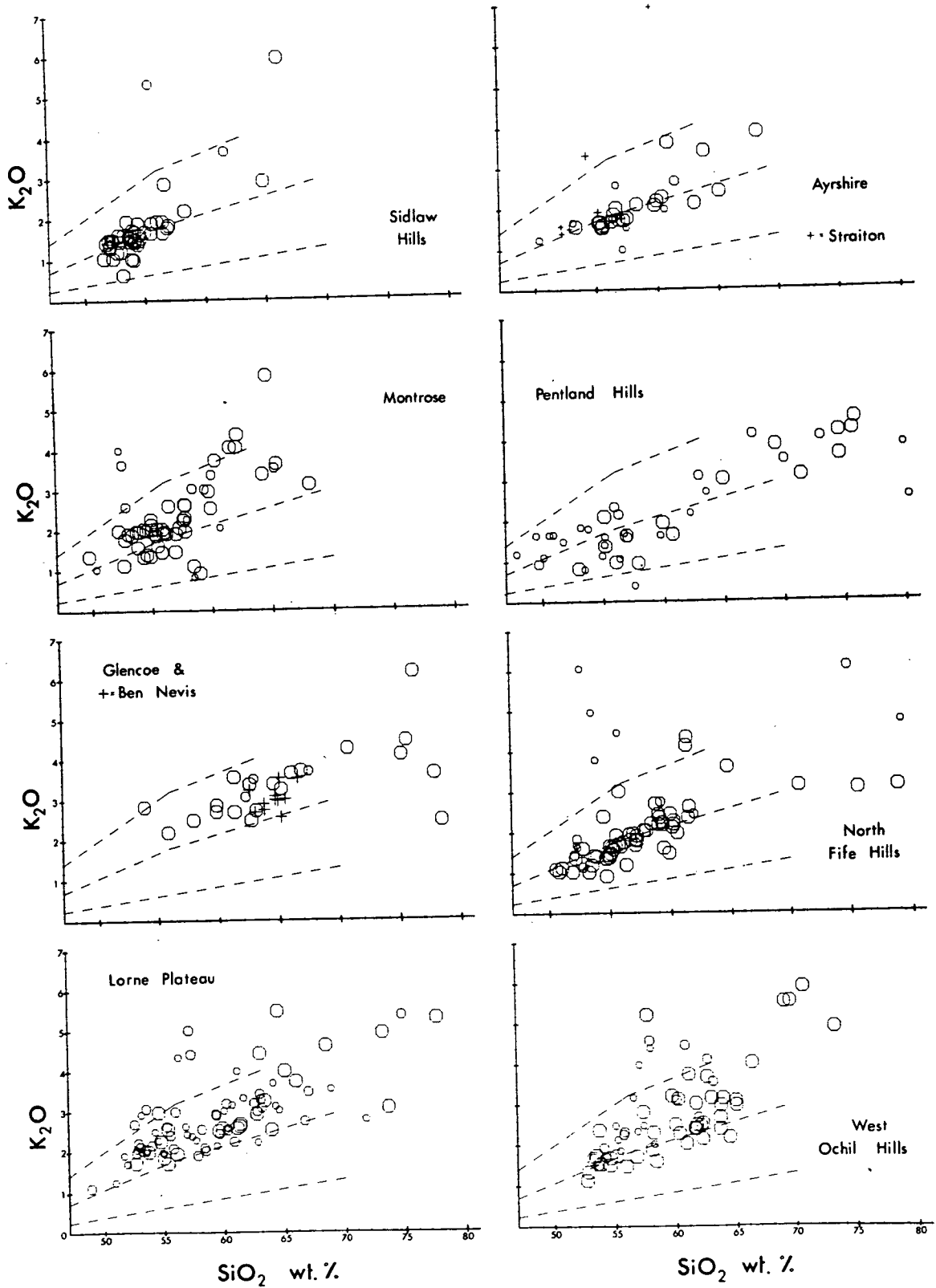
(b) Y/Nb is greater than 1, except in the Hoy lavas. This suggests a non-alkaline suite (Pearce and Cann, 1973).

(c) Ti and Al contents of phenocryst clinopyroxene are low, generally falling within the non-alkaline field of Le Bas (1962), with the exception of those from the Hoy lavas.

These three features imply that the suite is non-alkaline, but concentrations of LIL elements and Zr are often comparable to those of alkaline suites. In particular, the classification of Peccerillo and Taylor (1976) describes many rocks as shoshonitic (Fig. 9.1); but using the above criteria these rocks are not alkaline.

(d) Few rocks show much iron enrichment relative to Mg, and with the notable exception of some samples from Shetland (Fig. 8.3) almost all samples fall within the

Fig. 9.1 : K_2O : SiO_2 variation diagrams for the main O.R.S. volcanic regions, with boundaries from Peccerilo and Taylor (1976) between shoshonitic, high-K, calc-alkaline and tholeiitic suites (as Fig. 8.3). Conventions as section 3.3.



calc-alkaline field of Miyashiro (1974).

(e) Phenocryst pyroxene seldom has atomic $Mg/(Mg+Fe)$ lower than 70, even in siliceous rocks. Exceptions occur at Shetland and at Straiton, Ayrshire, where exsolution relationships indicate the former presence of pigeonite.

(f) In the three regions of the province where volcanic rocks outcrop over a wide area (SW Highlands, North Midland Valley, South Midland Valley) all silica concentrations from 50 to 80% are well represented. The smaller outcrop areas into which these may be divided often show a preponderance of a more restricted silica range, but this may be due to the locations of these areas relative to eruptive foci. In these three regions, rocks with <53 and $>65\%$ SiO_2 are relatively less common. Of the other outcrop areas, only the Cheviot Hills provide a volcanic suite in which basic rocks ($<60\%$ SiO_2) may never have been present.

(g) Alumina concentrations are never lower than 14.6% in basic and intermediate lavas, and samples with around 16% Al_2O_3 are common. Many therefore plot within the tholeiitic field on the Al_2O_3 - normative plagioclase composition diagram of Irvine and Baragar (1971).

(h) Rocks with high concentrations of Ni (>60 ppm) and Cr (>100 ppm) are abundant throughout the province. Many such samples are silica-rich, and several have $>65\%$ SiO_2 . Rocks with around 57% SiO_2 , 180 ppm Ni and 350 ppm Cr are common in the Midland Valley. Most Ni-, Cr-rich samples have low alumina ($<16.5\%$).

Features (d) to (f) strongly suggest that the rocks are best described as calc-alkaline, with the rocks of Shetland transitional to tholeiitic. The high Ni and Cr of the low-alumina rocks could suggest that far less separation of mafic phases has occurred during ascent than in most modern calc-alkaline suites: this can resolve the ambiguity of point (g), for separation of mafic phases will result in higher alumina. This suggests that the term "high alumina basalt" (Kuno, 1960) is of little genetic relevance in describing the mafic members of calc-alkaline suites.

(i) A wide range in lava chemistries at constant silica is present in the rocks of each outcrop area. This can only be attributed to fractional crystallisation in the various geographic subareas of Shetland: elsewhere variation in ratios of incompatible trace elements such as Zr/Nb implies a complex contamination history for the magmas.

(j) Many outcrop areas show broadly constant or in some cases decreasing concentrations of Zr and Nb with increasing silica. Pearce and Norry (1979) noted this unusual behaviour of 'incompatible' trace elements only in continental margin calc-alkaline suites. High concentrations of LIL elements comparable to those in the O.R.S. province are only to be found among modern calc-alkaline suites in those developed on continental margins e.g. the western U.S.A. (Ewart, in press).

9.2 : SPATIAL VARIATION IN MODERN CALC-ALKALINE SUITES

Modern calc-alkaline suites are almost exclusively associated with zones of lithospheric plate convergence. To some extent a semantic equivalence has grown up, and volcanic rocks associated with plate convergence are often loosely termed calc-alkaline, while calc-alkaline rocks have been used as evidence for the existence and interaction of minor plates in areas not clearly related to major plate convergence. The close spatial and temporal relation of the O.R.S. volcanic province to the closure of Iapetus (section 1.1) confirms that this province was developed at a zone of plate convergence.

More specifically, most modern calc-alkaline suites overlie Benioff zones of intermediate-deep focus earthquakes, and thus characteristically form arcuate volcanic zones, in some way genetically related to lithospheric subduction. This association has led to the use of calc-alkaline volcanic suites as evidence for palaeo-subduction, and the O.R.S. suite has been used by Phillips et al. (1976) as evidence for termination of northward subduction under Scotland during the Devonian. The occurrence of modern calc-alkaline volcanic rocks in the western U.S.A. and Turkey (e.g. Lambert et al., 1974), where no Benioff zones have been recognized, suggests that care should be taken in the direct equation of calc-alkaline magmatism with active subduction.

Petrographic and chemical variation across and along subduction-related magmatic arcs has received much attention in the literature. Kuno (1966) observed variation across the Japanese arc from tholeiitic ('pigeonitic') volcanoes nearest the trench in the east, through calc-alkaline ('hyperstheneic') volcanoes to alkaline volcanoes in the west. Dickinson and Hatherton (1967) observed that a close relationship existed between the K content of andesites at constant silica and the depth of the Benioff zone beneath the volcano, and hence with depth (h) to the subducting lithosphere. K content at constant silica was determined from a regression line drawn on a K_2O-SiO_2 variation diagram. Ninkovich and Hays (1972), Nielson and Stoiber (1973) and Dickinson (1975) showed that the K- h relation was closely dependant on the type of magmatic arc, with those located on continental margins showing the highest K for constant h . Similar variation for many other LIL and high field strength elements has been summarized by Jakeš and White (1972) and by Arculus and Johnson (1978), but the data is often vague, and Arculus and Johnson (1978) describe a number of examples where K- h variation does not appear to occur. Variation along a magmatic arc was described from the Lesser Antilles; variation along the arc has also been described in Indonesia (Whitford, 1975) where a southeastward decrease in $^{87}Sr/^{86}Sr$ was used to infer decreasing crustal contribution in this direction.

In addition to the spatial variations, Jakeš and White (1972) have also drawn attention to broad chemical

changes occurring during the evolution of a magmatic arc. Tholeiitic volcanism was believed to dominate the early stages of arc evolution, with alkaline (?shoshonitic) volcanoes occurring late in the arc development. The evidence for this is frequently ambiguous (Arculus and Johnson, 1978).

The origin of these spatial and temporal variations has been discussed by many authors, but detailed discussion is often hampered by the lack of comprehensive chemical data. Cawthorn (1977) noted that the variation in K content at constant silica described by Dickinson (1975) was critically dependant on the origin of the positive correlation between K_2O and SiO_2 . If this were due to fractional crystallisation then K_{55} , $K_{57.5}$ and K_{60} as defined by Dickinson (1975) would be functions of the silica content of the bulk extract. For example, high partial pressures of oxygen could lead to fractional crystallisation of magnetite (Osborn, 1962), resulting in lower K at constant silica than magmas separating a more silica-rich assemblage. Fractional crystallisation of amphibole-bearing assemblages (Cawthorn and O'Hara, 1976) would also lead to relatively low K at constant silica. A similar criticism applies if the silica variation is generated by variation in the degree of partial melting of a common source: variation in residual phases could lead to variation in K content at constant silica. However, variation in both partial melt residua and fractionating assemblage could be related to depth of magma generation.

It is clear that the true nature of spatial and temporal variation in calc-alkaline suites can only be elucidated if the origin of the silica variation is known, or if we can infer the compositions of primitive magmas from which the lava compositions seen at the surface may be derived by crystal separation. In both cases, it is essential to consider a comprehensive body of accurate chemical data, rather than restricting discussion to K_2O and SiO_2 .

9.3 : SPATIAL CHEMICAL VARIATION IN O.R.S. MAFIC ROCKS

The O.R.S. volcanic province is most unusual for calc-alkaline suites in its great abundance of rocks with high Ni and Cr. Some 20% of the rocks collected have >100 ppm Ni and >150 ppm Cr; these include rocks from the SW Grampian Highlands, the North and South Midland Valley, Arran, St. Abb's Head, Orkney and Shetland. 600 and 1200 ppm respectively are close to the maximum Ni and Cr concentrations observed in natural liquid compositions; fractional crystallisation of mafic minerals from such compositions results in rapid depletion in Ni and Cr, for distribution coefficients are high for these elements in mafic phases (Gill, 1978).

For example, if such compositions were parental to the rocks of the O.R.S. volcanic province, then an assemblage with $D(Ni, bulk) = 7$ could generate the 100 ppm Ni of many of these rocks with only 25% crystallisation.

Higher $D(\text{Ni}, \text{bulk})$ is likely if olivine formed a major part of the crystallising assemblage, while large contributions from clinopyroxene or spinel would result in major depletion in Cr. It is clear that crystal separation of mafic phases can not produce more than 25% relative variation in LIL elements in rocks with >100 ppm Ni. Furthermore, Ni and Cr concentrations can be used as indices of differentiation, and more than some 20% relative variation of LIL elements at constant Ni and Cr can not be generated by separation during ascent of different proportions of mafic phases.

Fig. 9.2 demonstrates that approximately 6-fold variation in Ba and Sr exists among rocks with >100 ppm Ni in the O.R.S. volcanic province. The strong positive correlation between Ba and Sr may not be generated by separation of plagioclase during magma ascent: it is therefore concluded that any primary magmas parental to these rocks must have shown comparable variation in Ba and Sr content. The very minor significance of separation of mafic phases during ascent is emphasized by the total absence of correlation between increase in Ba and Sr and decrease in Ni and Cr. The correlation between Ba and Sr demonstrated for Lorne in Chapter 4 forms part of the overall correlation throughout the whole province, and there is clear correlation between geographic position and content of Ba and Sr in rocks with >100 ppm Ni. Low concentrations are dominant in the South Midland Valley and high concentrations are dominant in the SW Grampian Highlands.

Fig. 9.2 a & b : Bulk rock variation diagrams for samples with
>100 ppm Ni and >150 ppm Cr.

Conventions as section 3.3

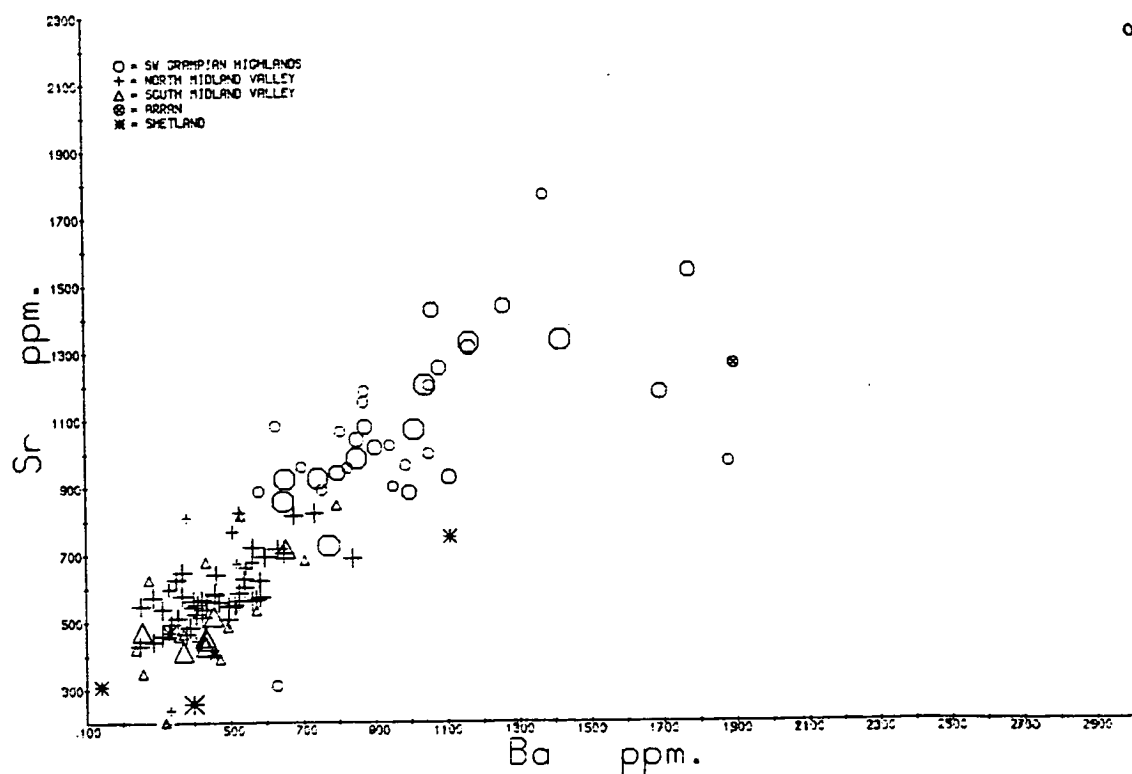
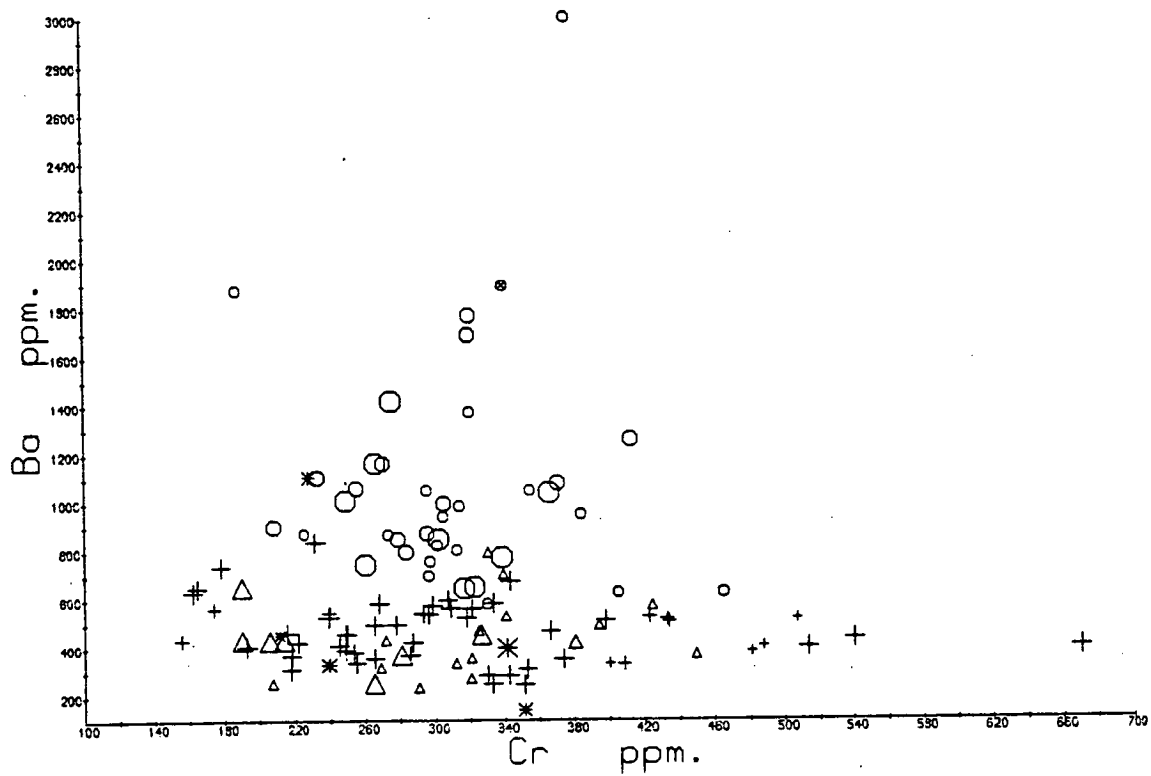


Fig. 9.2 c & d : samples with >100 ppm Ni and >150 ppm Cr

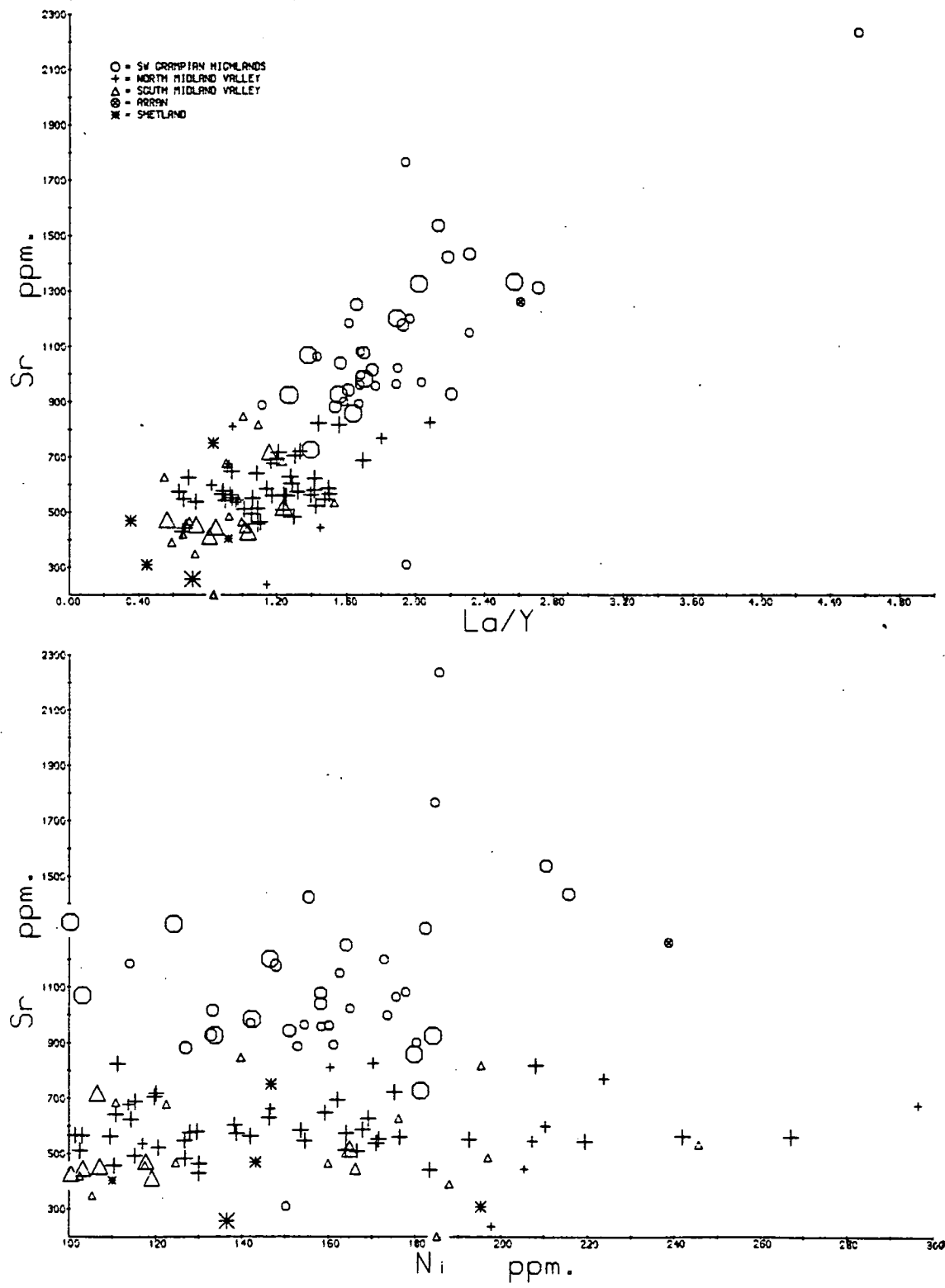


Fig. 9.2 e & f : samples with >100 ppm Ni and >150 ppm Cr

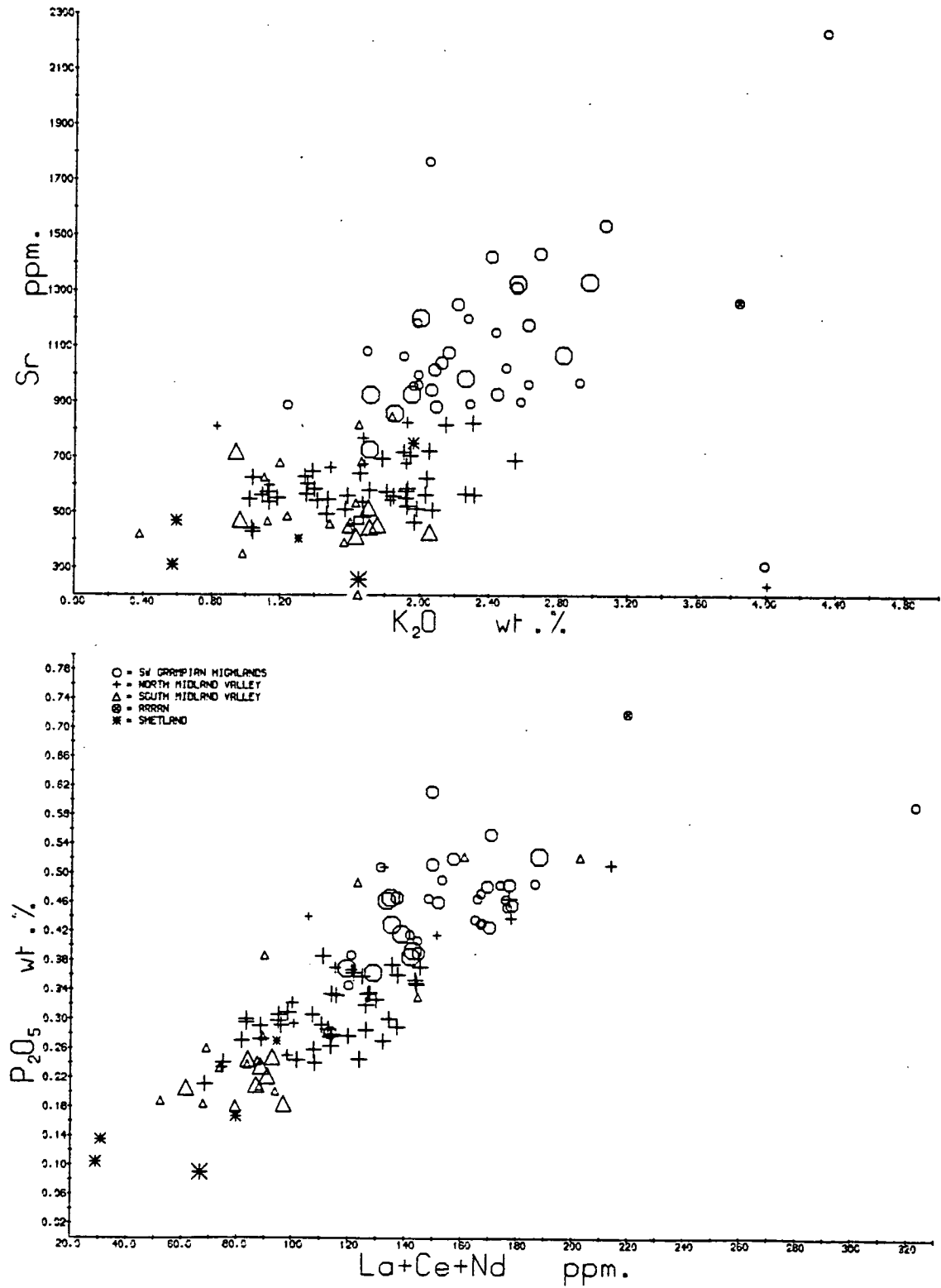
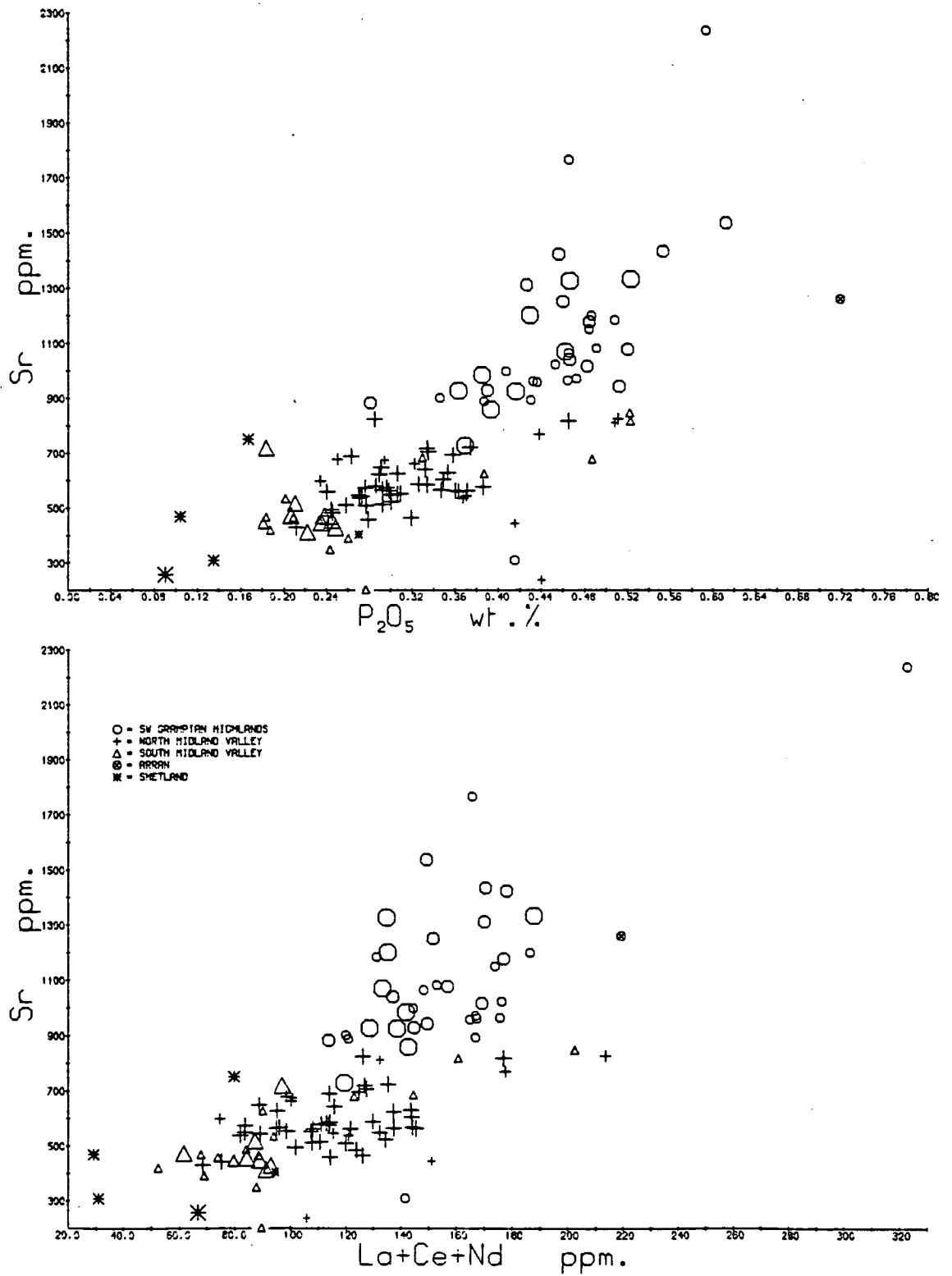


Fig. 9.2 g & h : samples with >100 ppm Ni and >150 ppm Cr



Similar correlations exist for Sr-La/Y and P_2O_5 -LREE, although the relationships between Sr-K, Sr-LREE and Sr- P_2O_5 are curved, with greatest variation in Sr between the SW Highlands and the North Midland Valley, while P and LREE variation is large between the South and North Midland Valley.

Confirmation that comparison is being made between otherwise similar rocks (e.g. for SiO_2 , Ni and Cr) is given by the great similarity between the average compositions of rocks with >100 ppm Ni from these three areas (analyses 1-3, Table 9.1). The striking equivalence of most elements is strong evidence for the existence of a fundamental process causing increase in Sr, Ba, P, LREE, K, (La/Y) and possibly Nb and Rb, and decrease in Y and possibly also Sc on a traverse from the South Midland Valley to the SW Grampian Highlands. Difference in the averages for other elements is perhaps significant for Ca and Mg: the high average LOI of South Midland Valley rocks suggests that this is probably a function of alteration. 25% and 75% quartiles are given for some of these parameters in Table 9.2: the variation is comparable to that displayed by the means, demonstrating that the means are not seriously dependant on atypical high or low values for elements in one or two samples.

This spatial variation in LIL elements is encountered in a traverse roughly perpendicular to the suture of Phillips et al. (1976). The variation is comparable to that described from many calc-alkaline suites (section 9.2).

TABLE 9.1 : Average analyses of samples with >100 ppm. Ni

1 = SW Highlands, 2 = North Midland Valley, 3 = South Midland Valley,

4 = St. Abb's Head/Eyemouth, 5 = Shetland

	1	2	3	4	5
SiO ₂	54.95	54.58	54.66	56.11	52.57
Al ₂ O ₃	16.46	16.37	16.86	16.35	17.08
Fe ₂ O ₃	7.95	7.77	8.10	7.31	9.40
MgO	5.37	6.52	5.09	6.27	6.22
CaO	6.91	7.33	8.36	6.44	7.61
Na ₂ O	3.82	3.60	3.72	3.36	3.88
K ₂ O	2.34	1.69	1.43	2.04	1.22
TiO ₂	1.32	1.36	1.28	1.17	1.03
MnO	0.10	0.11	0.10	0.08	0.27
P ₂ O ₅	<u>0.45</u>	<u>0.32</u>	<u>0.27</u>	<u>0.31</u>	<u>0.15</u>
Total	99.67	99.65	99.87	99.44	99.43
LOI	3.32	1.79	4.47	4.81	2.66
Ni	158	157	143	220	146
Cr	308	316	302	426	274
V	168	162	175	135	178
Sc	22	24	26	24	32
Cu	30	28	34	31	24
Zn	80	76	133	122	399
Sr	1103	589	515	510	437
Rb	40	37	34	48	49
Th	4	6	7	4	2
Zr	200	211	197	220	111
Nb	14	12	9	13	9
Ba	1045	465	436	534	486
La	37	28	22	30	16
Ce	81	61	49	61	30
Nd	38	29	25	29	14
Sm	7	6	6	5	2
Y	20	25	25	25	23
No.	38	53	22	12	5

TABLE 9.2 : Interquartile ranges for selected chemical parameters.

All samples with >100 ppm. Ni.

	South Midland Valley		North Midland Valley		SW Highlands	
	25 percentile	75 percentile	25 percentile	75 percentile	25 percentile	75 percentile
Sr	428	626	540	644	928	1201
K ₂ O	1.13	1.66	1.37	1.93	1.99	2.58
Ba	336	493	374	554	797	1105
La/Y	0.69	1.03	0.93	1.36	1.61	2.02
SiO ₂	51.7	57.2	52.5	56.5	53.1	56.1
Cr	265	339	242	360	274	330
No. of samples		22		53		38

9.4 : SPATIAL CHEMICAL VARIATION IN LESS MAFIC ROCKS

Direct comparison between the spatial chemical variation described in section 9.3 and that described by workers on other calc-alkaline suites is only possible if the entire range of volcanic products is considered, although the demonstration in section 9.3 of a wide range in primary magma compositions is believed to be more fundamental than variations in element concentrations at constant silica (section 9.2). This is particularly true where the origin of the silica variation is not understood, as is the case for most of the O.R.S. regions, with the prominent exception of Shetland.

The criticism by Cawthorn (1977) of the K-h relationship, that variation in K at constant SiO_2 can easily be generated by differences in the Si and K content of a fractionating assemblage (section 9.2), will apply to any element that shows correlation with silica. When an element shows no correlation with silica, variation in the SiO_2 content of the extract can not change the concentration of the element at a particular evolved silica composition. Sr shows little or no correlation with silica in O.R.S. lavas with less than about 65% silica (e.g. Fig. 9.3), and therefore spatial variation in Sr can not be generated by geographic changes in the silica content of an extract in a fractional crystallisation model. Regression lines for Sr against SiO_2 have been computed for each area using the program VARPLOT (Appendix D7; perpendicular-to-line

Fig. 9.3 : Sr : SiO₂ variation diagrams for the main volcanic regions.
Conventions as section 3.3.

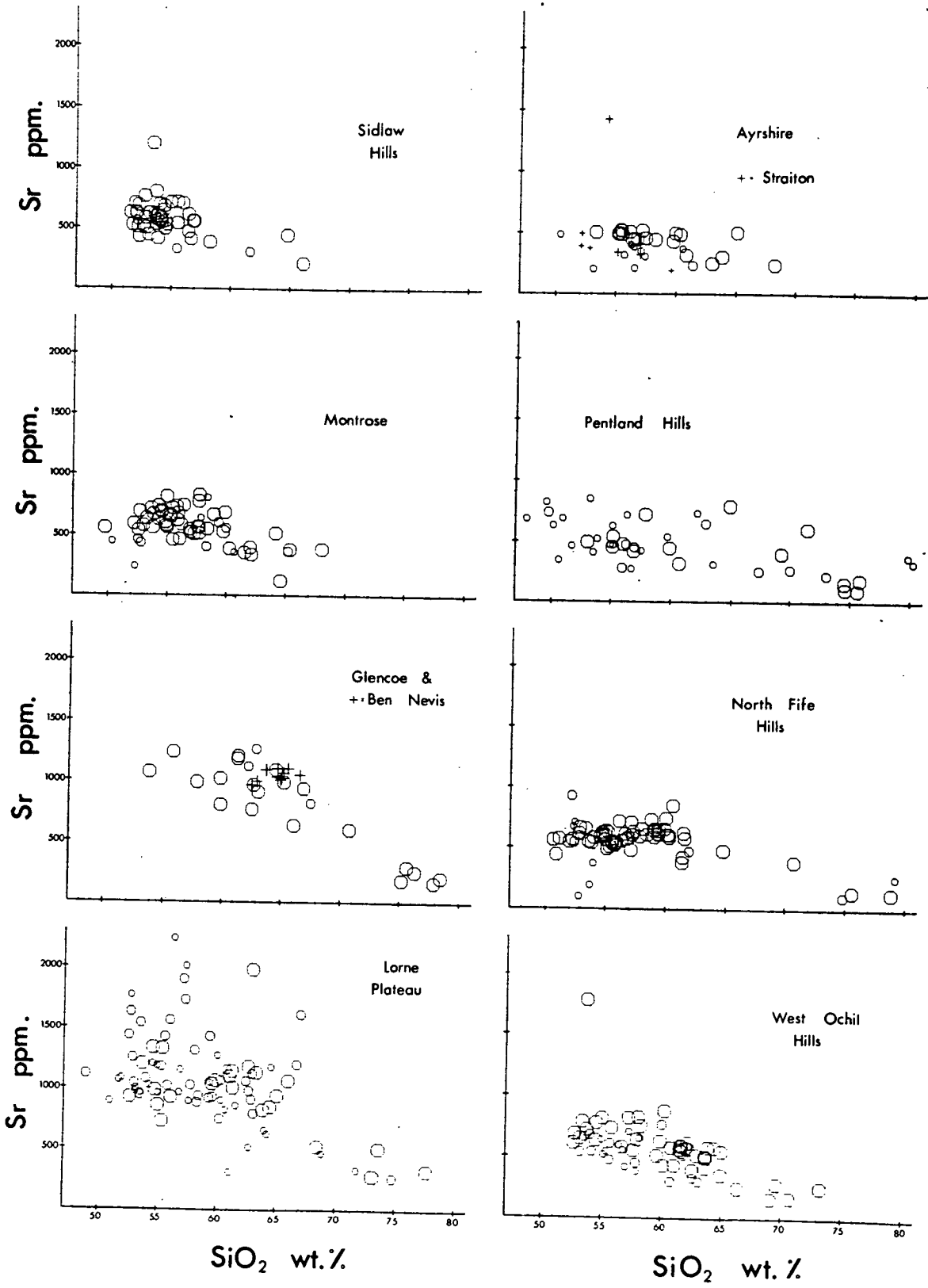


Fig. 9.4 a & b : Regression lines for each area for samples with <65% SiO_2 , <3% LOI. Symbols refer to the major regions:
 ○ = SW Grampian Highlands, + = North Midland Valley,
 △ = South Midland Valley, * = Shetland (Esha Ness)

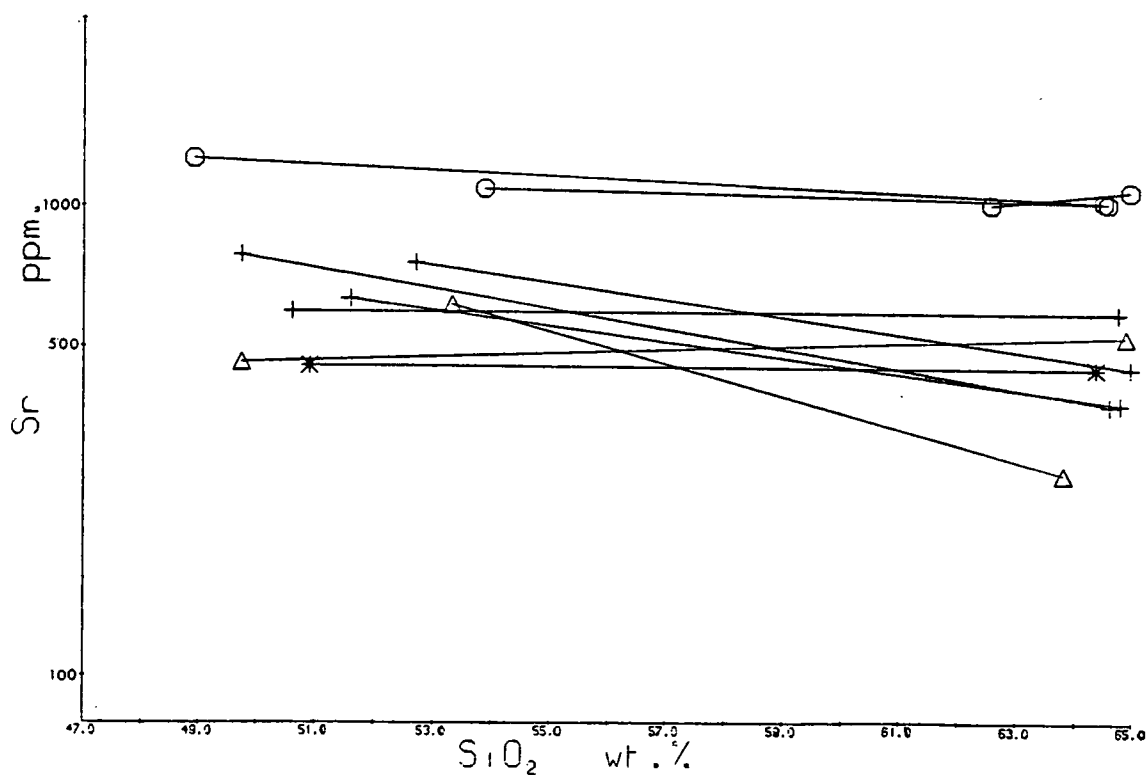
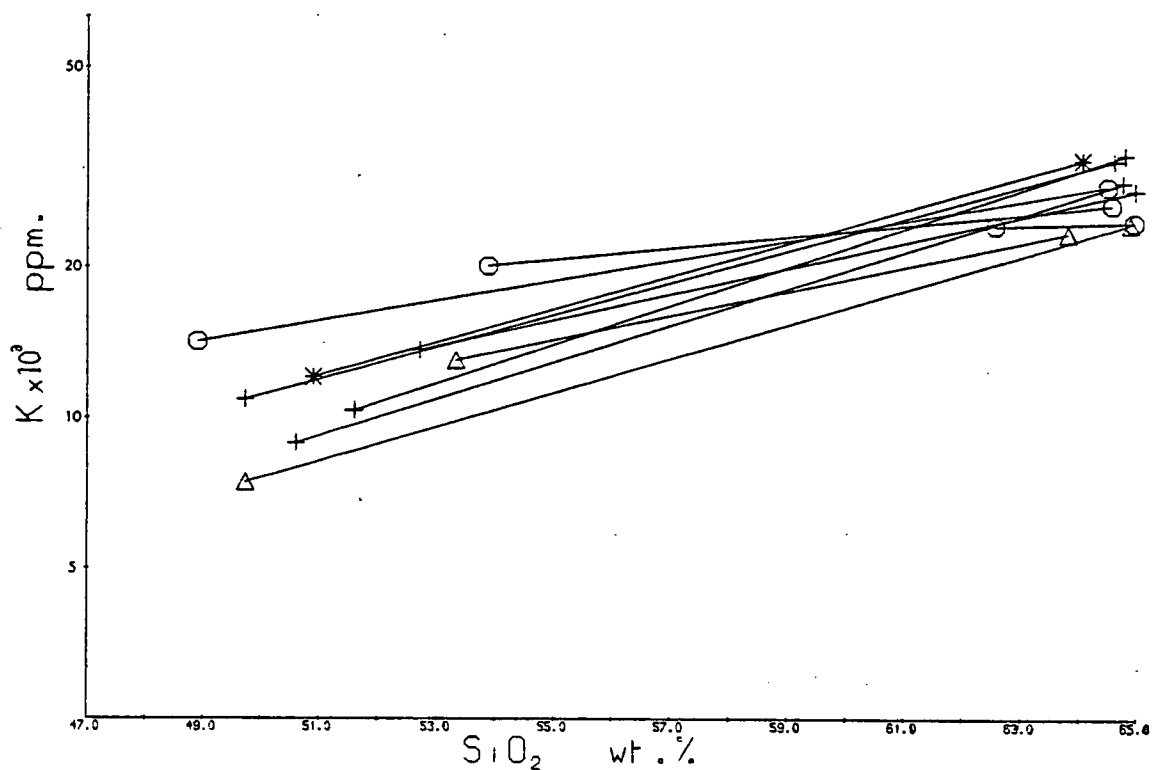
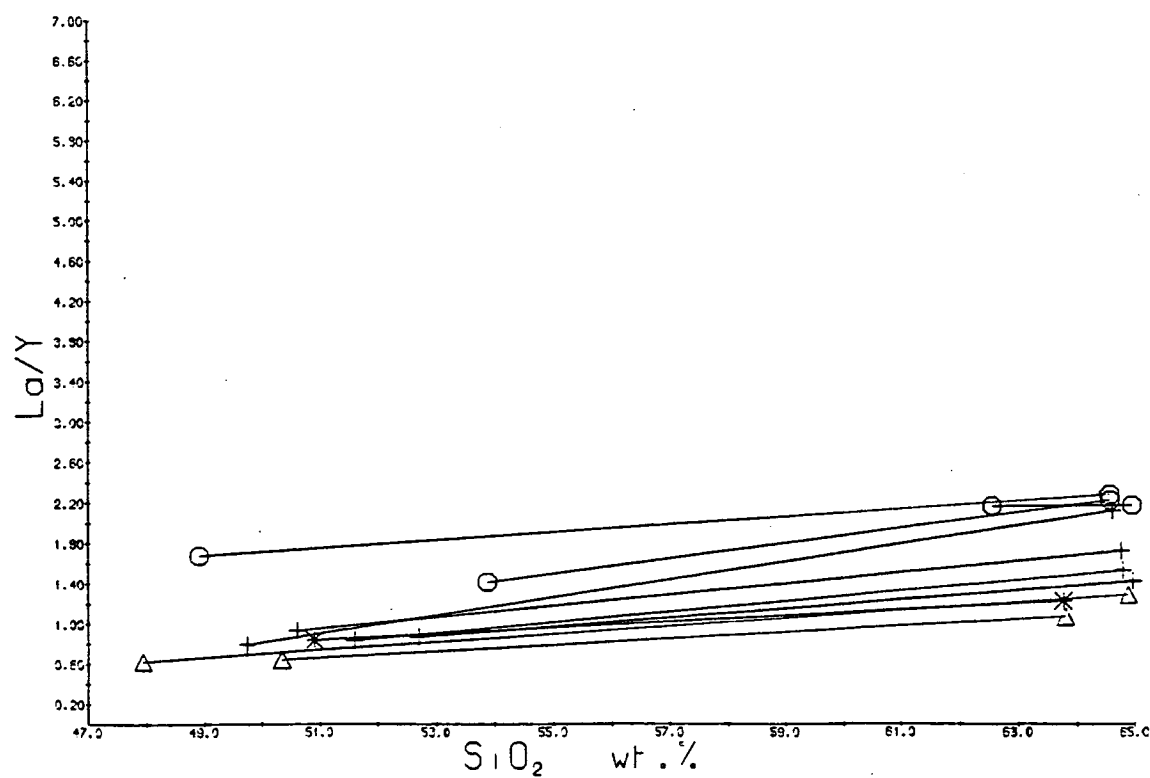
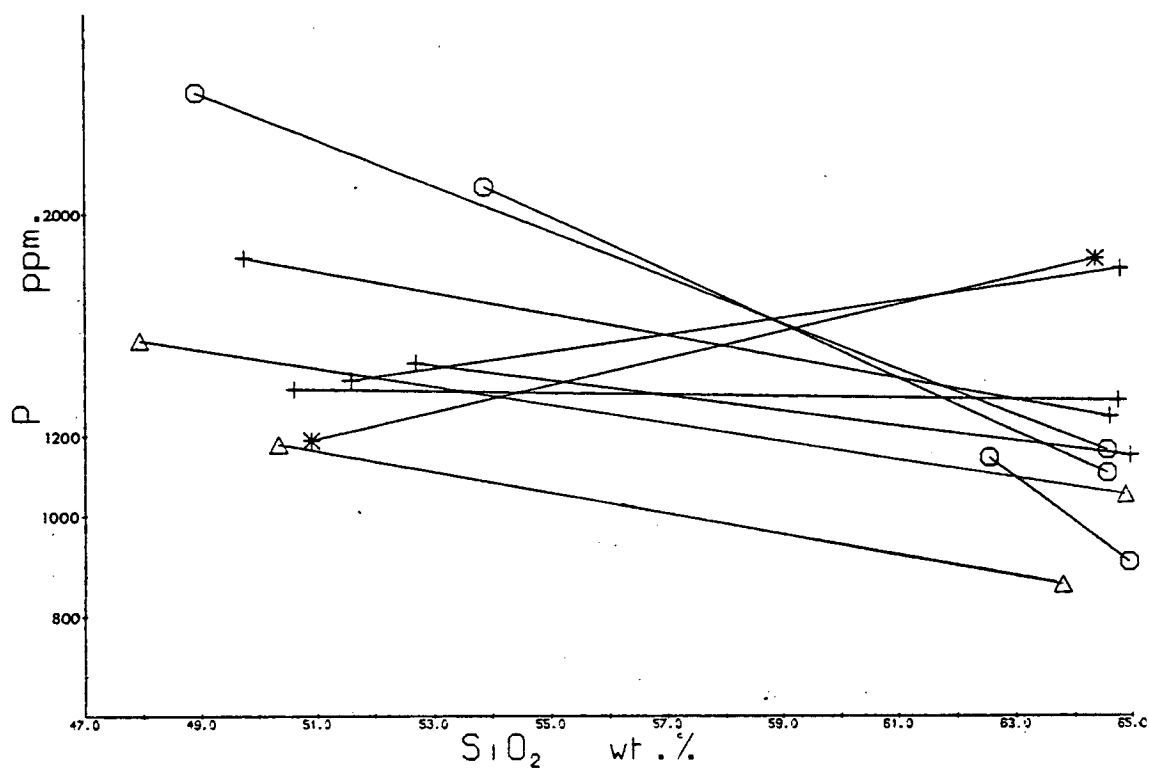


Fig. 9.4 c & d : Regression lines for each area for samples with $<65\%$ SiO_2 . Symbols as Fig. 9.4 a & b



procedure), and are given in Fig. 9.4. Sr concentrations in the SW Highlands, the North Midland Valley and the South Midland Valley are readily distinguished using this method, and the variation is similar to that described in section 9.3.

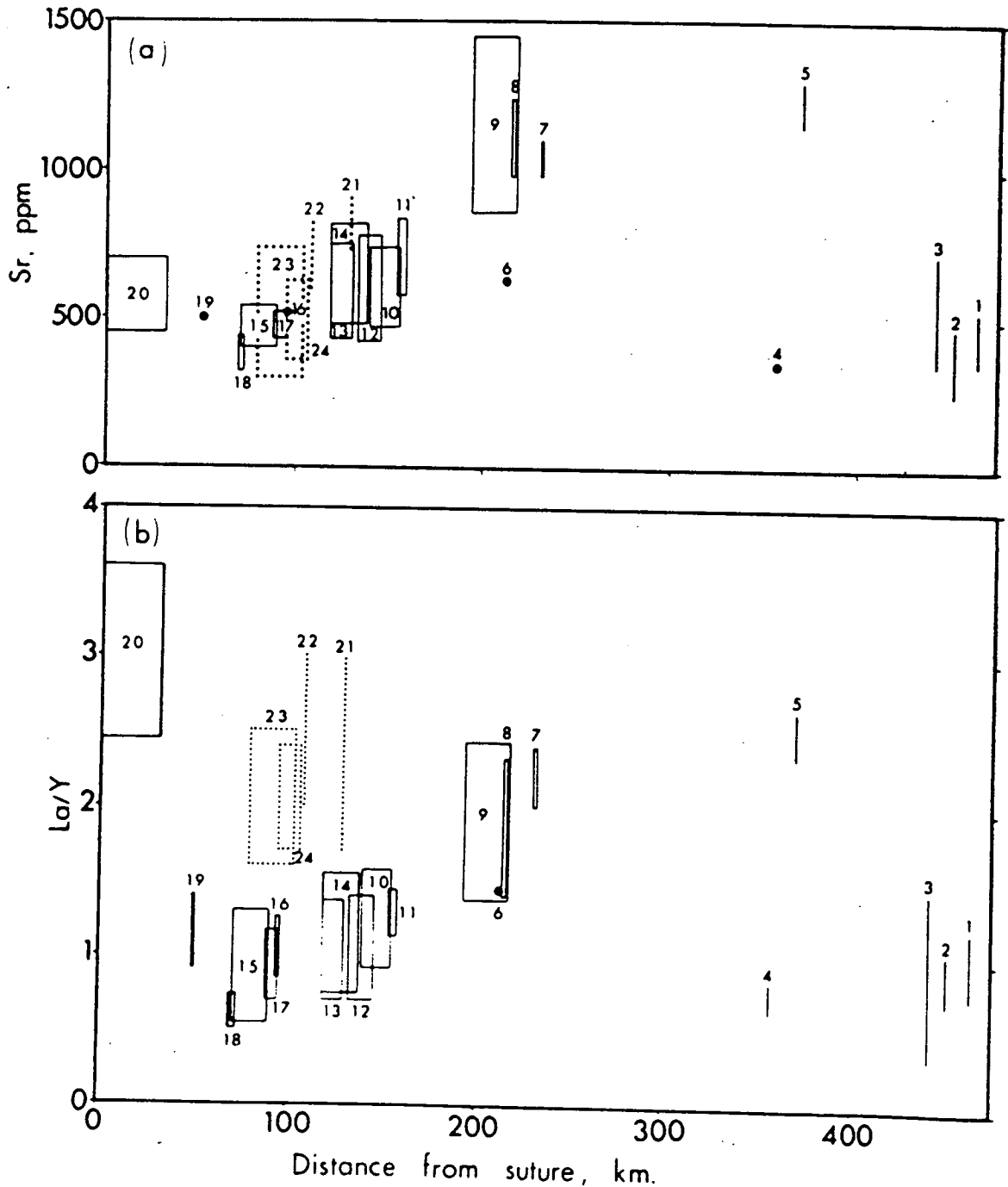
Despite the foregoing criticisms of the K-h relationship, regression lines have also been computed for many geochemical parameters which do show correlation with silica: for example, for K, La/Y and P_2O_5 , Fig. 9.4. The same spatial variation is shown, namely that at constant silica, samples from the SW Highlands have highest Sr, Ba, K, La/Y, P and LREE, while samples from the South Midland Valley have the lowest values of these parameters. These data are directly comparable to the spatial variations described from modern calc-alkaline magmatic arcs, related, by Dickinson (1975) and many other authors, to the depth to the descending lithospheric plate.

There is therefore abundant evidence that the Old Red Sandstone volcanic province was generated in response to subduction beneath the northwestern continental margin of the Iapetus Ocean.

9.5 : SUBDUCTION DIRECTION

Chemical variation in the O.R.S. volcanic province as a whole is not well described by distance perpendicular to the suture of Phillips et al. (1976). Fig 9.5 demonstrates

Fig. 9.5 : Ranges of Sr and La/Y plotted against distance from suture of Phillips *et al.* (1976). The cpx-hb-bi-phyrlic rocks of Lorne and some altered rocks are omitted from the ranges. Outcrop areas are shown as rectangles if they have significant width normal to the suture, and as a dot (e.g. area 6) if only a small number of samples is represented. The Irish and Arran areas are shown dotted for clarity. Numbers refer to: 1 = Esha Ness, 2 = Papa Stour, 3 = Sandness Formation, 4 = Shapinsay/Deerness, 5 = Hoy, 6 = Huntly, 7 = Ben Nevis, 8 = Glencoe, 9 = Lorne Plateau, 10 = Montrose, 11 = Highland Border, 12 = Sidlaw Hills, 13 = North Fife Hills, 14 = West Ochil Hills, 15 = Pentland Hills, 16 = Distinkhorn, 17 = Ayrshire Coast, 18 = Straiton, 19 = St. Abb's Head & Eyemouth, 20 = Cheviot Hills, 21 = Arran, 22 = Cushendall, 23 = Fintona, 24 = Curlew Mountains.



that the range in Sr and La/Y values exhibited by basic and intermediate rocks of each outcrop area only correlates well with distance from the 'suture' for areas in the North and South Midland Valley and in the SW Grampian Highlands. With respect to these regions, all areas with apparently anomalous low levels of Sr and La/Y lie geographically to the northeast of a line joining the South Midland Valley and Lorne (Fig. 1.1), while, with the exception of the Cheviot Hills and St. Abb's Head, all areas with apparently anomalous high levels of La/Y and Sr (Ireland and Arran) lie to the southwest of this main volcanic region.

There is considerable difficulty involved in discussion of the significance of these relationships, for Fig. 9.5 does not include any measure of SiO_2 , Ni or Cr, and comparison between the siliceous rocks of Ireland and rocks from the rest of the province is hazardous. The following points should be noted:

(a) A lava with >100 ppm Ni and >150 ppm Cr is present on Arran (AR2). This has very high concentrations of LIL elements, comparable with those at Lorne (Fig. 9.2).

More siliceous rocks from both Arran and Cushendall have higher concentrations of LIL elements than those from further southwest in Ireland (Fig. 8.2), and higher than those of siliceous rocks in the Midland Valley.

(b) The most mafic sample from Huntly (NG1) has 90 ppm Ni and 157 ppm Cr. It is therefore unlikely that concentrations of LIL elements in this sample have been greatly changed by fractional crystallisation of mafic

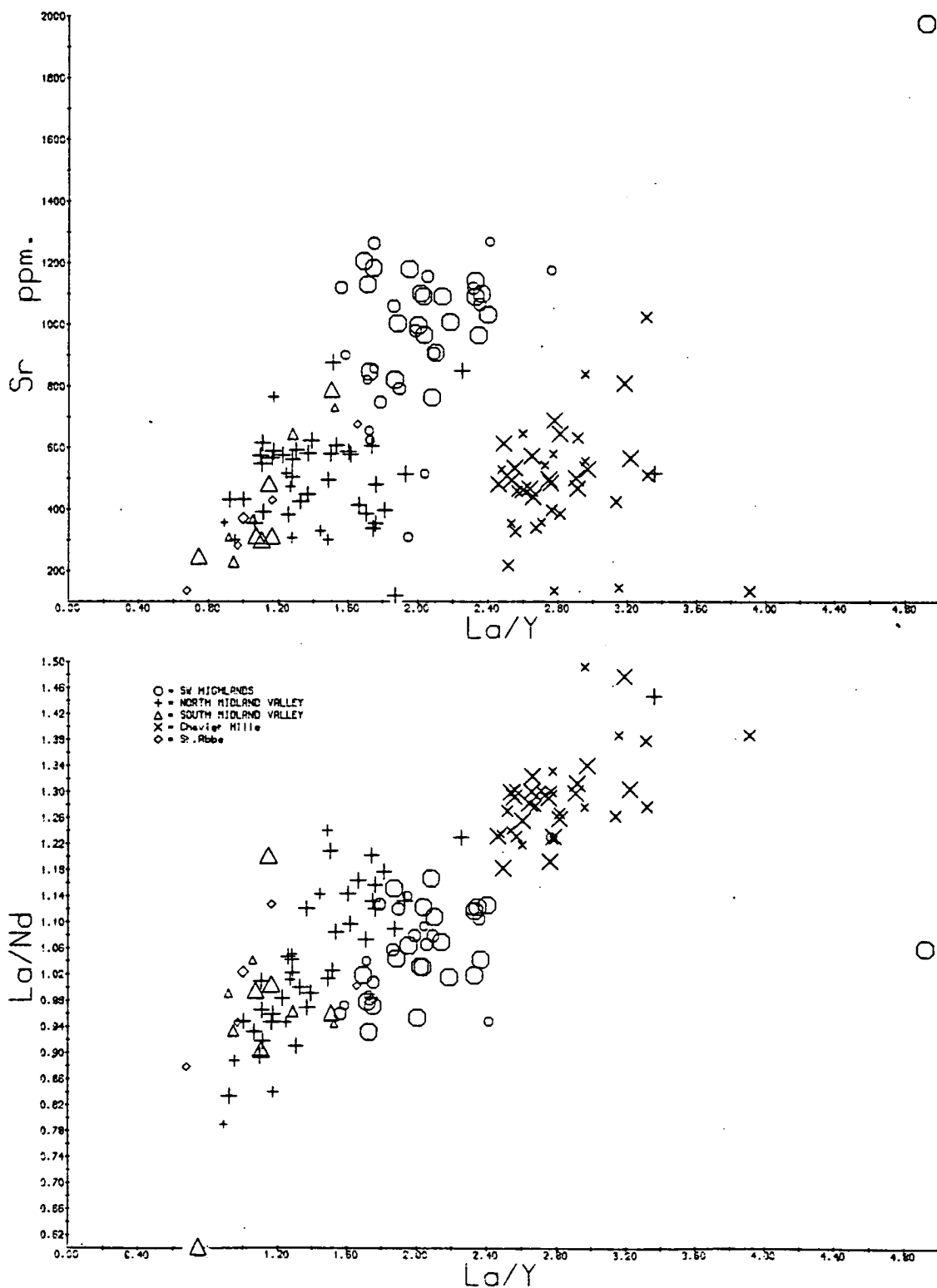
phases. Both Sr and La/Y are lower than in SW Highland rocks and comparable to their levels in the North Midland Valley. More siliceous samples from Huntly also have relatively low Sr and La/Y, as do the Highland-derived volcanic clasts in the O.R.S. conglomerates of Kincardineshire (section 5.1a).

(c) Chemical variation in the volcanic rocks of Shetland is controlled by fractional crystallisation, and values of K at constant silica for Shetland are a little higher than those in the North Midland Valley. However, the few Ni- and Cr-rich rocks present all have much lower concentrations of LIL elements (Fig. 9.2). These are the only Shetland rocks directly comparable with the Ni-, Cr-rich lavas of the rest of the province. The average analysis of these rocks is given in Table 9.1: while concentrations of ~~the~~ Sr, P, LREE and K are much lower than those for areas on the Scottish mainland, the analyses are not wholly comparable because of differences in SiO₂. Shetland lavas are transitional between calc-alkaline and tholeiitic (Fig. 8.3).

(d) The older lavas of Orkney (Eday Flags) are closely comparable with mafic lavas in Shetland (section 8.6), and have equally low LIL element concentrations. The younger lavas of Orkney (Hoy) are alkaline and are perhaps unrelated to the rest of the province.

(e) The lavas of the Cheviot Hills have La/Y values comparable to those of Lorne, but Sr and Ba are much lower, even in equally siliceous rocks. La/Nd is substantially higher than at Lorne (Fig. 9.6): it is

Fig. 9.6 a & b : Bulk rock variation diagrams for samples with between 60 and 65% SiO_2 . N.B.1 : similarity to Fig. 9.2 c; N.B.2 : Anomalous behaviour of Cheviot samples. Conventions as section 3.3



important that while enrichment of LREE relative to HREE (Y) shows considerable spatial variation, enrichment within the LREE (La/Nd) does not, with the exception of the Cheviot lavas.

(f) Due to alteration, the behaviour of Sr and Ba in the St. Abb's Head lavas is not known. The average analysis of St. Abb's Head Ni- and Cr-rich lavas is given in Table 9.1. While not directly comparable with elsewhere (SiO_2 , Ni, Cr, V), concentrations of LIL elements appear to be similar to those in the North Midland Valley (column 2).

If the correlations between LILE concentrations and La/Y displayed in Fig. 9.2 are believed to be the result of subduction-related processes (section 9.7), it is reasonable to suggest that the Cheviot lavas, and possibly those of St. Abb's Head, were not related to the same subduction zone as the remainder of the province. Supporting evidence for this exception comes from the unusual petrography and chemistry of rocks in these areas, and perhaps in their unusual positioning on an accretionary sedimentary wedge.

If this exception is accepted, the simplest tectonic model that can explain the spatial variation in LIL element concentrations in the province requires a major change in strike of the surface expression of the subduction zone off the east coast of Scotland. It is proposed that the plate convergence responsible for the Old Red Sandstone volcanic province took place in a nearly east-west direction, and that the southeast margin of the American-Scottish plate was

an arcuate zone of active plate consumption, concave northwards.

Such a subduction geometry would allow the tholeiitic/calc-alkaline transitional rocks of Shetland to lie relatively close to the surface trace of the subduction zone, while the LILE-rich rocks of the SW Highlands and Arran would lie furthest from the surface trace. The position suggested in Fig. 9.7 is critically dependant on several assumptions:

- (i) That, with the exception of the Cheviot Hills and St. Abb's Head, all the volcanic rocks are related to the same subduction zone. Multi-subduction zone models could easily account for the observed variation, but they are not necessary.
- (ii) That the volcanic rocks are not widely disparate in their ages. This may not be a valid assumption for the relationship of Shetland and Orkney to the mainland, but the Huntly and Arran rocks are generally considered to be part of the Lower O.R.S.
- (iii) That the levels of La/Y and LILE were directly related to the depth to the Benioff zone (section 9.7).
- (iv) That the angle of dip of the Benioff zone was relatively constant throughout the province. Variation in the angle of dip does not however allow much change in the position of the surface trace.

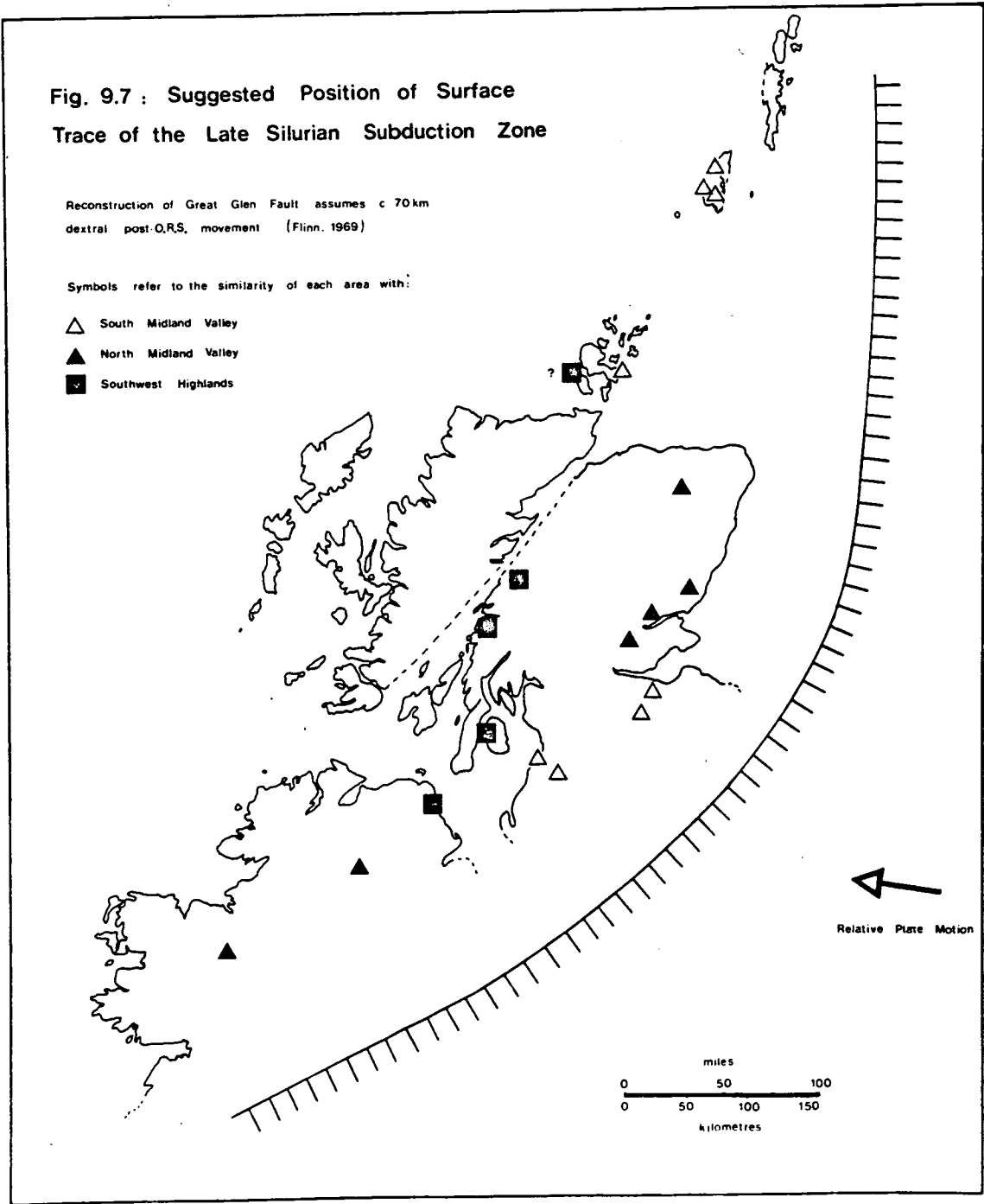
A number of additional lines of evidence support the suggestion of a change in strike of the subduction zone from

**Fig. 9.7 : Suggested Position of Surface
Trace of the Late Silurian Subduction Zone**

Reconstruction of Great Glen Fault assumes c 70 km
dextral post-O.R.S. movement (Flinn, 1969)

Symbols refer to the similarity of each area with:

- △ South Midland Valley
- ▲ North Midland Valley
- Southwest Highlands



ENE in southern Scotland and Ireland to NNE in the North Sea:

(a) The change in strike of the Great Glen Fault and of Dalradian metasediments from ENE in the SW Grampian Highlands to N in Shetland. While both of these probably pre-date the development of the O.R.S. province, they may be indicative of a regional change in strike existing until final closure of Iapetus. The presence of a possibly ophiolitic complex on Unst and Fetlar, Shetland, provides additional evidence for the proximity of Shetland to a subduction zone, although these again probably pre-date the O.R.S. volcanic rocks.

(b) Chemical and isotopic variation among the younger granites of the Scottish Highlands is not well characterized by distance from the ENE-striking suture of Phillips et al. (1976). Instead, the chemical and isotopic composition of the granites appears to vary from east to west (Stephens, pers. comm., 1979). The north-south orientation of a belt of syenitic plutons in the northern Highlands from Ben Loyal to Glendessary may also be significant, although these are now known to be Ordovician (van Breemen et al., 1979).

(c) Phillips et al. (1976) extrapolate their suture ENE from Scotland to join the southeastern front of the Scandinavian Caledonides (their Fig. 9). This would imply that the entire Scandinavian nappe pile, and the east Greenland Caledonides, were developed on the continent to the northwest of Iapetus, a most unlikely possibility in view of the generally southeastward

translation of the Scandinavian nappes (Strand and Kulling, 1972, p.50). While the suture position is more a function of the shape of the opposing continental masses than of subduction zone position, the occurrence of Lewisianoid basement in Shetland (Pringle, 1970) and of abundant allochthonous continental basement in the Scandinavian nappes strongly suggests that both the suture, and the trace of the subduction zone by which closure occurred, must be located between Shetland and Scandinavia. This implies a major change in strike for the suture in the North Sea, and perhaps a corresponding change in subduction zone strike.

It is evident that the change in strike of the subduction zone suggested by the chemical data fits the tectonics of the area more satisfactorily than the consistently ENE striking suture and E-W striking northern subduction zone of Phillips *et al.* (1976). It should be noted that the subduction direction suggested is almost perpendicular to that used by Phillips *et al.* (1976) in their model of oblique collision, and therefore casts doubt on many of the conclusions reached by these authors.

9.6 : THE SILURO-DEVONIAN OROGENY IN BRITAIN

The British Isles are unique among the Atlantic Caledonides in their lack of major tectonism and metamorphic activity associated with final closure of Iapetus. If nappe tectonics be considered diagnostic of collision orogeny,

then collision orogeny did not take place in Britain at the time of closure. Despite this, abundant evidence for orogeny is preserved in the great thicknesses of Old Red Sandstone conglomerates in the Midland Valley of Scotland. It is believed that this apparent paradox can be resolved by considering the implications of sections 1.3 and 9.5.

(a) Timing of subduction

The convincing evidence for northwestward subduction preserved in the Southern Uplands accretionary sedimentary wedge (McKerrow et al., 1977) indicates that subduction was active from at least the Caradoc to the Wenlock. Pre-O.R.S. volcanic rocks suggested by Mitchell and McKerrow (1975) to be due to this subduction are the Wrae volcanics (now known to be peralkaline, Thirlwall, in prep.) and the 'andesite' clasts in Southern Uplands greywackes (described by Kelling, 1962, p.126, as petrographically comparable to some of the rocks of Bail Hill, Sanquhar, now known to be an alkaline volcanic complex, M. McMurtry, pers. comm., 1979). The only volcanic rocks north of the suture of Phillips et al. (1976) which can confidently be related to subduction are therefore those of the Old Red Sandstone, but these are commonly thought to be of Devonian age, post-dating the last accretionary slice in the Southern Uplands.

Calc-alkaline volcanism possibly post-dating subduction has been suggested in the Cascade Range, U.S.A.: the occurrence of bronzite-andesites at Mount Shasta,

California, has been reported by Anderson (1977), who interpreted them as the result of the "melting of a refractory source rock", initiated by continued volatile loss from a stationary segment of subducted lithosphere. The bronzite-andesites of the O.R.S. province are not comparable with these, however, for they are rich in LIL elements. A time delay between an increment of subduction and its associated magmatic event is not unlikely, but no calc-alkaline volcanic province is known that wholly post-dates its associated subduction.

Recalling the unsatisfactory state of the evidence for a Devonian age for the Scottish Lower O.R.S. (section 1.3), it is suggested that the bulk of the Scottish Lower O.R.S., and possibly some of that described as Middle O.R.S. (Shetland), may in fact be of Silurian age, and directly associated with the subduction responsible for the Southern Uplands accretionary prism of McKerrow *et al.* (1977).

If the Scottish Lower Old Red Sandstone is of Silurian age, then the large thickness of conglomerates in the Midland Valley can not be used as evidence for end-Silurian orogeny, and the paradox noted earlier is partially resolved. It is therefore necessary to re-examine briefly the entire status of the Siluro-Devonian Orogeny in Britain.

(1) Scottish Highlands: all nappe tectonics and metamorphism is Ordovician or earlier (van Breemen and Boyd, 1972). Very minor open folds may be younger, but

it is probable that the Highlands acted as a nearly rigid block by the end of the Ordovician. The O.R.S. conglomerates probably indicate the uplift and erosion of the mountains of the Grampian Orogeny, of Ordovician age (Lambert and McKerrow, 1976).

(ii) Midland Valley: pre-O.R.S. rocks are only present in the south, where their relationship to the O.R.S. varies from ?conformity to unconformity. In both cases, there is a transition from marine to continental facies near the base of the Wenlock, and it is not improbable that such a transition could be accompanied by the development of local unconformity. Most of the folding in the South Midland Valley inliers may postdate the local Lower O.R.S.

(iii) Southern Uplands (and Girvan area): folding and cleavage development in the sediments of the accretionary prism could be mainly related to the accretionary process and sediment dewatering. The subaerial volcanic rocks of St. Abb's Head and the Cheviot Hills lie unconformably on the rocks of the prism, but they need not be younger than the youngest segment of the prism on which they rest. However, these volcanic rocks are not thought to be related to the rest of the province, and they may well be younger.

(iv) Lake District: Soper and Moseley (1978) have inferred major end-Silurian orogeny on the basis of a common penetrative cleavage direction in major rock groups of Arenig to Ludlow age, and suggested that this was dated by the contemporaneity of the final stages of

cleavage formation with the injection of the Shap Granite (394 Ma). However, the common direction does not necessarily imply that the cleavage was formed at the same time throughout the Lake District. In addition, there is no evidence that the Silurian rocks in the south of the Lake District were originally present throughout the area, for chemical (Fitton and Hughes, 1970) and age (Downie and Soper, 1972) differences between the Eycott and Borrowdale Volcanic Groups imply that these may no longer be used to infer the existence of a pre-Carboniferous Lake District anticline. Apart from the Silurian rocks in the south, and the immediately adjacent Ordovician, there is therefore little evidence for end-Silurian orogeny in the Lake District.

(v) Wales: there is reasonable evidence that cleaved Silurian rocks were originally present throughout much of North and Central Wales, and end-Silurian orogeny is accepted here.

It is concluded that major Siluro-Devonian deformation in Britain was probably restricted to the southern Lake District and Wales, and can not accurately be described as a major orogeny. The great contrast in structural complexity between this deformation and the end-Silurian nappe structures of Scandinavia therefore requires explanation.

(b) Direction of Subduction

The arcuate surface trace of the O.R.S. subduction zone has great implications for the geometry of plate movements in the British-Scandinavian sector of the Caledonides. Strongly curved magmatic arcs are known in modern Indonesia, and such arcs imply one of two geometrical possibilities:

- (i) Deformation of the descending plate, allowing perpendicular plate convergence throughout the length of the subduction zone;
- (ii) A major transcurrent component to subduction in regions where the orientation of the surface trace of the subduction zone is subparallel to the relative direction of motion of the opposing plates.

It is probably not feasible to distinguish between these possibilities when all traces of oceanic crust have been destroyed, but it is believed that the second can be used to explain the tectonic contrast between Britain and Scandinavia at the end of the Silurian.

Major collision orogeny could be expected where the direction of relative plate motion was perpendicular to the surface trace of the subduction zone. Collision orogeny could therefore occur on the Shetland-Scandinavia sector of the subduction zone if relative plate motion was east-west. Plate convergence along the sector between Ireland and southern Scotland would then be less than 45° oblique to the

subduction zone, and would perhaps result in much less intense deformation. The occurrence of granulite facies gneissose blocks in Carboniferous vents close to the suture in central Ireland (Strogen, 1974), and the existence of a normal crustal thickness along the LISPB seismic section (Bamford et al., 1978) suggest that the opposing continents did come into contact in this sector, although some ambiguity exists in the geological interpretation of the seismic data. Further speculation on the actual geometry of collision is considered unjustified because of the lack of information concerning the shape of the northwest margin of the European plate.

It is believed that the rarity of calc-alkaline volcanic rocks of Silurian age on the European plate can be used as evidence against final closure being accomplished by the collision of two opposing subduction zones (c.f. Phillips et al., 1976), although the significance of the c. 400 Ma granitoids of northern England and southern Scotland, and of the Cheviot and St. Abb's Head lavas, remains to be investigated. These lavas and plutons are thought to be of early Devonian age, a little younger than the O.R.S. volcanic province to the north of the Southern Uplands Fault. More detailed modelling will need to be based on an accurate geochronological study of the O.R.S. lavas, together with a trace element chemical study of the plutonic rocks.

9.7 : ORIGIN OF SPATIAL CHEMICAL VARIATION

The complex chemical variation described from most of the O.R.S. volcanic province was ascribed to multi-source contamination models in sections 4.4, 5.5 and 6.3. As discussed in section 9.3, the wide variation in LILE element concentrations of rocks with >100 ppm Ni and >150 ppm Cr can not be generated by fractional crystallisation, and requires the existence of primary magmas with a wide range of LILE concentrations in a single area, and an increase in overall LILE concentrations correlated with increasing depth to the inferred Benioff zone. Since correlation between LILE concentrations is colinear for variation both within a single area and throughout the whole province, it is believed that any mechanism proposed to explain LILE variation with depth to the Benioff zone must also be able to provide LILE variation within a single area.

The existence of a descending lithospheric plate allows five possible contributory sources to the eventual magma composition: the upper and lower continental crust; the mantle; the subducted lithosphere and any sedimentary material subducted with the descending plate. The greater the number of sources invoked in a final model the harder this becomes to test, and therefore models will be discussed in order of increasing complexity.

(a) Single source models

The high Ni and Cr concentrations of many of the rocks imply derivation of parental magmas by the partial melting of a Ni- and Cr-rich source material. Both upper crustal material and subducted sediments are likely to contain less Ni and Cr than many of the lavas, and if the subducted oceanic crust was comparable to modern mid ocean ridge basalts, Ni and Cr would again be lower than their concentrations in many O.R.S. lavas (Sun et al., 1979, Fig. 2). The cumulates and mantle underlying the subducted oceanic basalts are likely to be highly refractory: it is not believed that significant volumes of melt could be derived from this source. Little is known of the chemical characteristics of the lower continental crust, but it is unlikely to have much Ni and Cr, assuming that it is not ultramafic.

The only single source that can provide adequate Ni and Cr is therefore the mantle. It was observed in section 4.4 that generation of thick sequences of LILE-rich volcanic rocks such as the Lorne Plateau lavas requires the total removal of many LILE from unreasonably large volumes of even fairly enriched mantle (2x chondrite). A single mantle source region is therefore required to be highly enriched in LIL elements. If this also involved enrichment in Rb/Sr and Nd/Sm then the values of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ could be used to indicate the longevity of the enrichment. The relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ at Lorne (Brown, 1975) suggests that either

enrichment had not been long in existence, requiring a recent influx of LIL elements, or that Rb/Sr was not enriched. Depth-correlated variations in LILE concentrations could then be generated by an increase in mantle LILE with depth.

Such a model for the K-h variation has been discounted by many authors e.g. Dickinson and Hatherton (1967) and Cawthorn (1977). It is believed to be unlikely because of the extreme nature of the necessary enrichment in LILE, and the development of the enrichment not long before volcanism would require an additional source of incompatible elements. Furthermore, the failure of Rb, Zr and possibly Th and Nb to show depth variation (Fig. 9.8, Table 9.1), and the negative correlation between Y and depth, suggests either that enrichment was restricted to a particular group of incompatible elements, or that these elements were located in refractory phases, and that the Y-bearing phase (?garnet) became more refractory with depth. Both of these possibilities are thought to be unlikely, and the difficulty of producing the observed variation in incompatible element ratios within a single area is believed to be strong evidence against any single source model.

(b) Dual source models

Using the same argument as previously, the high Ni and Cr of many rocks requires that some part of these melts must originate in the mantle. Since the main difficulty

Fig. 9.8 a & b : Bulk rock variation diagrams for samples with
>100 ppm Ni and >150 ppm Cr.

Conventions as section 3.3

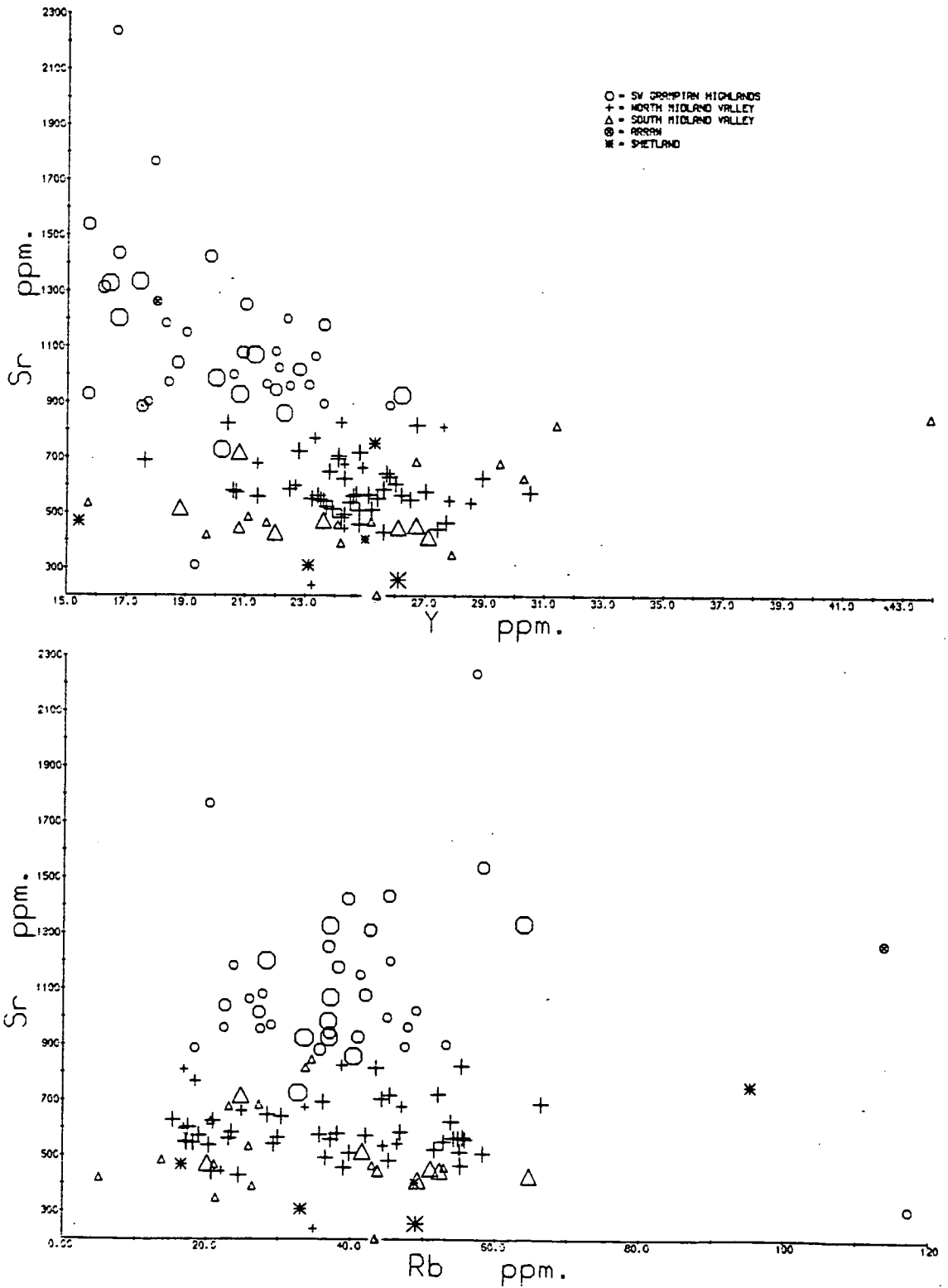


Fig. 9.8 c & d : samples with >100 ppm Ni, and >150 ppm Cr

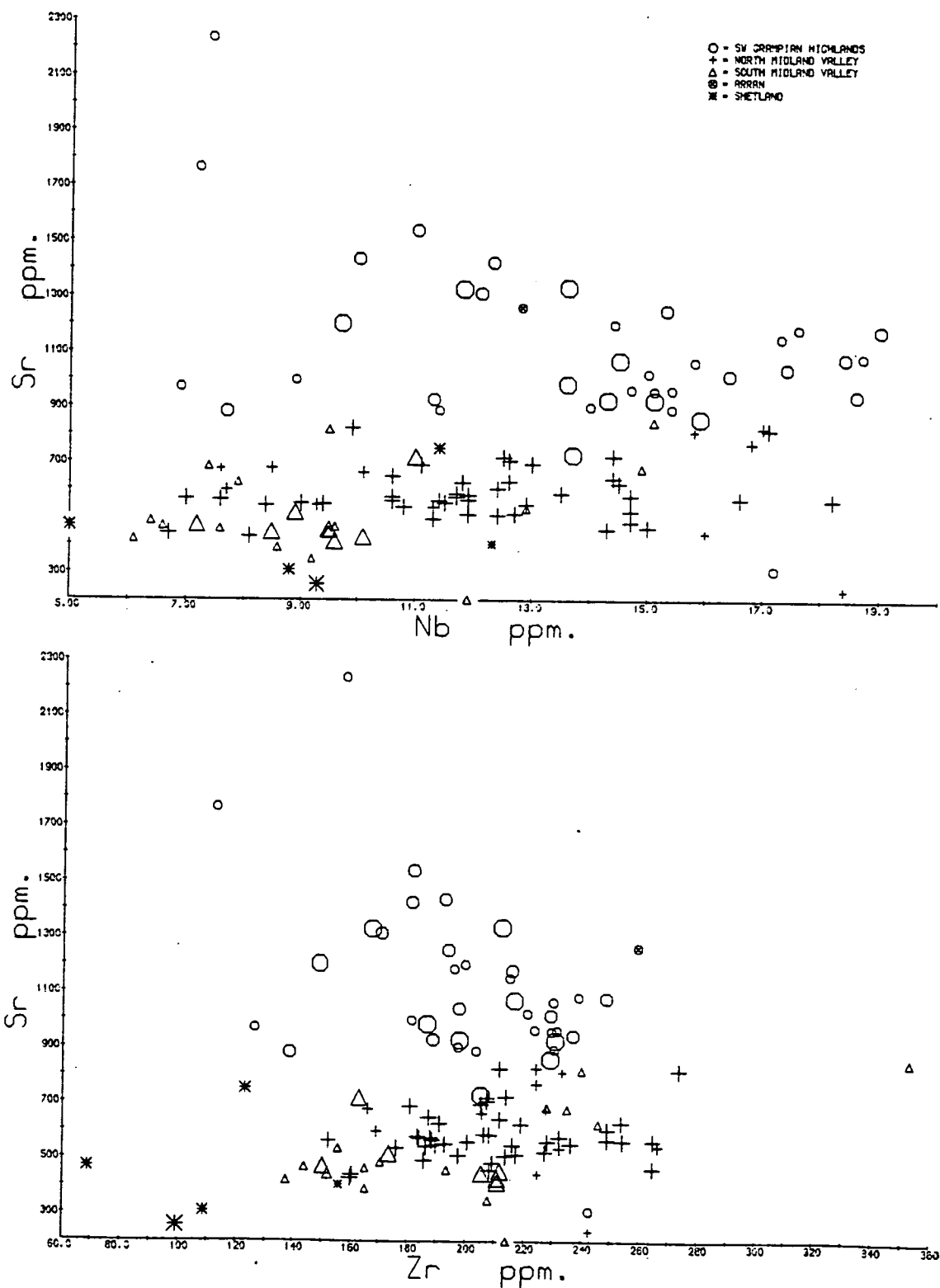
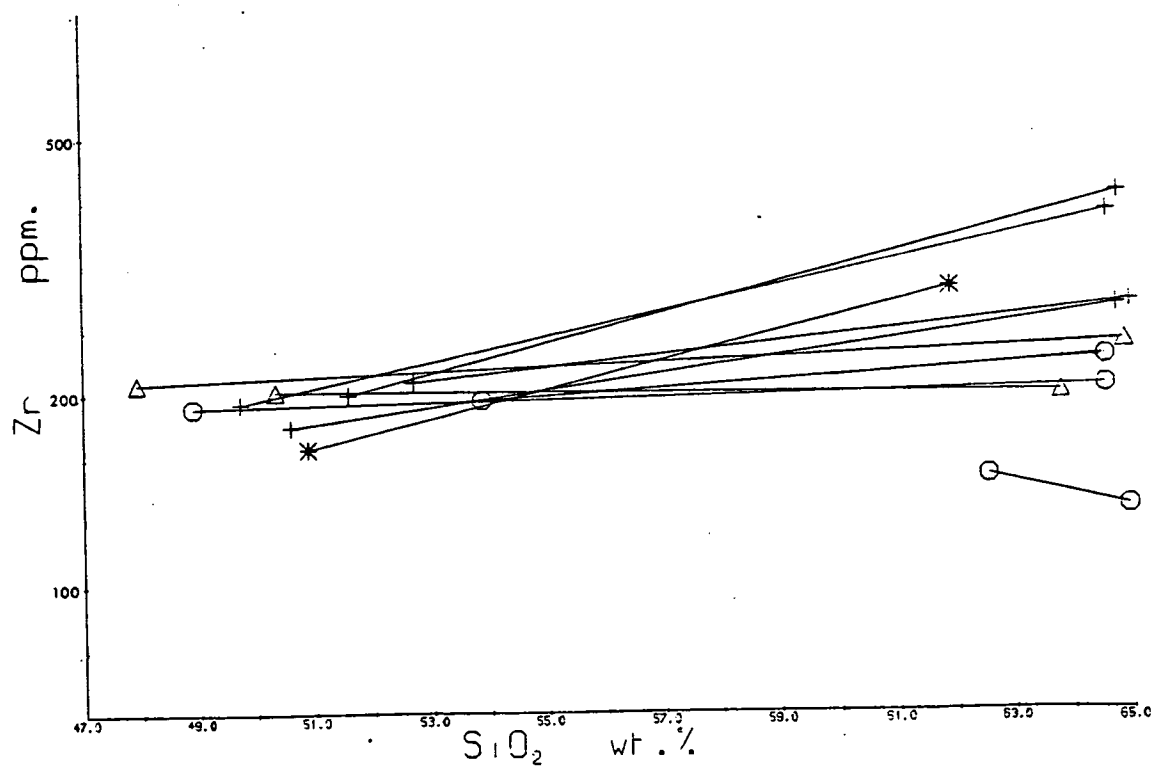
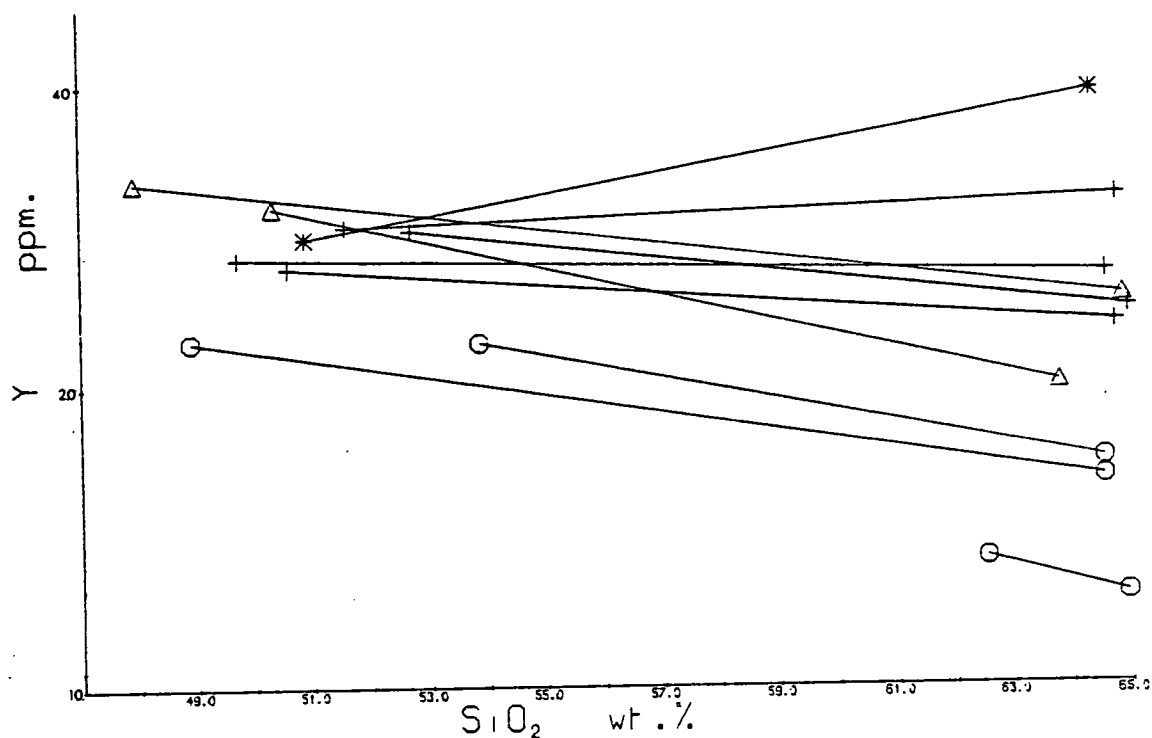


Fig. 9.8 e & f : Regression lines for each area for samples with 65% SiO_2 . Symbols refer to the major regions:

○ = SW Grampian Highlands, + = North Midland Valley,

△ = South Midland Valley, * = Shetland (Esha Ness)



with single-source mantle derivation is the high concentrations of incompatible elements, the basic function of an additional source region is to provide a contaminant rich in incompatible elements, varying proportions of which can be added to a mantle melt to provide a wide range of incompatible element concentrations with only minor change in major element composition.

Generation of higher LIL element concentrations through the interaction of mantle-derived melt with thicker crust to the northwest can not satisfactorily account for the low levels of these elements in Huntly and Shetland. The low initial $^{87}\text{Sr}/^{86}\text{Sr}$ of the Lorne lavas was used in Chapter 4 to infer that the high Sr was not crustally derived, but interpretation of this isotopic result is hazardous because of the northwestward decrease in Rb/Sr. It is very difficult to envisage a model for this Rb/Sr depletion involving crustal contamination. Derivation of the high concentrations of incompatible elements by contamination with lower crustal material is unlikely to produce an increase with depth to the subduction zone. Furthermore, if the lower crust was of Lewisian character, it is improbable that a contaminant rich in incompatible elements could be derived from it.

It is difficult to suggest criteria which could indicate the extent to which subducted sediments contributed to the magmas. They are probably capable of providing a source for small quantities of melt very rich in

incompatible elements, but it is difficult to suggest a reason for the increase in LIL element concentrations with depth to the Benioff zone. This requires a greater relative volume of sediment-derived melt or melts richer in LILE with increasing depth. Neither of these possibilities is thought to be likely, and the failure of Zr, Rb and Nb to increase with depth requires an unusual combination of refractory phases.

Interaction of subducted oceanic crustal material and overlying mantle can occur by transfer of either melts or hydrous fluids. In either case, the existence of an increase in LIL element concentrations with depth to the Benioff zone implies that the contaminant becomes richer in LIL elements with depth or that the relative proportion of contaminant to mantle-derived melt increases. Cawthorn (1977) has reviewed the suggestions of several authors for the origin of K-h₂O variation involving a melt contribution from the slab. These include the breakdown of hydrous phases in the slab, buffering of the K₂O content of the magmas by sanidine, and decrease in $D(K, \text{bulk slab})$ with pressure. Models involving particular phases are specific for K, and can not generate the variation observed in the O.R.S. province for many other LIL elements.

Little evidence is available for the behaviour of LILE distribution coefficients with pressure: it is thought to be most unlikely that those for Sr, Ba, LREE, P and K in an eclogitic assemblage would decrease by the large amount

required with no corresponding change in those for Rb, Zr and Nb. Change in relative proportions of slab and mantle melt is unlikely to result in contamination by a greater proportion of slab melt at greater depths, unless slab dehydration at shallower levels results in greater melting of the overlying mantle. Change in proportions of contaminant and mantle melt requires lower concentrations of Rb, Zr and Nb in deeper slab melts: this would probably require the retention of these elements in refractory slab phases, and is thought to be unlikely.

It is probable that a slab-derived hydrous fluid would be able to transport LIL in preference to high field strength elements from the slab into the overlying mantle, in a manner analogous to the behaviour of these two groups of elements during metamorphism. This might therefore provide a model for the separation of the two groups of incompatible elements, not readily accomplished by melting processes. The high degree of light rare earth enrichment at Lorne could be produced without the need to invoke residual garnet, or separation of garnet during ascent, for Y would not be readily transported by the hydrous fluid.

The hypothesis satisfactorily explains the failure of Zr, Ti and Y to correlate with the LIL elements, and slight correlation of LILE with Nb could be ascribed to minor transport of Nb as ionic complexes. However, Rb is likely to be one of the most readily transported LIL elements in a hydrous fluid. Furthermore, it is not clear how

contamination by slab-derived hydrous fluid can generate the depth increase, for the bulk of the dehydration of the subducting lithosphere is likely to take place at relatively shallow levels. The PT regime of the descending lithosphere is not sufficiently well-known to permit accurate prediction of the stability limit of amphibole, which is probably the most important hydrous phase, although phases such as hydrogarnet have been proposed at higher pressures. It is nevertheless believed that the quantity of hydrous fluid released by the descending lithosphere will decrease with increasing depth, and that therefore increase of LILE with depth by this model requires major increase in $D(\text{LILE, hydrous fluid/slab})$ with pressure. This has been demonstrated by Mysen (1979) for LREE in a garnet-peridotite, but is thought unlikely to be the case for all the elements involved.

(c) Zone-refining

Best (1975) suggested that the K-h relation could be produced if magmas (or hydrous fluids) generated in the vicinity of the subducted lithosphere were able to zone-refine (or scavenge) incompatible elements from the overlying mantle wedge, resulting in higher K with an increased path length to the surface. The enrichment process is only limited by the distribution coefficient for a particular element between the fluid and the mantle phase assemblage, and variation within a single outcrop area can be attributed to differences in the rate of fluid ascent, or

to heterogeneity in the mantle resulting from the passage of earlier fluids. This mechanism would be most effective for incompatible elements present at grain boundaries, in fluid inclusions or in defect structures, but the ascending fluid would probably not incorporate incompatible elements held in minor phases, unless it was sufficiently superheated to allow melting of these phases.

Various minor mantle phases have been invoked to explain trace element characteristics of 'primary' magmas; for example, phlogopite (Beswick 1976) and apatite (Beswick and Carmichael, 1978). If such phases are present then the incompatible element concentrations of a particular zone-refining primary magma will be a function of the concentrations acquired at the site of melting, the ascent rate, the path length to the surface and the distribution of minor phases along this path. The failure of Zr, Rb, possibly Th and to a lesser extent Nb to show depth-correlated variation might suggest the presence in the mantle of minor phases rich in these elements. These phases are not required to be refractory, as is the case in previously discussed models, and the wide variation in these elements uncorrelated with Sr or LREE in a single outcrop area, e.g. Lorne, could be due chance melting and incorporation of these phases into some of the ascending fluids.

This interaction between ascending fluids and incompatible elements occurring both within discrete phases

and dispersed through the mantle can probably account for most of the observed spatial and local variation in relative and absolute abundances of incompatible elements in the Ni- and Cr-rich rocks. The absence of constant ratios between the incompatible elements that increase most with depth can be ascribed to the partial buffering of most elements by minor phases. For example, K_2O shows little increase relative to Sr between the North and South Midland Valley, while P_2O_5 and LREE appear to increase more rapidly than Sr over this part of the depth range (Fig. 9.2). The close correlation between P_2O_5 and $\Sigma LREE$ and the curved Sr-P, Sr- $\Sigma LREE$ relations could suggest minor buffering of P and LREE concentrations by apatite in the north, but otherwise it is difficult to suggest the identity of the minor phases. For example, the failure of Rb to show a depth increase coupled with the intermediate behaviour of K could suggest the presence of phlogopite, but it is doubtful whether $D(K/Rb, phlog)$ is sufficiently low to provide readily apparent variation in K but none in Rb. Ilmenite is perhaps the most plausible phase to prevent a Zr-h relation, but the existence of a slight Nb-h relation is difficult to reconcile with $D(Zr/Nb) < 1$ for most phases. The decrease in Y with depth (Fig. 9.8) can not be satisfactorily explained by this process, unless interaction with a greater height of garnet-bearing mantle can result in loss of Y from the ascending fluids. This could also produce the slight decrease in Sc with depth (Table 9.1).

While the scavenging/zone refining process provides

the most satisfactory dual source explanation for the depth variation and for variation within a single area, some doubts must be expressed concerning the dynamics of the process. The zone-refining presumably occurs by diffusion of incompatible elements into the ascending fluid: if ascent was diapiric then diffusion rates are probably too slow to provide sufficient enrichment. The alternative is to invoke percolation of the ascending fluid through the mantle: this may involve equilibration with the mantle throughout ascent for the major elements. Insufficient high pressure experimental work is available to suggest the sort of compositions that might result, but the hypothesis requires some of these to be very siliceous: seven of the rocks with >100 ppm Ni and >150 ppm Cr have over 59% SiO_2 , and bronzite-andesites with 56-59% SiO_2 are very common. Many rocks much more siliceous than these also have high Ni and Cr, frequently in excess of 60 and 100 ppm respectively. The zone-refining hypothesis could imply that these too had passed through the mantle, for such rocks display a similar variation in incompatible element concentrations (e.g. Fig. 9.6a), and can not be derived by fractional crystallisation of any of the more mafic magmas (sections 4.4d, 5.5c, 6.3c). High pressure experimental determination of the phase relations of some of these compositions would be of great value.

A further problem arises concerning the genesis of many rocks poor in Ni and Cr. While the few of these that are rich in incompatible elements may probably be generated

by fractional crystallisation (e.g. the "trachyandesites" of Montrose, section 5.1e), many have equivalent or lower concentrations of incompatible elements than the Ni- and Cr-rich rocks of the same area (e.g. the East Hills/Dunnichen Member, section 5.1b). It was concluded in section 5.5c that these were most likely to represent partial melts of a Ni-, Cr-poor source, although their derivation by fractional crystallisation from primitive incompatible element-poor magmas, never seen at the surface, could not be precluded. If the latter was the case, then the entire spatial variation of mafic rocks in the O.R.S. province would have to be a result of chance: this can not be accepted. It is possible, however, that relatively little separation of mafic phases is required to reduce Ni and Cr to these levels, and that the parental magmas need not have been much poorer in incompatible elements.

Alternatively, the Ni-, Cr-rich magmas could be parental to the low-Ni, -Cr rocks if differentiation took place prior to contamination. If this differentiation occurred at relatively shallow depths (<60 km), then the contamination process must have involved the mixing of magmas produced at these levels with the fluids which had ascended through and zone-refined the mantle wedge. Serious volumetric problems are encountered here, for the great advantage of the zone-refining process would be lost, whereby the incompatible element-depth variation is believed to be due to zone-refining through different path lengths to the surface. An extra variable would be introduced into the

chemical equation: the relative proportion of zone-refining fluid to sub-crustal melt. The relatively constant levels of K and Sr in many parts of the Midland Valley (e.g. Figs. 9.1, 9.3 for the Sidlaw Hills, the North Fife Hills and Ayrshire) are most unlikely to be due to high level mixing, for it would be expected that at least some of the high level magmas parental to rocks such as those of Dunnichen and East Hills would reach the surface. The relatively uniform levels of these elements are far better explained by allowing a wide range in Ni, Cr and SiO_2 concentrations in the primary magmas formed in the vicinity of the subducted slab. A third source component is therefore believed to be necessary to generate the volcanic rocks of the O.R.S. province: the subducted slab.

The melting processes in the vicinity of the subducted slab are not understood, for their chemical features are difficult to isolate from the effects of later contamination. It is possible that the positive K- SiO_2 correlation has its origin in this region, with the K later augmented by zone-refining. The striking La/Y- SiO_2 and Ti-Y correlations in the rocks of many areas may also originate at this early stage in petrogenesis.

(d) Petrogenetic summary

It is believed that a model along the following lines could have generated the chemical variation of the rocks of the O.R.S. volcanic province:

- (i) Generation of melts in the subducted slab and in the immediately overlying mantle with a wide range in SiO_2 , Ni and Cr concentrations. Subducted sediment may also play a part in initial magma generation.
- (ii) Percolation of melts through the overlying mantle wedge, resulting in the zone-refining of incompatible elements from grain boundaries, and sometimes the melting of minor phases rich in LIL and high field strength elements. The increase in incompatible element concentrations from the South Midland Valley to Lorne is directly related to the increased path length available for zone-refining to melts arising from successively deeper levels.
- (iii) Minor separation of mafic phases in the later stages of ascent can reduce Ni and Cr concentrations and could possibly destroy evidence for major element equilibration with mantle.
- (iv) Minor fractional crystallisation at crustal levels may generate a few rocks greatly enriched in Zr, Nb etc. e.g. the "trachyandesites" of Montrose. Major fractional crystallisation at this level appears to have taken place in Shetland.
- (v) Melting of the lower continental crust with hybridisation may generate some of the most siliceous magmas, with lower incompatible element concentrations than in many more basic magmas.

The great complexity of the chemical variation inevitably means that the evidence for some of these

conclusions is a little unsatisfactory, and further work, particularly isotopic and experimental, is required before detailed petrogenetic models can be suggested for the various rock groups. It is believed that further work on rocks of the province, possibly leading to refutation of some of the above conclusions, would be of great value, for some of the implications of the model discussed above are of considerable importance for the genesis of all calc-alkaline rock suites. The zone-refining process will result in a mantle heterogeneously depleted in grain boundary incompatible elements, but not necessarily infertile: any melts forming at a later date should show the effects of this (e.g. the Scottish Carboniferous volcanic rocks). Further, there is no reason to suggest that the zone-refining process should be restricted to calc-alkaline rocks, and any magma generated below the uppermost mantle is probably capable of zone-refining during its passage to the surface.

ACKNOWLEDGEMENTS

I am most grateful to Dr. J.G. Fitton and Dr. B.G.J. Upton for suggesting this research project, for their constant interest and encouragement throughout, and for their helpful comments on the various stages of this thesis.

I am very grateful to Professor Sir Frederick Stewart and Professor G.Y. Craig for placing the facilities of the Grant Institute of Geology at my disposal. The receipt of a Natural Environment Research Council Research Studentship is gratefully acknowledged.

I also wish to thank everyone with whom I have discussed the various ideas presented herein, especially my fellow research students Messrs. A.M. Graham and P.M. Jackson.

I would also like to express my appreciation to the following persons for the large amount of technical advice and assistance that I have received throughout the course of this research.

Mr. K. Cameron and his assistants for making most of the thin sections and probe slides, and for help in making the others.

Dr. J.G. Fitton, Dr. E. Boyle and Mr. G.R. Angell for assistance and advice on XRF techniques.

Dr. P.G. Hill, Mr. C. Begg and Mrs. S. O'Hara for their great help in electron microprobe techniques, and in particular for their immediate assistance at any mishap and for their maintenance of an extremely efficient microprobe laboratory.

Dr. G. Yarwood for my introduction to the Edinburgh computer system; the authors of the various computer programs that I have used, particularly Dr. D.J. Humphries; and the staff of the Edinburgh Regional Computing Centre, without whose assistance little of this work could have been completed within three years.

Mrs. D. Baty and Mrs. K. Swanson for photographing and printing some of the diagrams, and for their assistance with draughting.

Mrs. T. Grieve for assistance in the library.

Mr. P. Aspen for the efficient curation of my samples.

Several people kindly donated specimens for analysis; I should particularly like to thank Messrs. M.A.E. Brown, D.C. Greig and R.W. Elliot of the Institute of Geological Sciences, Edinburgh, and Mr. E. Kellock.

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APPENDIX A : PRE-ANALYTICAL PROCEDURES

A1 : SAMPLE COLLECTION

Samples were collected with the object of displaying the full range of chemical and petrographic variation found in the rocks of each area of volcanic outcrop, with each part of that range being represented by the samples least affected by alteration. While collection has been primarily from lava flows, in some areas samples have been collected from minor intrusions into the volcanic pile, and from clasts of volcanic origin in Old Red Sandstone conglomerates. Coastal, quarry and riverside exposures were best suited to the collection of less altered samples, for collection could here be restricted to the compact central portions of flows, instead of the characteristically autobrecciated and vesicular tops and bases. In most areas, however, exposure is limited, and unusual rock types have been collected despite their state of alteration. The shortage of exposure, and variation in appearance of altered rocks, have probably led to underrepresentation of some rock types, but it is thought that this is not a serious problem.

Where possible, samples of at least 4" (10cm) diameter were collected, and as much weathered material as possible was removed in the field. Sampling was based on a geographic division of the province into 15 outcrop areas, and samples are identified by prefixing numbers with letters indicative of the outcrop area. The rocks of any one outcrop area are not necessarily genetically related.

A2 : SELECTION OF SAMPLES FOR ANALYSIS

All samples collected have been examined petrographically, initially to determine their degree of alteration and the likely effect of this on a possible analysis. Where several well-defined petrographic types were identified, the less altered samples of each type were selected for analysis. As far as possible, the analysed samples represent the full range of primary petrographic variation present in the samples collected from each area. A total of 597 samples have been analysed, and are listed in Table A1. In order to maintain constant analytical quality, only new analyses have been used, and the majority of the samples have been collected by the author.

Table A1 : List of samples analysed, localities and brief petrographies.

Abbreviations: ol=olivine; opx=orthopyroxene; cpx=clinopyroxene; hb=hornblende; pl=plagioclase; ksp=alkali feldspar; qz=quartz; bi=biotite; ap=apatite; mt=spinel; ilm=ilmenite; cc=calcite.

% refers to approximate volume percent phenocrysts.

Alteration state numbers (PAS) are: 1=ol fresh; 2=opx fresh; 3=both cpx,pl fresh; 4=either of cpx,pl fresh; 5=none fresh (Chapter 2).

Where an alternative specimen number is quoted, the sample

is from another worker's collection: SA12-21, SH36-41, OC152-153 and OR1-4 are from the Scottish collection of the Institute of Geological Sciences (S-numbers); OR5-8 were collected by Kellock (1969); S18-52 were collected by Gandy (1973a; M-numbers); and AR10 and AR11 were collected by Dr. J.E. Dixon.

Sample	Grid Reference	Phenocrysts	%	PAS	Comments
<u>LORNE</u>					
L1a24	NM980349	cpx-pl-bi-hb-?opx-mt-ap-qz	25	5	
L3a1	NM924371	ol	5	4	
L4a1	NM924373	ol-mt	15	4	
L5a14	NM922375	opx-cpx-pl-bi	25	5	
L8a1	NM871319	ol	10	3	
L9a7	NM888338	ol-cpx	10	3	
L10a8	NM886339	opx-cpx	5	3	
L11a8	NM886339	opx-cpx	5	4	
L12a1	NM902342	ol	7	4	
L13a1	NM904342	ol	8	4	qz-cc amygdales
L14a8	NM909343	opx-cpx-qz	3	3	
L18a1	NM903338	ol-?cpx	6	4	
L19a1	NM883312	ol	13	4	
L21a7	NM885309	ol-opx-cpx-qz-?pl-?ap	5	3	
L22a20	NM864275	qz-?pl-?hb	4	4	pl xenocrystal
L23a1	NM859278	ol-?pl	1	3	
L24a7	NM915343	ol-cpx	7	3	
L25a1	NM924343	ol	7	4	
L26a7	NM933345	ol-cpx	9	3	
L28a13	NM968341	pl-opx-cpx-ap-mt	25	4	
L30a13	NM961327	pl-opx-cpx-ap-mt	20	4	
L34a45	NM986337	ol-pl-hb-cpx	20	5	
L35a21	NM985342	pl-?hb		5	ignimbrite
L38a20	NM985305	?opx	0	5	cc veins
L41a20	NN044285	opx-?hb	0	4	
L42a19	NN040285	pl	5	5	?autobreccia
L43a22	NM980288	pl-mt-?ksp	20	5	?dyke-rock
L44a1	NM908334	ol	7	3	
L45a8	NM904318	opx-cpx	5	3	
L50a45	NM911299	ol-cpx-pl-hb-qz	7	3	
L51a9	NM914296	ol-opx-cpx-?hb	6	3	
L52a9	NM916285	ol-opx-cpx-?hb	8	5	
L54a22	NM831280	cpx-bi-ap-?pl	15	5	Ferry Plug
L55a22	NM823258	?bi-?cpx	0	5	Gallanach neck
L56a1	NM791278	ol	10	3	
L58a1	NM793279	ol	7	4	
L61a47	NM889284	?ol-?opx-?hb-qz	5	5	
L63a47	NM887265	ol-opx-bi-pl-?hb-?cpx	5	5	
L64a7	NM892265	ol-cpx	6	3	
L65a7	NM816237	ol-cpx	14	3	
L67a1	NM821235	ol	7	3	
L68a1	NM889248	ol-?qz	8	3	pl-rich ?autoliths
L71a1	NM908242	ol-?opx	5	5	
L73a12	NM922240	ol-cpx-pl	15	3	
L75a19	NM922242	pl-hb-bi-mt-?ol	6	5	
L77a19	NM932226	pl-hb	15	5	

L79@13	NM947234	opx-cpx-pl-mt-ap	25	4	
L82@25	NN113289	pl, schistose screen in Etive complex			
L86@13	NN013290	opx-cpx-pl-mt-ap	32	5	
L87@3	NN012290	cpx-qz	24	5	
L91@3	NN013283	cpx-qz	20	5	
L92@19	NN014282	pl-bi-ap-?hb	6	5	
L95@13	NN018278	opx-cpx-pl-mt-ap	22	5	
L97@7	NN027265	ol-cpx	9	3	
L98@6	NM937282	pl-opx-hb-mt-ap	22	5	
L99@19	NM946278	pl	1	5	
L100@6	NM944278	pl-opx-hb-mt-ap	30	5	
L101@9	NM944283	ol-opx-cpx	7	3	
L102@13	NM947286	pl-opx-cpx-mt-ap	32	4	
L113@15	NM824217	?hb-cpx-bi-qz	18	3	
L120@19	NM804201	pl-qz-opx	15	5	
L121@13	NM813213	pl-opx-cpx-mt-ap	34	4	
L122@26	NM843198	ol-cpx	6	3	cc-bi aggregates
L125@15	NM834225	?hb-cpx-bi	12	3	
L126@7	NM857201	ol-cpx	6	3	
L128@13	NM897205	pl-opx-cpx-mt	50	3	
L129@1	NM912204	ol	4	4	
L130@19	NM915205	pl-hb-bi-opx	6	5	
L131@5	NM924307	pl-opx-mt-ap	30	5	
L132@5	NM912199	pl-opx-mt-ap	36	4	
L133@1	NM846193	ol	5	5	cc veins
L137@26	NM875170	ol-cpx	10	4	cc-bi aggregates
L140@1	NM854163	ol	5	3	
L141@1	NM847156	ol	10	3	
L146@7	NM958154	ol-cpx	14	3	
L148@1	NM992241	ol	15	3	
L150@21	NM984235	pl-bi-?ksp-mt-ap	35	5	
L151@1	NM978238	ol	6	4	
L152@1	NM975235	ol	10	3	
L153@1	NM965232	ol	9	3	
L155@7	NM946238	ol-cpx-mt	11	3	
L156@19	NM956252	pl-opx-hb	8	5	
L157@13	NM956257	pl-opx-cpx-mt	50	5	
L158@13	NN013238	pl-cpx-?opx	30	5	
<u>GLENCOE</u>					
GC1@7	NN138555	ol-cpx	5	4	Group 1
GC3@44	NN144547	pl-opx-hb-bi-mt-ap	24	3	Gp 4
GC4@44	NN148538	pl-opx-hb-bi-mt-ap	27	3	Gp 4
GC5@21	NN153536	qz-pl-mt		5	Gp 5
GC6@17	NN155536	pl-bi-mt	45	5	Gp 7
GC8@19	NN158548	pl		5	Gp 2
GC10@14	NN162571	pl-opx-cpx-bi-qz	3	3	Gp 1
GC11@11	NN173568	ol-pl	10	5	Gp 1
GC12@10	NN174566	ol-cpx-opx-pl	3	3	Gp 1
GC13@19	NN181564	pl-?bi-ap	5	5	Gp 2,
					autobrecciated
GC16@19	NN196564	pl-?ksp-bi-?hb-mt	10	5	Gp 2
GC17@21	NN202563	pl-qz		5	Gp 2, ?lava
GC18@13	NN208562	pl-mt-?cpx-?opx	10	5	Gp 2
GC19@25	NN178511	?Gp 1 andesite hornfelsed by Cruachan Granite			
GC20@25	NN172516	pl-?opx-?hb	15	5	?Gp 4
GC23@6	NN172519	pl-hb-mt-?opx	18	5	Gp 4
GC24@21	NN172522	pl-qz-bi-ap		4	Gp 5
GC25@19	NN228527?	pl		5	Gp 2, hornfelsed

GC26a16	NN157583	opx-cpx-pl-mt-hb-qz	4	3	Gp 2
GC28a13	NN139552	opx-cpx-pl	5	4	Gp 1
GC29a16	NN147552	pl-opx-hb-cpx-mt-ap	28	3	Gp 4
GC30a22	NN160560	pl-hb-bi-mt-ap	33	4	NNE dyke
GC31a19	NN143548	pl-bi	5	5	Gp 2, ?autobrecciated

BEN NEVIS

BN1a24	NN157729	pl-opx-mt-hb-bi-ap	18	4	?autobrecciated
BN2a21	NN160728	pl-hb-opx-cpx-mt-ap	18	3	?tuff
BN3a24	NN165722	pl-hb-opx-cpx-bi-mt-ap	37	3	
BN4a16	NN165722	pl-hb-cpx-opx-mt-ap	22	4	
BN5a24	NN164721	pl-hb-cpx-opx-bi-mt-ap	27	3	
BN6a16	NN162719	pl-hb-cpx-opx-mt-ap	10	4	
BN7a16	NN162718	pl-hb-cpx-opx-mt-ap	34	3	
BN8a16	NN165712	hb-pl-mt-cpx-?opx-ap	16	4	
BN9a16	NN167713	pl-hb-cpx-?opx-mt-ap	10	5	
BN10a16	NN157715	pl-cpx-opx-hb-mt-ap	19	3	
BN11a24	NN154716	pl-cpx-hb-mt-bi-?opx-ap	15	3	

MONIROSE REGION, pre-Arbutnott group

SC1-9 all from clasts in conglomerates

SC1a6	N0879855	pl-?hb-?opx-ap	15	5	} Stonehaven Gp
SC2a6	N0879855	pl-opx-?hb-mt	40	5	
SC3a19	N0879855	pl-qz-hb-bi-mt-ap	45	4	
SC4a16	N0880853	pl-hb-opx-cpx-mt-qz	40	3	Dunnotar Gp
SC5a19	N0879853	pl-hb-opx-mt	25	4	Stonehaven Gp
SC6a19	N0880849	pl-ksp-qz-bi-?hb-mt	20	4	} Dunnotar Gp
SC7a25	N0880849	pl-?ksp-?hb-ap	8	5	
SC8a16	N0880849	pl-opx-cpx-hb-ap	8	5	
SC9a24	N0881847	pl-opx-cpx-hb-bi-mt-ap-?qz	30	4	
SC10a14	N0881848	pl-opx-cpx-bi-mt-ap	35	4	Strathlethan Fm.
SC11a1	N0880828	ol	2	3	Tremuda Bay
SC12a7	N0878796	ol-cpx	1	3	Crawton
SC13a12	N0881797	ol-cpx-pl	20	3	Crawton
SC14a1	N0870768	ol	1	3	Todhead Point
SC15a19	N0870768	qz-pl-?ksp	15	5	clast, Crawton
SC16a21	N0275542	qz-pl etc.		4	ignimbrite

MONIROSE REGION, post-Crawton group

MT1a11	N0505439	ol-pl	1	3	East Hills
MT2a11	N0458424	ol-pl	5	3	Corbie Den
MT3a1	N0519446	ol-?pl	1	3	East Hills
MT4a11	N0536447	ol-pl	1	3	East Hills
MT5a18	N0549451	ap-?ol	0	4	East Hills
MT6a1	N0506502	ol	1	5	Dunnichen
MT7a1	N0549517	ol	1	5	Dunnichen
MT8a1	N0557519	ol-?pl	1	3	Dunnichen
MT9a18	N0589496	ap-ol	1	4	Ferryden
MT10a10	N0822802	pl-opx-cpx-ol	10	2	Bruxie Hill
MT11a13	N0824805	pl-opx-cpx	10	2	Bruxie Hill
MT12a11	N0828787	ol-pl	15	3	Bruxie Hill
MT13a10	N0822791	pl-ol-opx-cpx	15	3	Bruxie Hill
MT14a12	N0816754	pl-ol-cpx	8	3	Bruxie Hill
MT15a13	N0758802	pl-opx-cpx-?ol	25	2	Glenbervie
MT16a13	N0758802	pl-opx-cpx-?ol	25	2	Glenbervie
MT17a1	N0736704	ol-?pl	6	3	Garvock Gp
MT18a10	N0772691	opx-ol-cpx-pl	8	3	Morphie
MT19a10	N0778673	opx-cpx-pl-ol	20	4	St. Cyrus
MT20a1	N0796669	ol	10	5	Johnshaven

MT21@10	N0734661	opx-cpx-ol-pl	5	3	Morphie
MT22@11	N0752646	ol-pl	6	3	St. Cyrus
MT23@1	N0757648	ol	4	4	St. Cyrus
MT24@11	N0677518	ol-pl	2	3	Ferryden
MT25@11	N0662535	ol-pl	2	3	Ferryden
MT26@11	N0668520	ol-pl	8	3	Ferryden
MT27@18	N0632494	ap-ol-pl	2	5	Ferryden
MT29@18	N0622526	ap-ol-pl	3	4	Ferryden
MT30@12	N0253537	ol-cpx-pl-qz	1	3	Glenisla
MT31@12	N0254537	ol-cpx-pl-qz	1	3	Glenisla
MT32@10	N0254536	ol-opx-cpx-pl-qz	4	3	Glenisla
MT33@20	N0232544	opx-pl-?qz-?ap	0	3	Glenisla
MT34@13	N0292537	opx-cpx-pl-ap-mt	25	3	Glenisla
MT35@20	N0648555	?ol-?pl	0	3	Ferryden
MT36@28	N0727568	ol-opx-pl	10	3	Ferryden
MT37@28	N0734567	ol-opx-pl	10	3	Ferryden
MT38@1	N0729558	ol	2	3	Ferryden
MT39@1	N0732556	ol	8	3	Ferryden
MT40@11	N0732554	ol-?pl	4	3	Ferryden
MT41@5	N0724542	opx-pl	15	3	Ferryden
MT42@7	N0701488	ol-cpx	18	3	Ethie Haven
MT43@12	N0705484	ol-cpx-?pl	10	3	Ethie Haven
MT44@12	N0706483	ol-cpx-pl	10	3	Ethie Haven
MT45@12	N0705481	ol-cpx-pl-mt	10	1	Ethie Haven
MT46@5	N0074405	opx-pl-ap-?hb	50	5	clast
MT47@13	N0074405	opx-cpx-pl-mt-ap	40	4	clast
MT48@10	N0074405	ol-opx-cpx-pl-mt-ap	20	4	clast
MT49@1	N0065406	ol	8	5	Dunkeld
MT50@20	N0092425	ol-opx-cpx-pl	0	2	Dunkeld
MT51@16	N0173482	opx-cpx-pl-?hb-?ol	25	5	clast
MT52@22	N0173482	pl-?ksp-bi-hb-qz-ap	40	4	clast
MT53@16	N0191515	pl-opx-cpx-?hb-qz	8	2	Blairgowrie
MT54@13	NN637109	pl-opx-?cpx-mt	25	5	Callander
MT55@1	NN638114	ol-cc	10	5	Callander
MT56@1	NS515998	ol-cc	10	5	Aberfoyle
MT58@19	NN875264	pl-hb-bi-mt-ap-?ol	15	5	Crieff
MT59@19	NN877266	pl-hb-bi-mt-ap-?opx	18	5	Crieff
MT60@19	NN875265	pl-hb-bi-mt-ap	15	5	Crieff
<u>SIDLAW HILLS</u>					
S1@12	N0125199	pl-ol-cpx	20	3	
S2@12	N0124200	pl-ol-cpx	30	3	
S4@20	N0123201	pl-?ol	1	3	
S5@11	N0122207	ol-pl	5	3	
S6@11	N0118205	pl-ol	3	3	
S8@11	N0161198	pl-ol	10	3	
S9@12	N0148193	pl-ol-cpx	10	3	
S10@20	N0109222	pl-ol	0	3	
S12@12	N0138227	pl-cpx-ol	35	3	
S13@10	N0139242	pl-ol-cpx-opx	18	3	
S15@12	N0184246	pl-ol-cpx-mt	20	3	
S16@11	N0169255	pl-ol	2	3	
S17@20	N0183279	pl	0	3	
S18@11	N0206260	ol-pl	7	3	M121
S19@11	N0241281	pl-ol	8	3	M13
S20@18	N0241281	pl-ol-mt	5	4	M142
S21@12	N0208281	pl-ol-cpx	15	3	M128
S22@20	N0206289	ol	0	3	M129
S23@11	N0210288	pl-ol	7	3	M135

S24@11	N0207285	pl-ol	3	3	M136
S25@12	N0207300	pl-ol-cpx	10	3	M86
S26@11	N0220298	ol-pl	3	3	M88
S27@11	N0212303	ol-pl	2	3	M82
S28@12	N0215301	pl-ol-cpx	28	3	M83
S29@12	N0208300	pl-ol-cpx	12	3	M85
S30@11	N0209316	pl-ol	8	3	M1
S31@11	N0221317	pl-ol	10	3	M10
S32@11	N0225315	pl-ol	11	3	M53
S33@11	N0232312	pl-ol	15	3	M55
S34@11	N0234311	pl-ol	2	3	M58
S35@11	N0238306	pl-ol-cpx	16	3	M59
S36@11	N0244321	pl-ol-cpx	17	3	M61
S37@6	N0261314	pl-?opx-?hb-mt-ap	3	5	M99
S38@16	N0313309	pl-opx-cpx-?hb	15	4	M107
S39@11	N0315310	ol-pl	5	3	M110
S40@22	N0282318	pl		4	M112
S41@22	N0282318	pl-cpx-mt		4	M114, segregatio
S42@12	N0242355	pl-ol-cpx	8	3	M104
S43@12	N0247354	pl-ol-cpx	20	3	M31
S44@5	N0265352	pl-opx	5	2	M96
S45@1	N0282359	ol	4	3	M102
S46@1	N0316384	ol	4	3	M116
S47@11	N0306401	pl-ol	8	3	M32
S48@11	N0305400	pl-ol	10	3	M41
S49@1	N0315411	ol	8	3	M24
S50@11	N0319408	pl-ol	5	3	M26
S51@11	N0323411	pl-ol	8	3	M28
S52@10	N0310417	pl-ol-cpx-opx	4	2	M18
<u>OCHIL HILLS, WEST OF GLENFARG</u>					
OC1@11	NS815972	pl-ol-?mt	15	5	cc vesicles
OC2@10	NS814981	pl-ol-opx-cpx	40	4	
OC3@10	NS814979	pl-ol-opx-cpx	35	4	
OC4@13	NS815986	pl-opx-cpx-mt	30	4	
OC5@10	NN857045	pl-ol-opx-cpx	40	5	
OC7@13	NN835019	pl-cpx-opx-mt-?ol-?hb	35	3	
OC8@13	NN843019	pl-opx-cpx-mt-ap-?ol	30	3	
OC9@10	NN851018	pl-opx-cpx-ol-?mt	40	4	
OC10@18	NN855016	pl-mt	10	4	
OC11@5	NN855015	pl-opx-mt-?cpx	8	5	
OC12@10	NN888072	pl-ol-cpx-?opx-mt-qz	20	4	
OC13@12	NN883061	pl-cpx-ol-mt	45	3	
OC15@10	NN994037	opx-cpx-pl-ol	14	2	opx mantled by o
OC17@12	NN915047	pl-ol-cpx-mt	20	3	
OC18@12	NN915046	pl-ol-cpx	35	3	
OC19@13	NN913042	pl-cpx-?opx-mt-ap	18	4	
OC20@16	NN946057	pl-hb-cpx-opx-mt	35	3	
OC21@20	NN970054	ol-pl	0	3	?minor intrusion
OC22@10	NN986006	cpx-pl-opx-ol-mt-ap	60	3	sector-twinne c
OC23@16	NN997024	pl-opx-cpx-hb-mt	35	3	ol in aggregate
OC24@18	NN913039	?ol-pl-?mt	3	5	much cc
OC25@16	NN937072	pl-opx-cpx-hb-mt	35	3	
OC26@16	NN937070	pl-opx-cpx-hb-mt	35	3	
OC27@18	NN935066	pl-?hb-mt-cpx-ap	4	3	
OC28@10	NS802979	pl-cpx-opx-ol-mt	28	3	
OC30@22	NS827971	pl-?hb-?opx	10	5	
OC31@10	NS826973	pl-opx-cpx-ol-mt	30	4	
OC32@5	NS828973	pl-?opx	8	5	clast

0C33a5	NS829971	pl-opx-mt	30	5	clast
0C35a18	NS848972	?ol-?hb	2	4	
0C36a13	NS848975	pl-cpx-opx-mt-ap	20	5	
0C38a20	NS847979	pl-ol	2	4	
0C39a20	NS879991	pl	0	5	
0C41a6	NN870002	pl-opx-ap-mt-?hb	12	4	
0C42a10	NN881014	pl-ol-cpx-opx	20	3	
0C43a13	NS897995	pl-opx-cpx-mt-ap	30	4	
0C44a11	NS900987	pl-ol	10	4	
0C47a22	NS912977	pl-hb-bi-cpx-mt-ap		4	diorite
0C48a22	NS913977	pl-?cpx		5	aplite vein
0C50a10	NS998998	pl-cpx-opx-ol-mt	60	3	
0C51a13	N0003030	pl-opx-cpx-mt	40	4	clast
0C52a10	NN974019	pl-ol-cpx-opx-mt	65	4	clast
0C53a16	NN965013	pl-hb-cpx-opx-mt-ap	30	3	
0C54a14	N0024022	pl-opx-cpx-bi-mt-ap	25	3	
0C55a22	N0054046	pl-hb-mt	15	5	dyke
0C56a16	NN944069	pl-cpx-opx-hb-mt-ap	35	3	
0C57a18	NN947076	pl-opx-cpx-ap-mt	5	4	
0C58a19	NN977127	pl-bi-qz	10	5	
0C59a19	NN975128	pl-bi-qz-ap	15	4	
0C61a16	N0021104	pl-cpx-opx-hb-mt	30	3	
0C63a18	N0092065	pl-mt-ap	3	5	
0C64a20	N0033140	pl	3	5	
0C65a16	N0042128	pl-hb-opx-cpx-ol-mt-ap	25	3	
0C67a16	N0042128	pl-hb-cpx-opx-mt-ap	25	2	
0C69a5	N0107095	pl-opx-mt	15	5	
0C71a22	N0113083	pl	10	4	diorite
0C72a22	N0124092	pl-ol-cpx-bi-mt-ap		1	gabbro
0C73a11	N0132097	pl-ol	10	4	
0C74a12	N0132097	pl-ol-cpx	40	3	
0C75a12	N0055166	pl-ol-cpx	5	3	
0C76a1	N0064161	ol	8	3	
0C77a10	N0088126	pl-cpx-ol-opx-mt	20	3	
0C78a12	N0149137	pl-cpx-ol	10	3	
0C79a12	N0091180	ol-pl-cpx	5	3	
<u>NORTH FIFE HILLS</u>					
0C80a20	N0163143	pl-mt	0	3	
0C81a12	N0155131	pl-cpx-ol	30	4	
0C82a12	N0165118	pl-ol-cpx	15	3	
0C83a10	N0177112	pl-ol-cpx-opx	20	2	
0C84a10	N0195113	pl-cpx-ol-opx	10	2	
0C85a10	N0189134	pl-ol-opx-cpx	25	3	
0C86a38	N0249120	pl-ol-cpx-hb	3	3	
0C87a38	N0249122	pl-hb-ol-ap-mt	4	5	gabbroic xenolith
0C88a38	N0239127	pl-hb-ol-ap-mt	4	5	
0C88Aa34	N0239127	pl-hb-bi-ap-mt in glass			xenolith
0C88Da34	N0249122	pl-hb-ap-mt in glass			xenolith
0C88Ea34	N0249122	as 0C88D but finer-grained			
0C89a13	N0231133	pl-opx-cpx-mt-?hb	30	5	
0C90a1	N0228163	ol	8	3	
0C91a12	N0223166	pl-ol-cpx	30	3	
0C92a12	N0232168	ol-cpx-pl	4	3	
0C93a13	N0231179	pl-opx-cpx-mt	25	2	
0C94a13	N0233180	pl-opx-cpx-mt	30	3	
0C95a20	N0244176	pl-mt	0	3	
0C96a1	N0268171	ol	5	3	
0C97a20	N0282189	pl-mt	0	2	

OC98@13	N0337237	pl-opx-cpx-mt	30	2	
OC99@20	N0334219	mt	0	2	
OC100@11	N0331214	pl-ol	10	2	
OC101@1	N0356238	ol-pl	5	3	
OC102@11	N0358252	pl-ol	25	3	
OC103@13	N0363254	pl-opx-cpx	10	2	
OC104@11	N0365254	pl-ol	5	3	
OC105@1	N0357249	ol	2	3	
OC106@13	N0161333	pl-opx-cpx-mt	15	3	
OC107@22	N0375189	pl-opx		5	?intrusion
OC108@13	N0388173	pl-opx-cpx	2	2	
OC109@13	N0404192	pl-opx-cpx-mt	20	3	
OC110@12	N0422214	pl-cpx-ol	10	3	
OC111@22	N0419213	pl-bi-mt	4	5	Lucklaw Hill
OC112@12	N0430225	pl-ol-cpx-?opx-?hb	20	3	
OC113@11	N0446243	pl-ol	5	3	cc amygdale
OC115@11	N0393262	ol-pl	10	3	
OC116@4	N0389258	pl	20	3	
OC117@19	N0385258	?pl-bi	5	5	
OC118@11	N0407270	ol-pl	5	3	
OC119@11	N0402268	ol-pl	7	3	
OC120@12	N0400265	ol-pl-cpx	5	3	
OC121@12	N0418276	ol-pl-cpx	10	3	
OC122@9	N0426280	opx-cpx-ol-?pl	4	3	
OC123@9	N0426282	opx-cpx-ol-?pl	4	2	
OC124@9	N0426283	opx-cpx-ol-?pl	5	2	
OC126@19	N0397264	pl-bi-mt	4	3	tuffaceous
OC127@22	N0397264	pl-cpx-opx	25	5	?intrusion
OC128@19	N0397264	pl-bi-mt-ap	5	3	
OC129@1	N0424287	ol-mt	5	3	
OC130@18	N0447293	pl-?cpx	4	4	
OC131@10	N0451293	pl-opx-ol-cpx	25	3	
OC132@1	N0454293	ol-mt	8	3	
OC133@1	N0441276	ol-pl	10	2	
OC134@9	N0424265	opx-cpx-ol-?pl	6	3	
OC135@9	N0477333	cpx-pl-opx-ol	1	3	microphenocrysts
OC136@9	N0485338	opx-cpx-ol-?pl	5	3	
OC137@22	N0475355	pl-ol-cpx	25	3	?lava
OC138@9	N0504355	ol-opx-cpx-?pl	8	3	
OC139@22	N0489370	pl-ol-cpx	20	3	?lava
OC140@12	N0454311	pl-ol-cpx	10	3	
OC141@22	N0429329	rare ol,pl in doleritic	pl-cpx-opx	PAS=3	
OC143@22	N0392315	as OC141		3	
OC145@13	N0443310	pl-opx-cpx-mt	35	2	
OC146@19	N0444310	pl-bi-hb-mt	15	4	clast
OC147@18	N0446310	pl	2	4	
OC148@11	N0513375	ol-pl	5	3	
OC149@11	N0556386	pl-ol	15	3	
OC150@22	N0522417	pl-ol		3	doleritic
OC152@12	N0204165	ol-pl-mt-cpx	20	1	S60736
OC153@10	N0265174	pl-opx-cpx-ol	20	2	S54857
<u>PENTLAND HILLS</u>					
PE1@1	NT204677	ol	10	4	Warklaw Hill Gp
PE3@11	NT247692	pl-ol	1	4	much cc
PE3A@11	NT247692	pl-ol-mt	2	3	?Allermuir Gp
PE4@19	NT235667	pl-bi-mt	14	5	Capelaw Acid Gp
PE5@20	NT233668	pl	0	3	Capelaw Basic Gp
PE6@1	NT233663	ol	7	3	Allermuir Gp

PE8@11	NT223667	pl-ol	27	3	Capelaw Basic Gp
PE9@11	NT226658	pl-ol-cc	18	4	Allermuir Gp
PE10@20	NT226660	ol-pl	0	5	Allermuir Gp
PE11@12	NT207614	pl-ol-cpx	35	5	Carnethy Gp
PE12@29	NT186587	pl-?ksp-bf	4	5	Woodhouselee Gp
PE13@11	NT204675	pl-ol	21	4	Warklaw Hill Gp
PE14@5	NT161558	opx-pl	13	4	much cc
PE15@5	NT162558	pl-opx	16	2	
PE16@5	NT152550	opx-pl	17	2	
PE17@12	NT151550	pl-cpx-ol	16	4	qz vein
PE18@13	NT150549	pl-mt-cpx-ap-?opx	10	4	
PE19@29	NT119506	pl-?ksp-bf-qz	10	4	
PE20@29	NT083470	pl-?ksp-?hb-?bf	4	5	
PE21@6	NT041359	pl-hb-opx-mt	20	5	
PE22@20	NT034363	pl-?ol	1	4	
PE23@20	NT025363	pl-?ol	1	4	
PE24@7	NT003344	ol-cpx-?pl	5	4	
PE25@22	NS978346	bf-pl	0	5	Tinto Felsite
PE26@13	NT088440	pl-opx-cpx	21	2	
PE27@22	NS953344	pl-bf-qz	2	3	Tinto Felsite
PE28@22	NS954356	gt-pl-bf	4	5	Tinto Felsite
PE29@22	NS956339	pl	0	5	Pap Craig
PE31@22	NT184618	micropegmatite-bf-qz		4	Black Hill Felsi
PE32@28	NT187616	ol-?opx-pl	12	4	Allermuir Gp
PE33@20	NT190620	pl-?ol	2	4	Allermuir Gp
PE34@19	NT201636			5	Bells Hill Gp
PE36@19	NT201636			5	Bells Hill Gp
PE37@45	NT216642	ol-pl-cpx-?hb	5	3	Allermuir Gp
PE38@29	NT136454	bf-?pl	2	5	
PE39@29	NS989385	pl	2	5	
PE40@49	NS971373	ol-?hb-?opx-pl-bf	8	5	much cc
PE41@10	NS897332	pl-opx-cpx-ol	20	2	
PE42@6	NS895332	pl-hb-?opx-mt-ap	30	4	
PE44@11	NS865311	pl-ol	15	5	
PE46@20	NS854234	opx-?cpx-?ol	?	5	
PE48@1	NS710196	ol	5	4	
PE51@19	NS759249	pl-hb-bf-mt-ap	35	4	clast
<u>AYRSHIRE</u> (Carrick Hills unless otherwise stated)					
AY1@6	NS513343	pl-hb-opx-mt-ap	15	4	Distinkhorn
AY2@13	NS524348	pl-opx-?cpx-mt	15	5	Distinkhorn
AY3@11	NS567358	pl-ol	15	5	Distinkhorn
AY4@5	NS532352	pl-opx-?ol	15	2	Distinkhorn
AY5@10	NS502351	pl-ol-opx-?cpx	8	5	Distinkhorn
AY6@11	NS329172	pl-ol	20	4	
AY7@20	NS297179	pl-cpx-mt	1	3	
AY8@11	NS273181	pl-ol	10	3	
AY9@6	NS263174	pl-hb-?opx-?cpx	8	5	clast, much cc
AY10@28	NS268178	pl-opx-ol-mt	25	3	
AY11@5	NS269179	pl-opx-mt	25	4	
AY12@13	NS258170	pl-opx-cpx-mt	15	3	
AY13@5	NS258168	pl-opx-mt	20	2	
AY14@13	NS255166	opx-pl-cpx-?ol	15	3	
AY15@5	NS255164	pl-opx-?ol	10	5	
AY16@10	NS268178	pl-ol-cpx-opx	25	3	
AY17@12	NS248156	pl-ol-cpx	20	3	
AY18@5	NS252159	pl-opx	15	5	
AY19@13	NS254160	pl-cpx-opx-?ol	20	2	
AY19A@10	NS250160?	pl-ol-opx-cpx	35	3	

AY20@10	NS244139	pl-ol-cpx-opx	20	3	
AY21@22	NS238102	pl-?cpx	5	5	dyke
AY22@13	NS227100	pl-opx-cpx	15	3	
AY23@5	NS228101	pl-opx-?ol	20	4	
AY24@10	NS231103	pl-ol-opx-cpx	40	3	
AY25@10	NS205078	pl-ol-cpx-opx	30	3	
AY26@11	NS203077	ol-pl	5	5	
AY27@10	NS202076	pl-ol-cpx-opx	25	3	
AY28@5	NS278119	pl-opx	10	5	
AY30@1	NS456055	ol	5	5	Dalmellington
AY31@11	NS388034	ol-pl	5	5	Straiton
AY32@10	NS389033	pl-ol-cpx-opx	15	3	Straiton
AY33@22	NS355107	pl-opx-?bf-?cpx	70	5	?sill
AY34@22	NS349126	pl-?cpx-?hb-mt-ap	5	5	?sill
AY35@10	NS389019	pl-opx-cpx-ol	15	2	Straiton
AY37@10	NS393017	pl-opx-ol-cpx	40	5	Straiton
AY38@12	NS390016	pl-cpx-ol	45	3	Straiton
AY40@6	NX397994	pl-hb-opx-mt-ap	20	5	Straiton
AY41@1	NX398986	ol	2	4	Straiton
<u>CHEVIOT HILLS</u>					
C1@31	NT829277	pl-opx-?cpx-?ilm-ap	25	5	
C2@33	NT987269	pl-opx-?cpx-?ilm-ap	19	5	
C5@31	NT900353	pl-opx-cpx-?ilm-ap	34	5	
C7@30	NT884344	pl-opx-cpx-ilm-ap	43	2	
C8@30	NT868304	pl-opx-cpx-?ilm-ap	36	4	
C9@33	NT870303	pl-opx-cpx-?ilm-ap	44	2	
C10@31	NT880305	pl-opx-cpx-?ilm-ap	28	5	
C11@31	NT883307	pl-opx-cpx-?ilm-ap	40	3	
C12@30	NT884312	pl-opx-cpx-?ilm-ap	28	2	
C13@30	NT885313	pl-opx-cpx-?ilm-ap	30	3	
C15@33	NT860284	pl-opx-cpx-?ilm-ap	41	2	
C16@14	NT854266	pl-opx-cpx-?ilm-bf-ap	29	3	
C17@31	NT854263	pl-opx-cpx-?ilm-ap	29	4	
C18@32	NT853262	pl-opx-cpx-?ilm-ap	38	2	
C19@30	NT857261	pl-opx-cpx-?ilm-ap	38	3	
C21@31	NT853281	pl-opx-cpx-?ilm-ap	30	4	
C22@33	NU025126	pl-opx-cpx-?ilm-ap	25	5	
C23@22	NT958085	pl-bf-?ilm	15	5	Biddlestone Felsite
C27@30	NT890073	pl-opx-cpx-?ilm-ap	35	5	
C28@22	NT879078	qz-pl-bf	25	5	dyke
C29@32	NT876080	pl-opx-cpx-?ilm-ap	35	5	qz amygdales
C30@33	NT864112	pl-opx-cpx-?ilm-ap	40	4	
C31@31	NT846114	pl-opx-cpx-?ilm-ap	45	5	
C33@33	NT833110	pl-opx-cpx-ilm-ap	20	2	
C34@32	NT822106	pl-opx-cpx-?ilm-ap	20	5	
C35@52	NT819103	pl-ksp-cpx-bf-ilm-ap	16	5	
C36@31	NT824108	pl-opx-cpx-?ilm-ap	30	4	
C37@33	NT856113	pl-opx-cpx-?ilm-ap	33	5	
C38@32	NT996166	pl-opx-cpx-?ilm-ap	28	3	
C40@22	NT993164	pl-bf-ksp-qz-ap	35	5	dyke
C41@19	NT993160	?mafic mineral	1	5	clast
C43@32	NT914235	pl-opx-?cpx-?ilm-ap	28	4	
C44@31	NT877235	pl-opx-cpx-?ilm-ap	16	3	
C45@30	NT861235	ol-opx-cpx-?ilm-ap	30	2	
C46@33	NT869225	pl-opx-cpx-?ilm-ap	28	3	
C47@22	NT874234	pl-opx-?cpx-bf-?ilm-ap	50	5	dyke
C48@22	NT943267	pl-opx-cpx-bf-ilm-ap	29	3	?dyke

C49@4	NT942264	pl-?qz-?ilm-ap	30	5	
C50@14	NT898226	pl-opx-cpx-?ilm-ap-?bf	20	2	
C51@14	NT898223	pl-opx-cpx-ilm-ap-?bf	22	2	
C52@22	NT898223	pl-opx-bf-cpx-ilm-ap	30	3	?dyke
C54@33	NT826283	pl-opx-cpx-ilm-ap	27	2	
C55@52	NT853185	pl-ksp-cpx-bf-?ilm-?opx-?hb-ap	25	5	
C57@52	NT919101	pl-bf-?ilm-ap-?cpx	16	5	
C58@22	NT927116	pl-cpx-bf-?ilm-opx-ap	30	3	?dyke
C59@29	NT929113	pl-?bf	2	5	
C60@33	NT918112	pl-cpx-opx-?ilm-ap	25	5	
C61@32	NT908109	pl-cpx-?opx-?ilm-ap	20	5	
C62@22	NT959171	pl-opx-cpx-bf	32	2	Cheviot Granite
C64@25	NT962160	pl-cpx	?		hornfels
<u>ST. ABB'S HEAD AND EYEMOUTH</u>					
SA1@48	NU918683	ol-?opx	5	3	
SA2@48	NU917688	ol-opx	3	4	
SA5@48	NU912693	ol-?opx	5	4	
SA6@1	NU914693	ol-?opx	5	4	
SA7@48	NU918686	ol-opx	4	4	
SA8@1	NU918685	ol	4	4	cc amygdale
SA9@48	NU916686	ol-opx	5	4	
SA10@1	NU913687	ol	8	5	
SA11@1	NU912689	ol	8	4	
SA12@44	NU943561	pl-hb-opx-bf		5	S55969
SA13@6	NU951571	pl-hb-opx		5	S54186
SA14@1	NU950570	ol-?opx		4	S54163
SA15@6	NU941651	pl-hb-opx		5	S51899
SA16@6	NU941649	pl-?opx-?hb		5	S51902
SA17@51	NU921631	ol-pl-?cpx-?hb-bf-ap		4	S51875
SA18@13	NU942650	pl-opx-cpx		5	S50572
SA19@48	NU885649	ol-opx		4	S49457
SA20@1	NU954566	ol		3	S54167
SA21@6	NU898641	pl-hb-opx		5	S50541
<u>IRELAND</u>					
NI1@22	D2527	ol-opx-bf-?ksp-qz	10	5	Cushendall Porphyry
NI2@44	D2528	pl-opx-hb-?cpx-bf-ap	10	4	clast, Cushendal
NI3@44	D2528	pl-hb-opx-bf	18	4	clast, Cushendal
NI5@16	H6968	pl-opx-cpx-?hb	5	4	Fintona
NI6@16	H6968	pl-opx-cpx-?hb	8	3	Fintona
NI8@16	H6864	pl-opx-cpx-?hb	8	4	Fintona
NI10@5	H3956	pl-opx-mt-ap	5	5	Fintona
NI11@13	M5696	pl-opx-cpx-mt-?hb-qz	15	2	Curlew Mts
NI12@19	M5895	pl-qz-bf-opx	30	4	Curlew Mts
NI13@20	M5996	cpx-hb-?pl	1	3	Curlew Mts
<u>ARRAN</u>					
AR1@13	NR987372	pl-opx-cpx-mt-ap	25	4	clast
AR2@1	NR893367	ol	10	5	much cc
AR3@19	NR895365	pl-hb-bf-mt-ap	30	5	clast
AR5@19	NR895365	pl-hb-opx-bf-mt	35	5	clast
AR6@44	NR895365	pl-hb-opx-bf-mt	10	5	clast
AR7@19	NR895365	pl-hb-bf-ap	15	5	clast
AR8@13	NR895365	pl-opx-cpx-mt-ap	30	5	clast
AR9@13	NR895365	pl-opx-cpx-mt-ap	25	5	clast
AR10@13	NR381596	pl-opx-cpx-mt-ap		5	clast, AR77-27
AR11@22	NR381596	pl-hb-granophyre		3	clast, XAR7

HUNTLY

NG1@11	NJ521324	ol-pl	2	3
NG2@12	NJ518337	pl-cpx-ol	10	4
NG3@22	NJ406645	pl-hb-opx	20	5

SHETLAND

SH1-SH13, SH37-SH41 from Esha Ness, SH14-SH19, SH22-SH25 from Sandness Formation, SH20, 21 from Melby Formation, SH27-SH36 from Papa Stour.

SH1@52	HU228776	pl-?ksp-?ol/cpx-ap	15	5	
SH2@52	HU214769	pl-?ksp-?ol/cpx-?opx-ap	15	5	
SH3@52	HU212773	pl-?ksp-?opx-?ol-ap	20	5	
SH4@11	HU223805	pl-ol	2	3	
SH5@21	HU217807	ksp-pl-ap-?hb		5	
SH6@21	HU214806	ksp-pl-ap-?hb-cpx		4	
SH7@13	HU216805	pl-opx-cpx-mt-ap	10	3	
SH8@13	HU205783	pl-opx-cpx-mt-ap	35	4	
SH9@13	HU204782	pl-opx-cpx-mt-ap	35	3	
SH10@5	HU210795	pl-?opx	6	4	
SH11@19	HU239800	?pl	1	5	
SH12@52	HU242829	pl-?ksp-?ol/cpx/hb-ap-mt	15	5	
SH13@52	HU236810	pl-?ksp-?ol/cpx/opx-ap-mt	15	5	
SH14@19	HU325590	pl-ksp-?cpx-mt-ap	45	4	clast
SH15@11	HU327589	pl-?ol-?hb			greenschist
SH16@20	HU308579	chlor vesicles		3	
SH17@21	HU288565	?pl/ksp-qz		5	
SH18@20	HU290564	none	0	5	
SH19@20	HU274556	pl-ol	1	5	
SH20@19	HU185580	pl-mt-?bf-?hb	3	5	
SH22@20	HU226540	pl-?ol	1	4	
SH23@12	HU229539	pl-cpx-?ol	30	3	
SH24@11	HU230543	pl-?ol	3	4	
SH25@11	HU235543	pl-?ol	15	3	greenschist
SH27@11	HU185610	ol-pl	2	4	
SH28@19	HU186613	ksp-pl-?hb-mt	5	4	
SH29@4	HU167617	pl-?ol-?cpx	5	2	
SH30@10	HU167620	pl-opx-cpx-?ol	5	3	
SH31@11	HU167620	pl-ol	10	4	
SH32@11	HU149609	ol-pl	6	3	
SH33@19	HU162609	ksp-hb-mt	20	4	spherulitic
SH34@19	HU166592	ksp-hb-cpx	15	4	autobrecciated
SH35@19	HU180598	pl-ksp-opx-?hb-mt	20	4	
SH36@11	HU191586	ol-pl	4	3	S30602
SH37@11	HU243798?	ol-pl	5	4	S43372
SH38@1	HU241787	ol, much cc	5	4	S43409
SH39@12	HU207787?	ol-cpx-pl	2	3	S43630
SH40@52	HU251851	pl-?ksp-opx-cpx-mt-ap	15	4	S43347
SH41@52	HU242845	pl-?ksp-opx-cpx-mt-ap	15	4	S43344
<u>ORKNEY</u>					
OR1-OR4	from Hoy; OR5-OR8 from Deerness and Shapinsay				
OR1@12	HY176008	pl-ol-?cpx	?20	5	S60792
OR2@12	ND195989	pl-ol-cpx-?hb	?25	3	S60793
OR3@12	HY220036	ol-cpx-pl	?25	1	S60794
OR4@12	HY214040	ol-pl-cpx	?15	1	S60795
OR5@22	HY563032	ol	5	3	DL92
OR6@22	HY591038	pegmatitic		4	DL27

OR7@11 HY527149 ol-pl
OR8@11 HY527149 ol-pl

10 4 DL76, zeolitised
15 5 DL78, zeolitised

A3 : REDUCTION OF SAMPLES TO POWDER

Since most of the rocks are fine-grained and fairly homogeneous, only small sample weights, about 200g, are thought to be required to obtain a representative analysis. This hypothesis has been tested by the collection of more than one sample from a single flow on a number of occasions: analyses of these compare closely (e.g. OC93/94, OC87/88). Several samples crushed by Gandy (1973a) have been re-crushed, and both powders analysed. The results (Table A.2) compare well despite the phenocryst-rich nature of the rocks.

Samples selected for analysis were as far as possible trimmed of their weathered surfaces and reduced to about 1.5 in (4 cm) diameter using a Cutrock hydraulic splitter. Little powder was produced during splitting, and any surfaces contaminated by steel from the splitter were discarded. The rock fragments were then reduced to about 0.5 in (1 cm) diameter chips and powder using a Sturtevant open-door roll jaw-crusher, the powder being retained with the chips. Where possible, chips showing alteration features (e.g. amygdales) were discarded. Use of the jaw-crusher may result in minor contamination by steel, although none has been observed on inspection of the chips. The chips and powder were then ground for about 2 min using a tungsten carbide Tema swing mill. The resulting powder is no longer gritty to the touch when wet, and will pass 100 mesh. Grinding probably results in partial oxidation of iron (Fitton and Gill, 1970), and in contamination by W and Co, not affecting the present study. Samples S18, S21-27, S29, S31-42 and S44-46 were ground by Gandy (1973a) using a steel Tema mill; this contaminates the sample with Ni and Cr (e.g. Table A.2), and therefore samples of which sufficient was available were reground using a tungsten carbide mill, and for others Ni and Cr values are not quoted.

All equipment was thoroughly cleansed with acetone between samples, and the jaw-crusher was pre-contaminated at the beginning of each crushing session.

TABLE A2: Comparison between powders of S21 (M128) and S35 (M59) crushed by Gandy (1972) using a steel Tema mill, and by the author using a tungsten carbide Tema mill.

	steel Tema		WC Tema			steel Tema		WC Tema	
	S21	S35	S21	S35		S21	S35	S21	S35
SiO ₂	53.74	55.56	53.29	56.01	Ni	516*	488*	95	120
Al ₂ O ₃	16.80	16.60	16.87	16.40	Zn	64 ⁺	83 ⁺	73	73
Fe ₂ O ₃	8.54	8.01	8.43	8.10	Th	9 ⁺	8	4	4
MgO	5.70 ⁺	4.97 ⁺	5.55	4.69	Rb	34	45	32	45
CaO	7.95	7.13 ⁺	7.95	6.90	Sr	801 ⁺	717 ⁺	813	695
Na ₂ O	3.62	3.64	3.66	3.73	Y	29	25	28	26
K ₂ O	1.54	1.90 ⁺	1.52	1.97	Zr	213 ⁺	207	206	207
TiO ₂	1.49 ⁺	1.39	1.45	1.40	Nb	11	13	10	13
MnO	0.12	0.10	0.13	0.09	Cr	219*	234*	127	162
P ₂ O ₅	0.35 ⁺	0.33	0.33	0.34	Ce	66	68	66	66
Sc	23	18	22	17	Sm	5	4	7	8
V	176	139	167	136	Nd	34	29	35	31
Cu	52 ⁺	24	49	23	* = contamination by steel from Tema + = outside 95% confidence limits, based on reproducibility, Tables B1, B3.				
Ba	523 ⁺	631	503	639					
La	29	30 ⁺	28	35					

APPENDIX B : X-RAY FLUORESCENCE ANALYTICAL TECHNIQUES

B1 : INTRODUCTION

Precise and rapid analytical procedures were made necessary by the large number of samples selected for analysis. The acquisition by the Grant Institute of a Philips PW1450/20 sequential automatic X-ray fluorescence spectrometer allowed the choice of XRF methods for all elements, in principle capable of rapid, precise and accurate measurements. The analytical techniques devised and the computer software written to handle the data are described in the following sections.

B2 : SAMPLE PREPARATION

The quality of an XRF analysis is dependant on a number of sample features, the relative importance of which is governed by the wavelength of X-rays used for analysis. Long wavelength radiation (K lines for elements of atomic number less than 20) is only weakly penetrative, and is strongly affected by minor mineralogical inhomogeneities close to the sample surface, and also by the surface finish. Accordingly, for the analysis of these elements, use of a pellet pressed directly from powder is not advisable and some form of homogenization procedure is required. Methods described in the literature involve fusion with a borate flux, and the grinding and pelleting of the glass so produced (e.g. Rose *et al.*, 1963), or the direct casting of the melt to produce a glass disc (e.g. Norrish and Hutton, 1969; Harvey *et al.*, 1973). The former method is unsuited to accurate analysis because of uncertainties in the amount of moisture adsorbed on the powdered glass. A direct casting fusion method based on that of Norrish and Hutton (1969) has therefore been used for preparation of samples for major element analysis. It should be noted that the 'major elements' are only definable for a particular rock: in the rocks analysed in this study, only Si, Al, Fe, Mg, Ca, Na, K, Ti, Mn and P had concentrations commonly above 1500 ppm, and hence these elements were treated as major elements. Following convention, these elements were determined as their oxides; the Fe²/Fe³ ratio was not determined because of the high degree of post-eruptive alteration, and a value of Fe₂O₃/(FeO+Fe₂O₃) wt.% of 0.2 was used in the normative calculations.

(1) Major Elements

The major elements provide nearly the total mass absorption of a sample, and therefore reference by calibration to samples of known different composition is unjustified. Possible methods of overcoming this difficulty include the use of standards very close in composition to the unknowns, or the use of an iterative correction procedure. The latter method relies to a great extent on the initial range of standards through which a first fit regression is calculated: if this is small, matrix

differences between the standards can lead to a meaningless regression line, and there are further difficulties in the selection of suitable mass absorption coefficients. The former method is time-consuming unless a method is chosen which involves dilution with an element with high absorption in the wavelength range of the major element K lines. This may conveniently be added as part of the flux in the fusion procedure of Norrish and Hutton (1969), and a mixture of lithium tetraborate, lithium oxide and lanthanum oxide is supplied commercially by Johnson Matthey Chemicals Ltd. as Spectroflux 105. Dilution by this in the constant flux:sample ratio of 5.3333:1 provides nearly constant composition samples, although they clearly differ in their pre-dilution chemistry. The extent to which the assumption of constant matrix is valid may be judged from the linearity of calibration graphs over large ranges in sample composition (Fig. B1).

Role of volatiles

On fusion, both sample and flux lose water and CO₂, and much of the iron in the sample is oxidised. This creates difficulty in the production of a constant flux:sample ratio, and two fusions are required, with intervening flux addition, to allow for flux volatiles. Two methods of treating sample volatiles are currently in use at the Grant Institute, one of which involves ignition of the sample at 1100°C before initial flux addition, thus requiring an extra preparation stage but leading to a total oxides sum close to 100%. In the second, extra flux is added to make up for volatile loss from the sample, giving total oxides of about 100%-H₂O-CO₂. All samples analysed in this study have been ignited prior to flux addition, and it is recommended that all samples with potentially high Loss on Ignition (LOI > 4%) should be ignited, because of the uncertain contribution to total mass absorption involved in adding extra flux.

Procedure

Sample powders were dried overnight in small glass jars in an oven at 110°C to remove adsorbed water (H₂O-), and about 1.05g was weighed into clean Pt-5%Au crucibles. Samples were ignited at 1100°C in a Gallenkamp furnace for at least 15 min, allowed to cool and then reweighed. Wt.% loss on ignition (LOI) was calculated. Ignition causes release of CO₂, H₂O, some Cl and possibly other volatiles, and gain of oxygen to allow almost complete oxidation of iron. This oxygen gain is relatively small, although in rare cases negative LOI may be reported. A consequence of this oxidation is that total iron may be calculated as Fe₂O₃.

Flux was then added to the ignited sample in the ratio 5.3333:1, a small amount of extra flux (c. 0.05g) being added to compensate for flux volatiles. The mixture was fused at 1100°C until the sample had completely dissolved (usually about 20 min unless the sample melted during ignition) and then allowed to cool. Platinum foil lids were

used to cover the crucibles in the furnace, to prevent contamination by furnace lining, and also whilst cooling, to prevent ejection of fracturing glass. Cooling was rapidly effected by placing the crucibles on a large block of stainless steel. The crucibles were reweighed and flux added to make up for flux volatile loss. This amount should be small (c. 0.01g) if sufficient was added after ignition, and hence its volatile content is trivial. The crucibles were transferred to Meker burners at about 1000°C, where the extra flux was dissolved. The crucibles were gently shaken to ensure melt homogeneity, and the melt poured onto graphite plattens inside stainless steel rings on a 240°C hotplate, followed immediately by quenching and moulding using an aluminium plunger, also at 240°C. The quenched glass discs were covered and allowed to anneal on the hotplate. Any remaining melt was shaken from the crucible and stored with the glass disc; the crucibles were plunged into water to cause cracking of any remaining glass adhering, and finally cleansed in warm 50% HCl for at least 20 min. Prior to reuse the crucibles were rinsed with distilled water and dried in an oven. In general, four crucibles were processed simultaneously, resulting in a production rate of about 2 discs per hour. The glass discs are essentially homogeneous and have a reproducible surface finish. Six discs of sample MT45 were produced to test reproducibility (Table B1); for Ca, Na, K, Ti and P this is comparable to the precision (Table B7), although for other elements it is a little worse. Total oxides for the six discs varied considerably within the range 99.2 to 100.1%, and SiO₂ correlates positively with total oxides, suggesting that the reproducibility is inferior because of slight errors in operation of the fusion procedure. This also illustrates the value of sample ignition, in providing an analytical check of constant total oxides (section B9).

Table B1 : Reproducibility of six discs of sample MT45.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO		
Mean	54.529	15.589	8.248	6.743	8.023		
± 2-sigma	0.342	0.114	0.101	0.069	0.025		
	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI	
Mean	3.317	1.356	1.281	0.115	0.347	1.542	
± 2-sigma	0.104	0.011	0.007	0.016	0.004	0.100	

(11) Trace Elements

The high degree of dilution involved in disc preparation leads to difficulty in the analysis of small quantities of elements, and although trace elements with concentrations in excess of 100 ppm may easily be analysed, counting times must be long to provide adequate precision. Accordingly, pressed powder pellets have been used: problems of heterogeneity and surface finish were not encountered as Sc was the lightest element analysed, and mathematical

corrections may be made for matrix absorption (section B8).

A sample weight of 7g was used, calculated by Fitton (pers. comm., 1977) to allow 99% absorption of NbK radiation in a matrix of very low absorption (pure silica). More strongly absorbing matrices have been analysed using as little as 4g, and no significant differences have been observed using the different weights (Table B2).

Table B2 : Analyses of SA1 using 4g and 7g pellets.

	Ni	Zn	Th	Rb	Sr	Y	Zr	Nb	Cr	Ce
4g	187.5	112.3	7.8	55.1	524.1	29.3	280.2	17.2	375.9	79.9
7g	187.9	112.3	5.7	54.8	521.0	28.6	281.2	17.3	379.9	80.7

	Sm	Nd	TiO2W	Sc	V	Cu	Ba	La	TiO2CR
4g	5.4	34.2	1.239	22.0	126.7	16.3	534.2	36.9	1.242
7g	3.8	35.8	1.256	21.6	122.1	17.7	540.9	37.7	1.242

After shaking the bottle of powder, about 7g of sample was transferred to polished tungsten carbide pressing apparatus and a backing of powdered boric acid was added to the hand-pressed pellet. The apparatus was then compressed at about 10 ton/in² for about 1 minute using a Research and Industrial Instruments Company 30-ton hydraulic press. Analysis of powders compressed at 9 and 11 ton/in² and for longer times has shown no significant differences. The procedure can allow the production of about 20 pellets per hour. The apparatus was thoroughly cleansed with acetone between samples. Reproducibility has been tested by making six pellets of MT45; the results (Table B3) are mainly comparable with the analytical precision (Table B7). The two exceptions are TiO2CR, where the inferior reproducibility may be the result of minor Ti discrepancy (section B9), and Th, where there is a large difference in the two mean values for MT45. The spectrometer run for precision took place one month later than the reproducibility run, and it is possible that the calibration had changed. This may also have bearing on the relatively high frequency of negative values quoted for Th (section B12).

Table B3 : Reproducibility of six pellets of MT45.

	Sc	V	Cu	Ba	La	TiO2CR	Ni	Zn	Th
Mean	24.4	167.0	49.9	543.6	31.1	1.309	138.3	67.9	10.6
± 2-sigma	0.4	4.6	1.2	8.5	2.1	0.036	0.8	1.1	2.3

	Rb	Sr	Y	Zr	Nb	Cr	Ce	Sm	Nd	TiO2W
Mean	17.3	601.1	25.8	249.1	12.4	289.8	73.3	8.8	34.1	1.331
± 2-sigma	0.9	4.5	0.8	1.5	0.9	4.0	2.3	4.6	1.7	0.016

B3 : STORAGE OF PREPARED SAMPLES

Labelled glass discs were stored in labelled 2 in (60 mm) square sealed plastic bags with any spare glass from the fusion procedure. They are very durable if correctly prepared, but retention of spare glass allows remelting on Meker burners and the recasting of the glass disc in case of shattering. Prior to analysis the analytical surface was wiped with a clean tissue, but great care was taken to avoid touching this surface, which leads to contamination by Na from perspiration. Glass discs have been stored for longer than six months and re-run without significant change in their analysis.

Pressed powder pellets were stored in boxes; they are fairly durable unless the sample is water-poor or rich in groundmass glass, when splitting of sample from backing may occur. This may be overcome by repelleting, or by the use of six drops of a 2% aqueous solution of polyvinyl alcohol (PVA) as a binding agent. This was found to have no significant effect on an analysis. Prior to analysis boric acid debris etc. was blown from the analytical surface.

B4 : USE OF MONITOR

The PW1450/20 allows pre-selection of a wide range of measurement conditions and procedures by means of the PW1395 programmer, and permits counting for a number of elements (up to 13 have been used) on four samples without operator intervention. An XRF program therefore produces fixed format output of cyclical nature, each cycle pertaining to four samples.

In order to eliminate some effects of long-medium term machine drift (e.g. temperature or generator induced), the first sample position has always been occupied by a monitor sample, chosen for reasons of durability to be a glass disc made by solution of compounds of the elements of interest in a borate flux. The flux should not contain La in the case of a trace element monitor.

Drift corrections were made by ratio, of peak P_s^i minus background B_s^i counts for element i on sample s divided by counts on monitor peak P_m^i over the same time, and the resulting 'count ratio' was used as the primary XRF measurement instead of the more traditional count rate. Thus:

$$R_s^i = (P_s^i - B_s^i) / P_m^i$$

where R_s^i = count ratio for element i in sample s .

Prior to the acquisition of a Philips PW1466/20 60-position automatic sample changer in July 1978, a slightly different procedure was in use, which involved ratio to $P_m^i - B_m^i$. This is not thought to have any advantage, but it results in a slightly different calibration. Major elements for samples GC1-26, L, BN, PE1-37, OC1-27 and a few

S samples, were analysed using this procedure.

Elements were present in high concentrations in the monitors to allow the rapid location of peak angles and to prevent significant worsening of precision through the ratio procedure. XRF printout consists of count ratios to four decimal places, and therefore precision would be worsened if monitor concentrations were more than an order of magnitude greater than sample concentrations. This procedure relies on the assumption that the monitor is unaffected by exposure to X-rays between calibrations. This might be noticed in systematic variation of calibration constants over several calibrations; this has not been observed (Table B4), and repeat analyses of samples within the same calibration over a period of 4 months show no systematic change.

Table B4 : Secular change in major element calibration constants

	Aug. 1978		Jan. 1979		July 1979	
	m	c	m	c	m	c
Si	59.93	4.46	59.73	4.52	59.82	4.61
Al	18.61	0.15	18.48	0.20	18.44	0.19
Fe	20.67	-0.11	20.68	-0.11	20.63	-0.11
Mg	38.04	-0.15	37.66	0.00	36.64	-0.19
Ca	15.30	-0.03	15.28	-0.03	15.21	-0.02
Na	15.53	-0.32	15.97	-0.26	15.43	-0.34
K	8.59	-0.05	8.61	-0.04	8.58	-0.04
Ti	4.98	-0.05	4.98	-0.05	4.97	-0.06
Mn	1.15	0.03	1.69*	-0.07	1.09	0.01
P	2.79	0.00	2.75	0.00	2.89†	-0.00

m=calibration gradient, c=intercept. *=Mn analysed using LiF220.
†=P analysed with different energy window.

The monitor also provides an indicator that the PW1450/20 is operating correctly, for times required for preset counts on the monitor are printed in the teletype output. Providing temperature-stable dispersing crystals are in use, monitor count rates should remain roughly constant, as should P_s^i/P_m^i and B_s^i/P_m^i for a given sample. This is usually true, but as yet unexplained exceptions have been observed on occasions of machine shutdown when using a tungsten anode X-ray tube. The value R_s^i , and hence the concentration, does appear to remain constant, however.

B5 : ANALYTICAL CONDITIONS

(i) Anode material of X-ray tube

Two high-voltage X-ray tubes are available at the Grant Institute, with chromium and tungsten anodes (Cr-tube and W-tube respectively). The latter tube is fitted with a relatively thick Be window, and is thus unsuitable for the excitation of long wavelength fluorescent radiation (NaK_{α} to $P_{K_{\alpha}}$), but provides a more intense continuum at short

wavelengths. There is thus a range of wavelengths for which the tubes provide comparable excitation: the cross-over point in efficiency is in the region of CrK_α . It is, however, better to analyze for the major elements together, so that the total oxides (section B9) may be used as an immediate analytical check. The Cr-tube is therefore used for Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe, despite its lower efficiency for the last two. The CrK_β tube line interferes with MnK_α , but this may be largely removed by use of an aluminium filter across the tube window, or, less satisfactorily, by use of a high resolution crystal (LiF220). The latter method was used for samples SH, OR, MT, SC, AY, NI, PE37-51, OC88D, OC88E and OC152-3, and the MnO values for these samples are slightly less precise than usual.

Trace elements Sc, V, Cu, Ba and La are also analysed using the Cr-tube, which is more efficient for ScK_α , VK_α and probably for LaL_α , than the W-tube, while CuK_α is free from WL_α tube line interference, and BaL_{β_2} is in an optimum excitation position relative to the CrK_α tube line.

The elements Ni, Zn, Th, Rb, Sr, Y, Zr, Nb, Cr, Ce, Sm and Nd were analysed using the W-tube, for all of which it is more efficient.

(ii) Analytical lines and interferences

Analytical lines and machine conditions are listed in Table B6. Lines were in general chosen to provide high intensity with minimal interference. The main interferences are listed in Table B5 together with the corrections made. Interference corrections have been made by use of a series of synthetic standards described in section B7. For Sc, V and Nd, corrections have been made by counting on the interfering line, and the correction may be expressed, for example, as count ratio Sc per count ratio CaK_β . Back-interference by the analytical line does not affect the calculation of concentration, for the same proportional back-interference also affects the standards. For Y, Zr and Sm, corrections have been made by counting on another line of the interfering element i.e. RbK_α , SrK_α and CeL_β , and corrections may be expressed as before. The remaining corrections have been made using a previously determined interfering element concentration, and thus corrections are made after matrix correction, and may be expressed as μ -corrected count ratio per ppm interfering element. Correction coefficients are in most cases calculated by computer regression (section B10); while only the gradient of the correction graph is used, the intercept should be close to the calibration intercept. It should be noted that in the first two methods correction should in theory not be made across a sample major element absorption edge. This is unfortunately unavoidable for ScK_α , but a range of major element compositions has been used in derivation of the correction, and variation in correction with composition is trivial.

TABLE B5: Interferences on chosen analytical lines and backgrounds.

Line	Interference	Approx extent of Interference	Correction made
Mn K_{α}	Cr K_{β}	Unimportant for Cr <1500 ppm	None
P K_{α}	Ca K_{β} (2nd order)	Unimportant for CaO <20%	Narrow energy window
Mg K_{α}	Ca K_{α} (3rd order)	? 0.1% MgO for 20% CaO	None
Sc K_{α}	Ca K_{β}	1 ppm. Sc per % CaO	Regression
V K_{α}	Ti K_{β}	180 ppm. V per % TiO ₂	Regression
La L_{α_1}	Ti K_{α}	5 ppm. La per % TiO ₂	Regression
Ti K_{β}	Ba L_{β_3}	0.00004 % TiO ₂ per ppm. Ba	Yes
	V K_{α}	0.0004 % TiO ₂ per ppm. V	Yes
Ni K_{α}	Y K_{α} (2nd order)	Unimportant for Y <400 ppm.	Narrow energy window
Y K_{α}	Rb K_{α}	0.22 ppm. Y per ppm. Rb	Regression
Zr K_{α}	Sr K_{α}	0.07 ppm. Zr per ppm. Sr	Regression
Nb K_{α}	La K_{α} (2nd order)	0.01 ppm. Nb per ppm. La	Regression
	Y K_{β}	Unimportant for Y <1000 ppm.	None
	U $L_{\beta_{2,4}}$	Unimportant for U <50 ppm.	None
Cr K_{α}	V K_{β}	0.05 ppm. Cr per ppm. V	Regression
Ce L_{β_1}	Nd L_{α_1}	Probably unimportant?	None
Nd L_{α_1}	Ce L_{β_1}	0.01 ppm. Nd per ppm. Ce	Regression
Sm L_{α_1}	Ce L_{β_2}	0.02 ppm. Sm per ppm. Ce	Regression
Cu background	Hf L_{α_1}	Unimportant for Zr <800 ppm	None
	Zr K_{α} (2nd order)		
Y, Zr, Nb backgrounds	U, Th	Unimportant for <500 ppm U, Th	None
Ce, Nd background	Cr K_{α}	Unimportant for Cr <800 ppm	None

TABLE B6: XRF analytical conditions

Line	Crystal	kV	mA	Colli- mator	Counter	Background offset 2 θ°	Lower Level	Window
SiK α	PE	50	45	C	F	+ 4.40	25%	60%
AlK α	PE	60	45	C	F	- 5.75	25%	60%
FeK α	LiF200	50	45	F	F	- 1.63	20%	60%
MgK α	TLAP	60	45	C	F	+ 2.70	25%	50%
CaK α	LiF200	50	30	F	F	- 3.00	25%	60%
NaK α	TLAP	60	45	C	F	- 2.25	30%	50%
KK α	LiF200	50	45	F	F	- 4.55	25%	60%
TiK α	LiF200	50	45	F	F	+ 4.74	30%	50%
MnK α	LiF200	60	45	F	F	- 1.00	15%	70%
PK α	Ge	50	45	C	F	+ 3.14	35%	40%
ScK α	LiF200	60	45	F	F	- 1.59	25%	60%
VK α	LiF220	60	45	F	F	- 2.62	30%	50%
CuK α	LiF200	60	45	C	F	+ 1.01	39%	26%
BaL β_2	LiF220	60	45	F	F	+ 1.75	15%	60%
LaL α_1	LiF200	60	45	C	F	- 1.08	30%	50%
NiK α	LiF200	60	45	F	F	+ 1.33	25%	50%
ZnK α	"	60	45	F	F	+ 0.80	25%	50%
ThL α_1	"	90	30	F	FS	-	20%	60%
RbK α	"	90	30	F	FS	+ 2.09	20%	60%
SrK α	"	90	30	F	FS	-	20%	60%
YK α	"	90	30	F	FS	+ 0.48	20%	60%
ZrK α	"	90	30	F	FS	-	20%	60%
NbK α	"	90	30	F	FS	- 0.40	20%	60%
CrK α	"	60	45	F	F	{+ 1.44 - 0.74	15%	60%
CeL β_1	"	60	45	F	F	-	15%	60%
SmL α_1	"	60	45	F	FS	- 0.48	20%	60%
NdL α_1	"	60	45	F	F	- 1.34	15%	60%
TiK β	"	60	45	F	F	- 1.54	30%	50%
CaK β	"	60	45	F	F	-	25%	60%

Crystals

PE = Pentaerythritol,
Ge = Germanium,

TLAP = Thallium acid phthalate
LiF = Lithium Fluoride

Collimators

C = coarse, F = fine

Counters

F = gas flow proportional counter
FS = flow counter and scintillation counter.

(iii) Background positions.

Background positions have been chosen to be as close as possible to the peak without interference. In general, only one background position has been used for each element, giving rise to a small matrix dependant error. The error is trivial for the major elements, and contributions to the background count from interfering minor elements are very small relative to the major element peak height. Care should be taken to avoid interference by the La spectrum from the flux, however. For trace elements, background position is critical, and change in peak angle should always be accompanied by a corresponding change in background angle setting.

For trace element i in sample s :

$$X_s^i = m^i \mu_s^i R_s^i + c$$

where X_s^i is the concentration of i in s ,
 μ_s^i is the mass absorption coefficient of s at the wavelength of the i analytical line - $\lambda_i = \lambda_{i,0}$ if the peak and background positions are close,
 m^i and c^i are the calibration gradient and intercept for element i respectively,
 R_s^i is the 'true' count ratio, related to that measured by

$$R_s^i \text{ measured} = R_s^i \text{ true} + B^*$$

where B^* is the small discrepancy between true and measured backgrounds. Therefore:

$$X_s^i = m^i \mu_s^i R_s^i \text{ measured} - m^i \mu_s^i B^* + c^i$$

The term $m^i \mu_s^i B^*$ is thus a small matrix dependant error, proportional to the count ratio discrepancy between measured and true background, which should give rise to calibration lines with matrix dependant intercept. This has never been observed. Additionally, for wavelengths shorter than the FeK_α absorption edge, it is approximately true that

$$\text{Background Intensity } B_s^i \propto 1/\mu_s^i \quad (\text{Anderman and Kemp, 1958})$$

and thus

$$B^* \propto 1/\mu_s^i$$

For such wavelengths, the $m^i \mu_s^i B^*$ term becomes nearly matrix independant, and will form part of the calibration intercept constant. Where interference corrections have to be made, it is advisable to reduce the B^* term as much as possible, and accordingly two backgrounds have been used for CrK_α . The steeply sloping continuum between ThL_α and NbK_α presents difficulties in the use of two backgrounds, for there are a number of Th and U L lines which could cause interference. Only one intermediate background position has therefore been used, and the background has been assumed linear between this and the two end backgrounds. This assumption has been checked by counting for a number of intermediate background positions on the United States

Geological Survey (USGS) standard samples.

(iv) Vacuum

All counting has been carried out under vacuum. While air has relatively small absorption for short wavelength radiation, the flow counter window is subjected to less stress if vacuum is permanent, and even for NbK_{α} substantially higher count rates are obtained.

(v) Angle and Pulse Height settings

The PW1450/20 allows pre-selection of goniometer angles and energy windows, and as these may remain unchecked for periods of one month or more, it is essential that they should be initially correctly set. The goniometer angle for a particular analytical line may change if the crystal d-spacing changes with temperature, or with a change in reflection geometry. The former only occurs with the penta-erythritol crystal (PE), and thus only affects Si and Al. While the monitor will correct for minor drifts, it is advisable to wait a few hours until the spectrometer has reached operating temperature before setting the angles for Si and Al. Change in reflection geometry usually produces substantial change in monitor count rates, and recalibration is advisable.

Automatic energy window selection is made possible by means of a variable potentiometer control of counter voltage, which is automatically set in relation to goniometer angle so that the first order reflection occurs at about the middle (50%) of the full energy window. This may drift if the initial counter high voltage changes, and, although the setting is seldom critical, the preset lower levels and windows in the XRF program on the PW1395 should be checked prior to recalibration. The monitors are convenient samples on which to check angles and energy distributions.

(vi) Counting times

In principle, counting times should be calculated from a required analytical precision, but use of a monitor complicates the calculation. Since the acquisition of the automatic sample changer, printout has consisted of count ratios to four decimal places, and it is difficult to allow for the rounding error in a precision-time calculation. A trial and error method has therefore been used, with precision being estimated by the repeated analysis of a single pellet or glass disc. Precision data for the analyses presented in this thesis are given in Table B7. Repeatability runs indicated that long exposure of single pellets or discs to X-rays did not cause deterioration.

For convenience in data processing, peak and background counts have been repeated four times each per sample for trace elements and 4 peaks, 2 backgrounds for major elements. This repetition allows the detection of

TABLE B7: Analytical Precision/Repeatability data.

	G2		AGV1		DTS1		MT45	
	Mean	$\pm 2\sigma$	Mean	$\pm 2\sigma$	Mean	$\pm 2\sigma$	Mean	$\pm 2\sigma$
SiO ₂	69.32	0.210	59.62	0.240	40.57	0.146	Ni	138.9 1.5
Al ₂ O ₃	15.48	0.058	17.12	0.062	0.40	0.006	Zn	68.6 1.7
Fe ₂ O ₃	2.74	0.015	6.92	0.035	8.93	0.036	Th	4.6 2.2
MgO	0.84	0.038	1.59	0.030	49.89	0.253	Rb	16.7 1.2
CaO	1.92	0.010	4.96	0.020	0.17	0.002	Sr	603.6 2.0
Na ₂ O	4.30	0.060	4.37	0.124	0.11	0.057	Y	25.5 0.5
K ₂ O	4.49	0.014	2.96	0.013	(-0.02)	0.001	Zr	249.8 1.7
TiO ₂	0.49	0.004	1.06	0.006	0.02	0.002	Nb	12.7 1.1
MnO	0.03	0.010	0.10	0.009	0.13	0.008	Cr	290.0 1.7
P ₂ O ₅	0.13	0.005	0.48	0.007	0.01	0.003	Ce	71.7 3.8
16 CYCLES PER SAMPLE							Sm	8.7 2.8
							Nd	34.1 1.6
							TiO ₂ W	1.34% 0.014

	SR6		S32		JB1		12 CYCLES	
	Mean	$\pm 2\sigma$	Mean	$\pm 2\sigma$	Mean	$\pm 2\sigma$		
Sc	15.7	0.4	21.7	0.6	26.2	0.5	Oxides in wt.%; trace elements in p.p.m.	
V	162.7	3.1	133.1	4.5	194.0	2.8		
Cu	29.9	0.5	22.2	1.0	53.9	0.8		
Ba	893.7	7.0	408.2	4.1	554.1	5.7	G2, AGV1, DTS1 and JB1 are international standards	
La	44.9	2.0	30.6	2.8	40.2	2.0		
TiO ₂ CR	0.73%	0.003	1.18%	0.003	1.27%	0.007%	S32, MT45 are samples from the present study	
19 CYCLES PER SAMPLE								
							SR6 is a basaltic andesite from the volcano Stromboli, Italy	

spurious counts (section B10). Unfortunately, the sample changer does not easily allow the use of different count times on peak and background, so that, for major elements, total peak time = 2 X total background time, and for trace elements, total peak time = total background time. There are minor exceptions in the cases of elements using the same background as another (Ce, Th, Rb, Sr, Y, Zr and Nb).

B6 : XRF OUTPUT

XRF output is printed simultaneously on teletype paper and onto punched paper tape. As the X-ray tube is the only analytical condition which must be manually selected, three programs are currently in use:

Program 90 : Major elements

91 : Cr-tube, trace elements Sc, V, Cu, Ba, La

91 : W tube, trace elements Ni, Zn, Th, Rb, Sr
Y, Zr, Nb, Cr, Ce, Sm, Nd

Specimen output of these programs is presented in Tables B8-B10. It will be noted that TiO₂ has been analysed in all three programs; it is used as an analytical check in the trace element programs (section B9).

B7 : STANDARDS

Glass discs for major element standards were prepared in the same way as the specimens (section B2). Standards used were USGS G2, GSP1, AGV1, BCR1, DTS1, PCC1; Centre de Recherches Petrographiques et Géochimiques (CRPG) GA, GH, BR; Geological Survey of Japan (GSJ) JG1, JB1 and National Bureau of Standards (NBS) NBS91 and NBS99A. Values were taken from Abbey (1977). These were all used without pre-ignition, but in addition ignited samples of the USGS and CRPG standards were used, with oxide % calculated from Abbey (1977) using the measured loss on ignition. This calculation may be easily performed using the computer program IGSTAN (source file: EGE007.IGSTAN). This effectively gives the USGS and CRPG standards double weighting. For computing purposes, ignited standards are named using the suffix -IG; sets of standards made with a new flux batch have a letter inserted between the sample name and the -IG, e.g. BCR1BIG. Hyphens should not be used in standard names during computer processing of the data. Fe for the ultramafic standards is not used in the calibration, and BR is given half weighting for silica (i.e. only the value for BRIG, BRBIG is used, not that of BR), because of possible matrix effects (section B8). No Mn value is quoted for NBS99A. The same standards were used for all the rocks analysed, although a new set was made up at the beginning of a new flux batch. A different selection of standards should be used if rocks are of more extreme composition.

Trace element standards require a slightly different procedure to the samples, for in using 7g of scarce international standard they must be almost permanent. Six drops of 2% PVA are therefore used as a pellet binder. PVA

TABLE B8 : Specimen output of XRF program 90 - major elements

PROGRAM NUMBER	2 3 4	2 2 2	01 02 03	SAMPLE 1		SAMPLE 2		SAMPLE 3		
				RATIO	TIME	RATIO	TIME	RATIO	TIME	
90										
14	1	400000	16349	8114	16349	8283	16349	7773	16349	} PEAKS Si K _α
14	1	400000	16413	8125	16413	8304	16413	7790	16413	
14	1	400000	16417	8142	16417	8303	16417	7788	16417	
14	1	400000	16425	8156	16425	8301	16425	7775	16425	
64	2	24	16425	25	16425	25	16425			} BACKGROUNDS
14	1	400000	16431	8166	16431	8340	16431	7806	16431	
64	2	24	16431	25	16431	26	16431			
13	1	200000	28083	9131	28083	10202	28083	8454	28083	
13	1	200000	28080	9169	28080	10181	28080	8486	28080	Al K _α
13	1	200000	28063	9149	28063	10169	28063	8478	28063	
63	2	107	28063	111	28063	109	28063			
13	1	200000	28127	9144	28127	10208	28127	8466	28127	
63	2	110	28127	115	28127	109	28127			Fe K _α
26	1	200000	7643	5755	7643	5133	7643	6165	7643	
26	1	200000	7614	5734	7614	5117	7614	6152	7614	
26	1	200000	7633	5745	7633	5140	7633	6165	7633	
76	2	41	7633	43	7633	42	7633			Mg K _α
26	1	200000	7654	5756	7654	5126	7654	6159	7654	
76	2	44	7654	43	7654	41	7654			
12	1	200000	46567	2025	46567	1242	46567	1765	46567	
12	1	200000	46558	2024	46558	1232	46558	1797	46558	Na K _α
12	1	200000	46644	2037	46644	1240	46644	1777	46644	
62	2	500	46644	471	46644	503	46644			
12	1	200000	46454	2014	46454	1226	46454	1779	46454	
62	2	489	46454	469	46454	501	46454			Ca K _α
20	1	400000	5466	3280	5466	1666	5466	4677	5466	
20	1	400000	5469	3303	5469	1664	5469	4677	5469	
20	1	400000	5465	3277	5465	1659	5465	4688	5465	
70	2	8	5465	6	5465	10	5465			K K _α
20	1	400000	5463	3298	5463	1650	5463	4666	5463	
70	2	6	5463	7	5463	9	5463			
11	1	20000	28687	4426	28687	6347	28687	5560	28687	
11	1	20000	28784	4454	28784	6256	28784	5411	28784	Ti K _α
11	1	20000	28446	4416	28446	6125	28446	5303	28446	
61	2	2041	28446	2014	28446	2073	28446			
11	1	20000	28363	4467	28363	6265	28363	5414	28363	
61	2	2093	28363	2093	28363	2054	28363			Mn K _α
19	1	400000	7385	1238	7385	2136	7385	1357	7385	
19	1	400000	7386	1240	7386	2332	7386	1358	7386	
19	1	400000	7391	1233	7391	2346	7391	1366	7391	
69	2	9	7391	8	7391	8	7391			P K _α
19	1	400000	7387	1235	7387	2327	7387	1370	7387	
69	2	6	7387	9	7387	9	7387			
22	1	200000	3577	3641	3577	2292	3577	3137	3577	
22	1	200000	3572	3634	3572	2286	3572	3118	3572	S K _α
22	1	200000	3587	3646	3587	2311	3587	3135	3587	
72	2	31	3587	30	3587	31	3587			
22	1	200000	3590	3656	3590	2271	3590	3159	3590	
72	2	28	3590	27	3590	27	3590			H K _α
25	1	10000	5626	5928	5626	8074	5626	6517	5626	
25	1	10000	5578	5868	5578	8056	5578	6548	5578	
25	1	10000	5619	5810	5619	7951	5619	6531	5619	
75	2	4257	5619	4336	5619	4225	5619			Cl K _α
25	1	10000	5536	6027	5536	7973	5536	6451	5536	
75	2	4160	5536	4114	5536	4191	5536			
15	1	40000	14248	1399	14248	901	14248	1268	14248	
15	1	40000	14400	1455	14400	878	14400	1282	14400	Br K _α
15	1	40000	14330	1416	14330	899	14330	1241	14330	
65	2	325	14330	320	14330	322	14330			
15	1	40000	14459	1435	14459	922	14459	1266	14459	
65	2	317	14459	254	14459	317	14459			
2	3	01								
3	3	02								
4	3	03								
90										
14	1	400000	16458	7975	16458	8453	16458	8118	16458	

	Sc	V	Cu	Ba	La	Ni	Zn	Th	Rb	Sr	Y	Zr	Nb	Cr	Ce	Sm	Nd	TiO ₂
SY3	*			*			*			*			*	*		*	*	
GSN				*			*									*	*	
PCC1				*	*	*	*			*	*		*	*	*	*	*	
UBN	x	x	x	x	x	*	*			*	*		*	*	*	*	*	
JB1													*					
JG1													*				*	
GSP1				*											*	*	*	
T1	*			*				*	*	*			*		*	*	*	
GH							*											
PKN	x	x	x	x	x		*	*	*	*	*		*		*	*	*	
DRN	x	x	x	x	x			*					*		*	*	*	
GA, BR, G2, AGV1 and BCR1 used for all elements																		
INTSGA2			*		*			*					*	*	*		*	*
INTSGB2	*		*		*	*	*			*				*			*	*
INTSBA2			*		*	*							*	*	*		*	*
INTSBB2	*		*		*	*	*			*	*			*			*	*
INTSGA3			*		*								*				*	*
INTSGB3	*		*		*	*							*				*	*
INTSBA3			*		*	*							*				*	*
INTSBB3	*		*		*	*							*				*	*
INTSGA4			*		*								*				*	*
INTSGB4			*		*	*							*				*	*
INTSBA4			*		*	*							*				*	*
INTSBB4			*		*	*							*				*	*
INTSG			*		*								x	*		x	*	*
INTSB			*		*								x	*		x	*	*
INTSA			*		*		x	x	x	x	x	x	x	*	x	x	x	*

TABLE B 11: Standards used in trace element calibrations.

* = omitted by program

x = omitted by not including in run

makes little difference to count rates, with the possible exception of the lightest elements, where a systematic error of up to 0.5 ppm may have been introduced. Because of the doubtful values of some elements for many of the standards, a far wider range of standards has been used than for the major elements; Table B11 lists the standards used for each element. For very different rock types, it is recommended that a different set of standards should be used in the calibration. Standard concentrations were again taken from Abbey (1977), with some additional data from the originators of the standards.

In addition to the international standards, a set of synthetic standards has been made by Dr. J.G. Fitton and the author. These are identified by the prefix INTS- (for INTERference Standard) and fall into two groups, two of roughly granitic composition (INTSG-) and two basaltic (INTSB-). Johnson-Matthey specpure major element oxides were fused at 1400°C in platinum dishes to produce about 100g of trace element free glasses of basaltic and granitic composition. These were ground in a tungsten carbide Tema mill, and glass discs were made from the powder to confirm the major element composition of the base glasses (Table B12). Mixtures of these with specpure TiO₂ were made to provide interference standards for Sc and V, and pellets were made of all these.

Table B12 : Major element composition of base glasses INTSG and INTSB, and of their derivatives.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂
INTSG	73.30	14.04	2.13	0.00	2.06	3.91	3.90	0.00
INTSB	50.05	13.80	10.25	9.64	10.39	2.91	1.02	2.00
INTSA	61.67	13.92	6.19	4.82	6.22	3.41	2.46	1.00
INTSATI	60.92	13.74	6.10	4.74	6.12	3.37	2.43	2.29
INTSBTI	49.07	13.53	10.05	9.45	10.19	2.85	1.00	3.92

Portions of the base glasses were then spiked with accurately known quantities of stoichiometric trace element compounds, to give element concentrations of between 1000 and 2000 ppm. Compounds used are listed in Table B13.

Table B13 : Trace element compounds used for spiking synthetic glasses.

Element	Rb	Sr	Y	Zr	Nb	Sc	V	Cr
Compound	RbCl	SrCO ₃	Y ₂ O ₃	ZrO ₂	Nb ₂ O ₅	Sc ₂ O ₃	NH ₄ VO ₃	K ₂ Cr ₂ O ₇

Element	Ni	Cu	Zn	Ba	La	Ce
Compound	Ni(CH ₃ CNO·CH ₃ CNOH) ₂	CuO	ZnO	BaCO ₃	La ₂ O ₃	CeO ₂

A pair of spiked glasses, suffixed -A and -B, was produced for both INTSG and INTSB, to allow different combinations of trace elements for interference corrections. The spiked glasses were then shaken in a polystyrene mixing vial using a Glen Creston mixer mill. To ensure homogeneity the spiked glasses were fused in the platinum dishes at

1400°C: the A series was fused first, and it would seem that this has lost Cu to the platinum, whence the B series has gained it. Cu values for these standards are therefore meaningless. It is possible that other elements have been similarly transferred, but only Ni and Cr show minor departures from the international standards calibration, and the synthetic standards are therefore not included in the calibrations for Ni and Cr. The resulting four glasses were ground in a tungsten carbide Tema mill and pellets made of the powders: these are INTSGA1, INTSBA1, INTSGB1 and INTSBB1. Three accurately weighed dilutions were made of the spiked glasses with base glasses, with mixing carried out by shaking in a mixer mill as before. Three more sets of four pellets were produced by this, suffixed 2, 3 and 4. All synthetic standards were pelletized using 2% PVA binding agent. The theoretical trace element composition of these sixteen pellets is given in Table B14.

Calibration consists of using the count ratios and the concentrations of the standards of Table B11 to determine m and c in the linear relation

$$X_s^i = m^i \mu_s^i R_s^i + c^i \quad (\text{section B5})$$

using regression procedures described in section B10.

B8 : MATRIX CORRECTIONS

The use of La203 in the flux for glass disc preparation and the five-fold dilution involved gives rise to a relatively constant matrix composition. It was therefore hoped that matrix correction would be unnecessary, and calibration lines were constructed from direct count ratio - concentration graphs. The ten graphs involved are presented in Fig. B1, and it is clear that a very high degree of linearity is obtained despite the wide variety of rock types used as standards, from dunite to granite. Linearity is particularly good for Mg, Ca, K, Ti and P, and it is improbable that matrix correction, with the attendant uncertainties in coefficients, could improve this. Matrix correction was applied to the silica calibration; while the resulting line was slightly different it was no more linear than the uncorrected calibration. Accordingly, for all elements determined on the glass discs, μ_s^i is given the value 1 in the equation at the end of section B7.

It is considered that a number of minor discrepancies do result from this lack of correction. In Fig. B1(a), it will be seen that BR and the ultramafic standards are divergent. Better total oxides are obtained if the calibration is placed closer to the ultramafic standards, and hence the SiO₂ value of BR is not used in the calibration, equivalent to giving BR half weighting for silica. A 100% specpure silica disc then has a total of about 101%: a similar effect probably accounts for the high frequency of >100% totals for analysed rhyolites. A minor discrepancy in iron contents of the ultramafic standards is also possibly a matrix effect, and these values are not used

TABLE B14: Theoretical compositions of synthetic trace element standards. All values in ppm.
Cu concentrations are incorrect due to exchange with Pt.

	Rb	Sr	Nb	Cr	Ni	Cu	Ba	La	Y	Sc	Zr	Zn	V	Ce
INTSBA1	1017	1017	1004	2528	2026	(1062)	1313	0	0	0	0	0	0	0
INTSGA1	2109	1125	1058	1058	1018	(1031)	2534	0	0	0	0	0	0	0
INTSBA2	414	414	409	1030	826	(433)	535	0	0	0	0	0	0	0
INTSGA2	877	468	440	440	423	(429)	1054	0	0	0	0	0	0	0
INTSBA3	83	83	82	206	165	(87)	107	0	0	0	0	0	0	0
INTSGA3	208	111	104	104	100	(102)	250	0	0	0	0	0	0	0
INTSBA4	19.4	19.4	19.1	48.2	38.6	(20.2)	25.0	0	0	0	0	0	0	0
INTSGA4	41.7	22.3	20.9	20.9	20.1	(20.4)	50.1	0	0	0	0	0	0	0
INTSBB1	0	0	0	0	0	(0)	0	1402	961	988	?4530	1053	1020	1047
INTSGB1	0	0	0	0	0	(0)	0	1017	998	998	1044	1011	1050	1037
INTSBB2	0	0	0	0	0	(0)	0	577	395	406	?1864	433	420	431
INTSGB2	0	0	0	0	0	(0)	0	430	422	422	441	427	444	438
INTSBB3	0	0	0	0	0	(0)	0	136	93.5	96	?441	102	99	102
INTSGB3	0	0	0	0	0	(0)	0	97	95	95	99	96	100	99
INTSBB4	0	0	0	0	0	(0)	0	28.5	19.5	20.1	?92.1	21.4	20.7	21.3
INTSGB4	0	0	0	0	0	(0)	0	18.6	18.2	18.2	19.1	18.5	19.2	18.9

Fig. B1 a & b : Major element calibration graphs

Symbols: $\blacklozenge$ = 'granites' (GA,GH,G2,JG1); $\blacksquare$ = 'ultramafics' (PCC1,DTS1,UBN)
 $\blacktriangle$ = 'intermediate rocks' (AGVi,GSP1,GSN,DRN,T1);
 $\bullet$ = 'basalts' (BR,BCR1,JB1); $\triangle$ = others (SY3,NBS91,NBS99A,FKN)

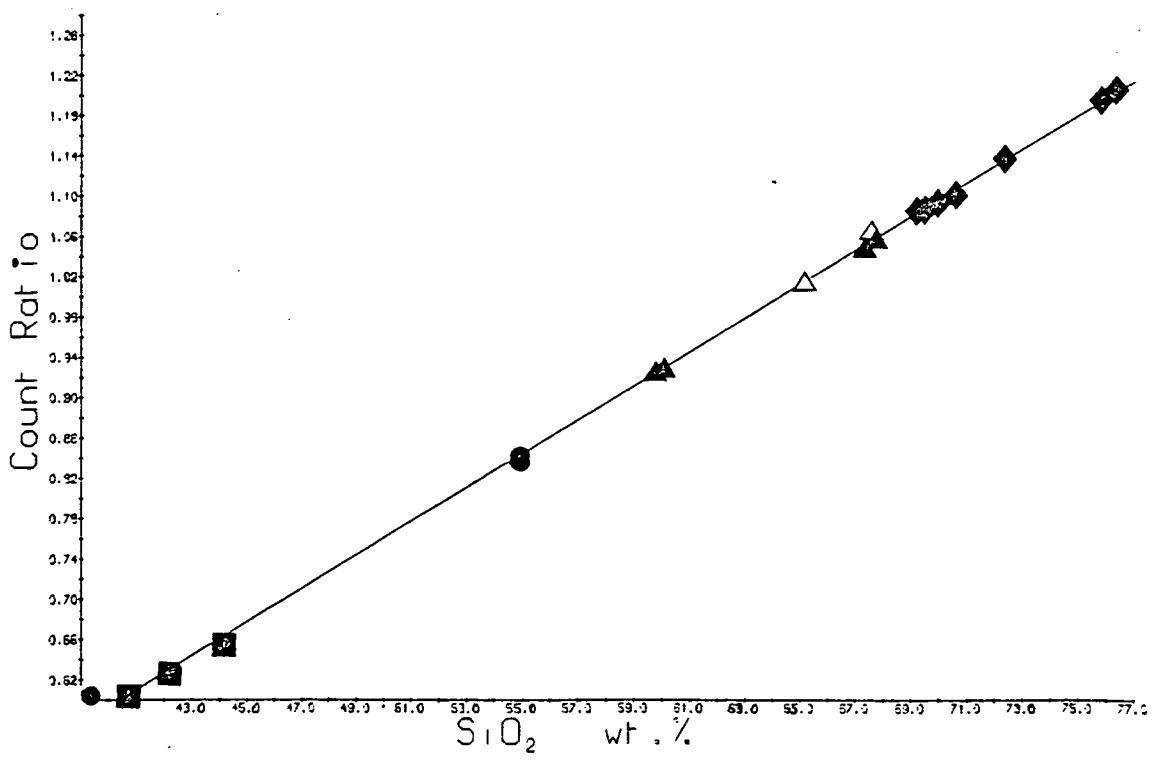
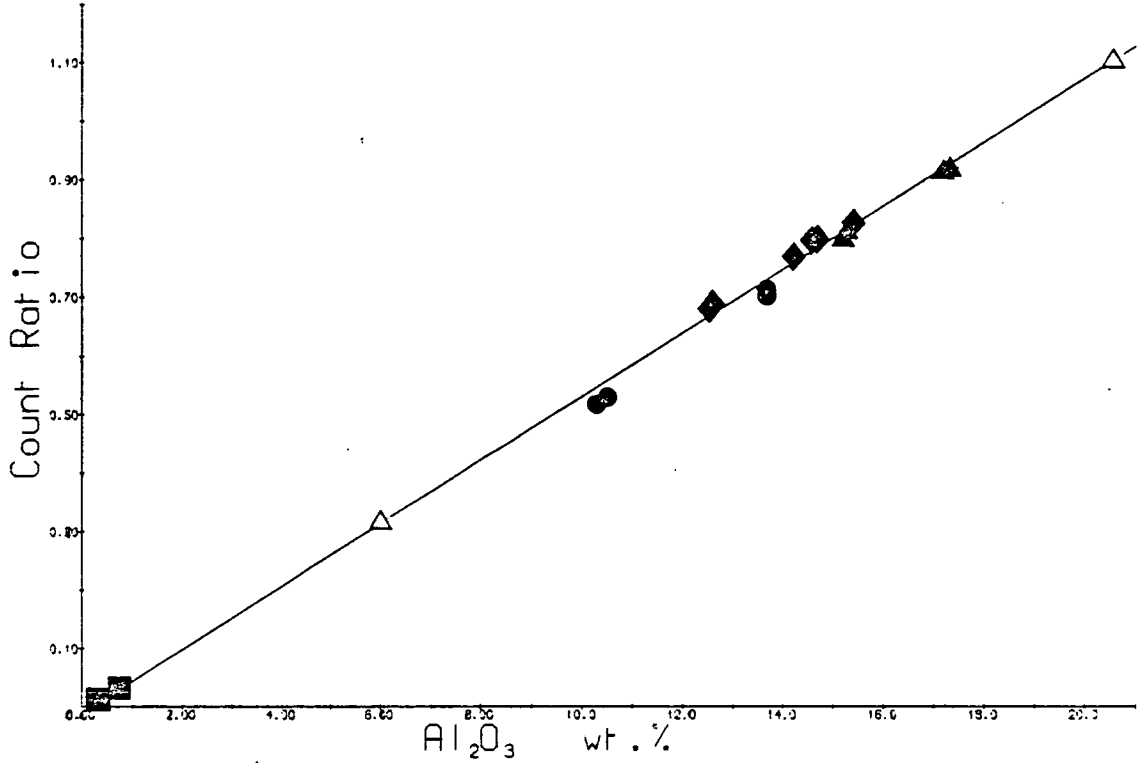


Fig. B1 c & d : Major element calibration graphs

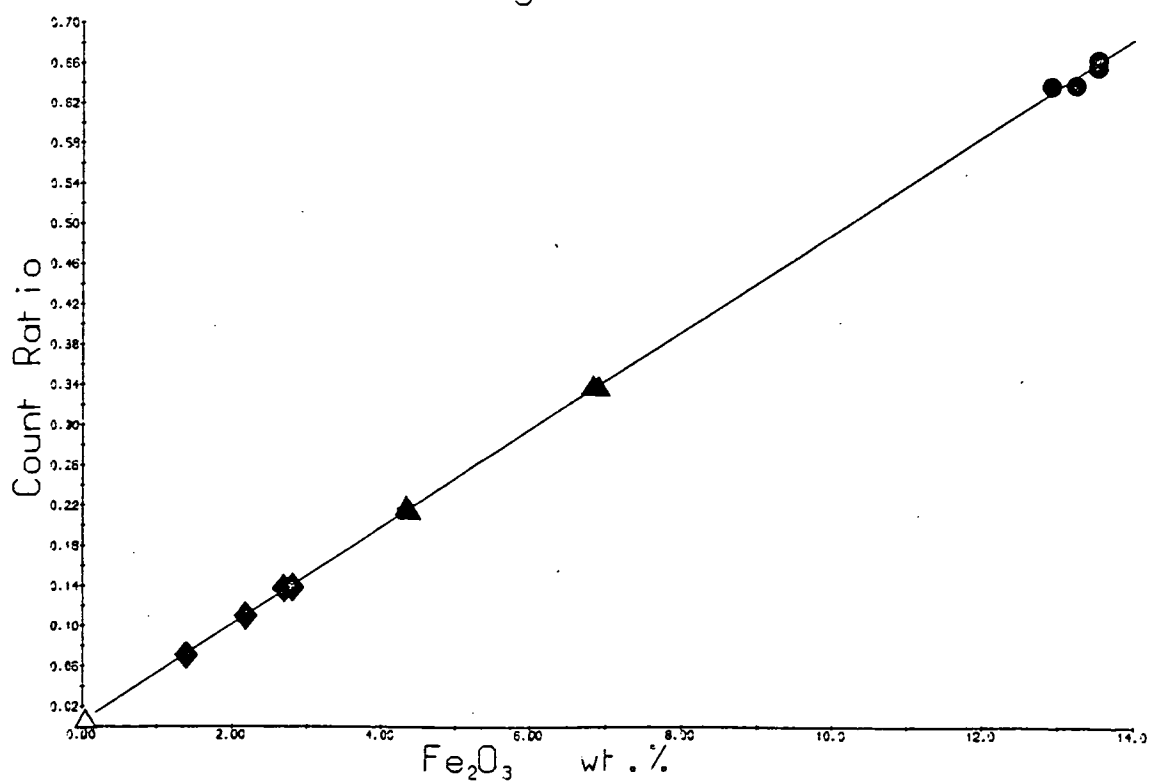
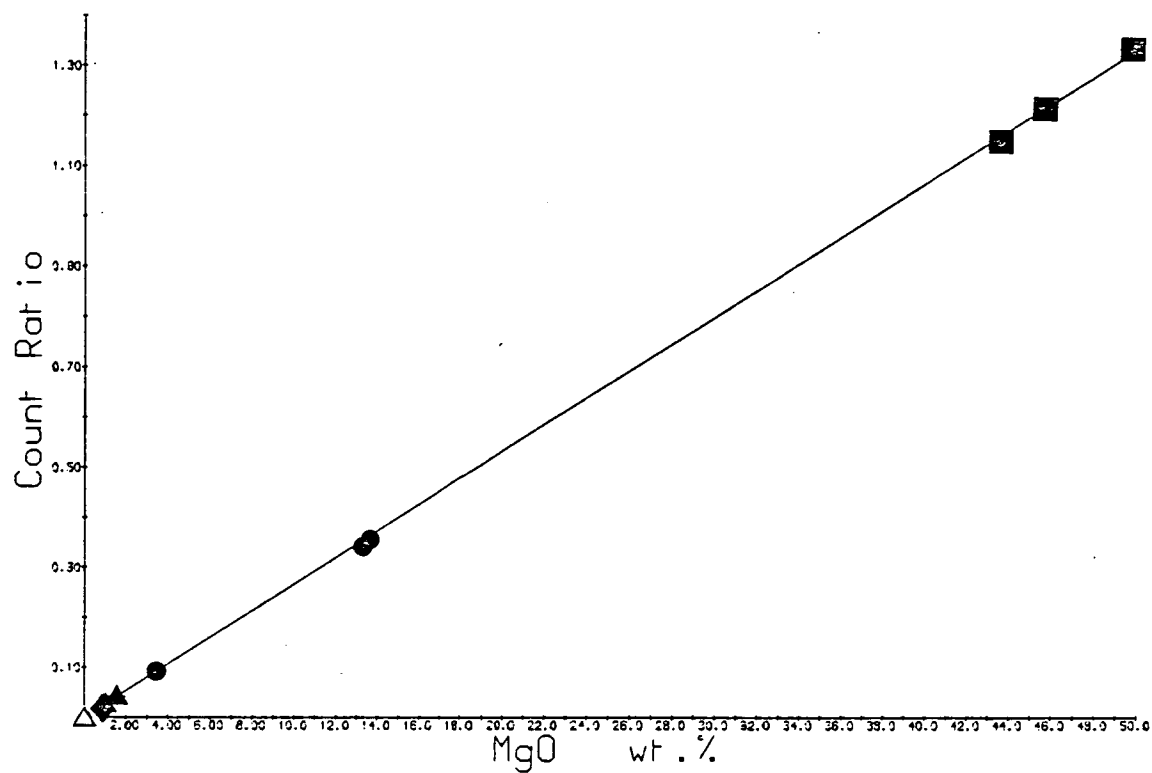


Fig. B1 e & f : Major element calibration graphs

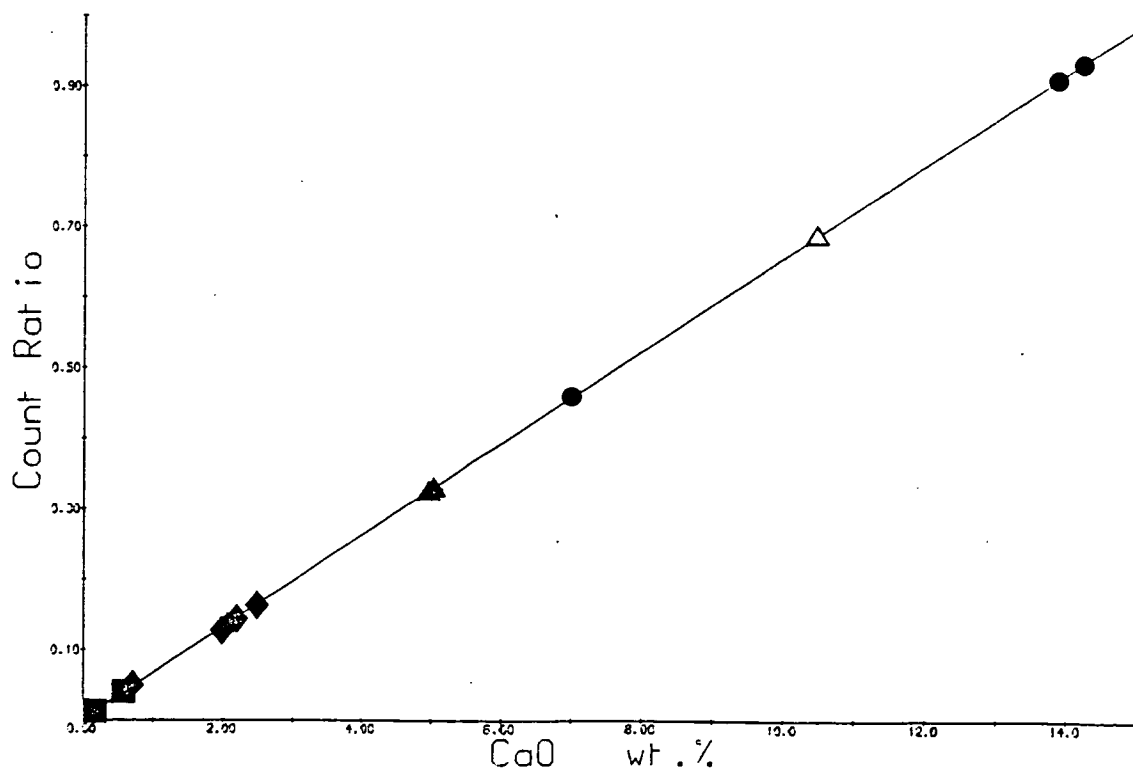
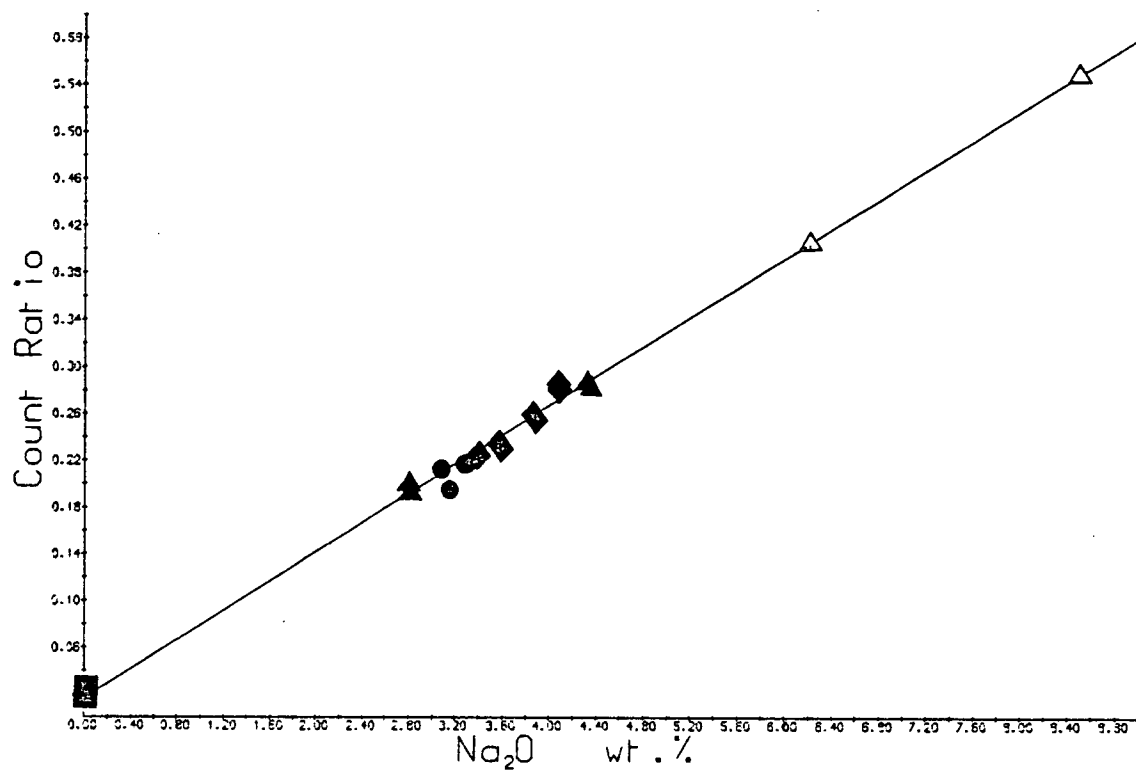


Fig. B1 g & h : Major element calibration graphs

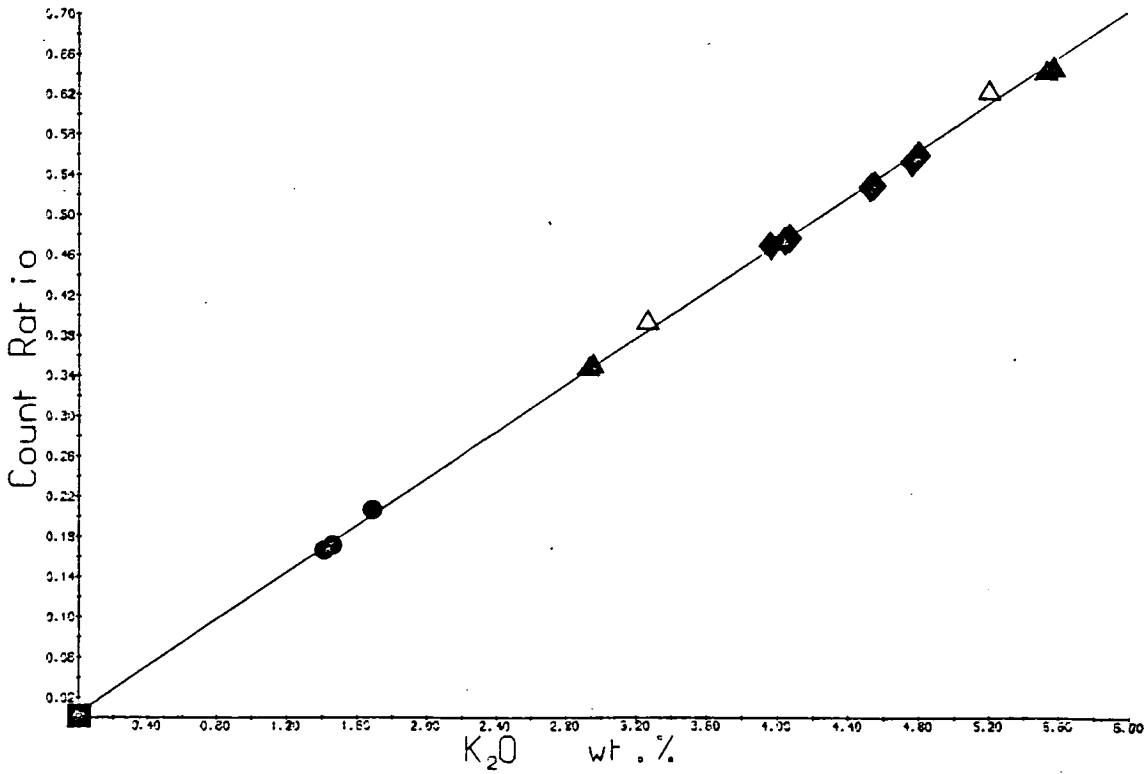
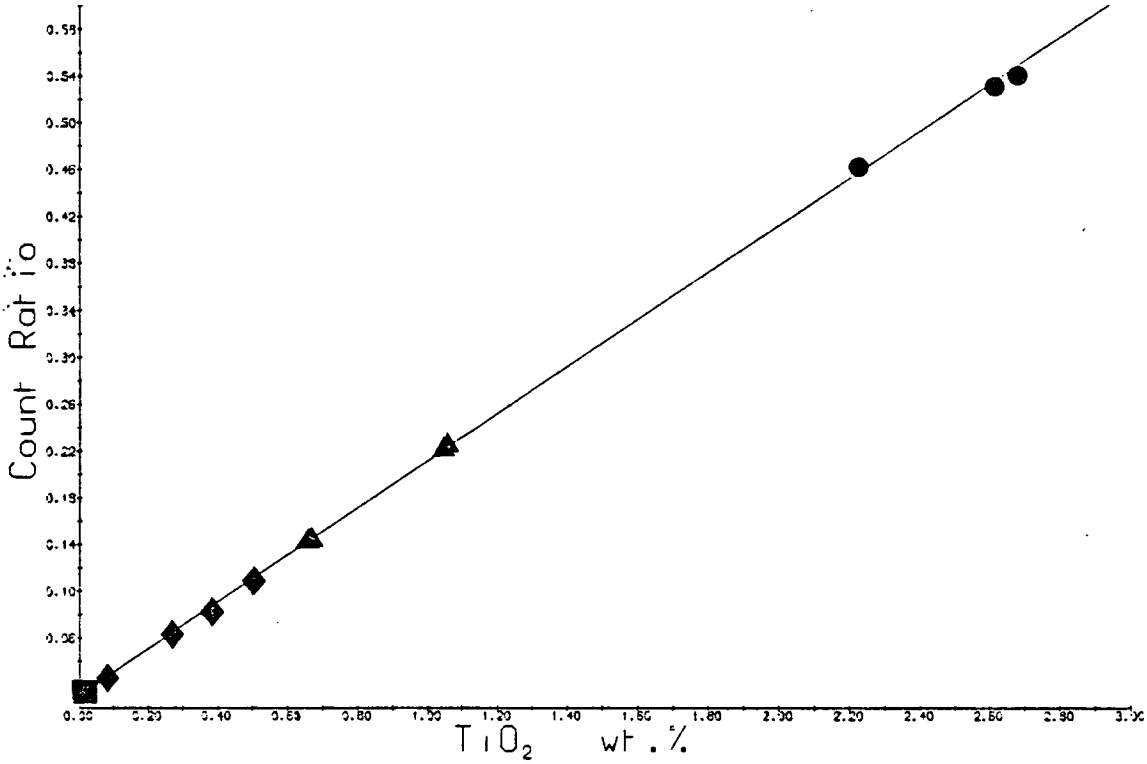
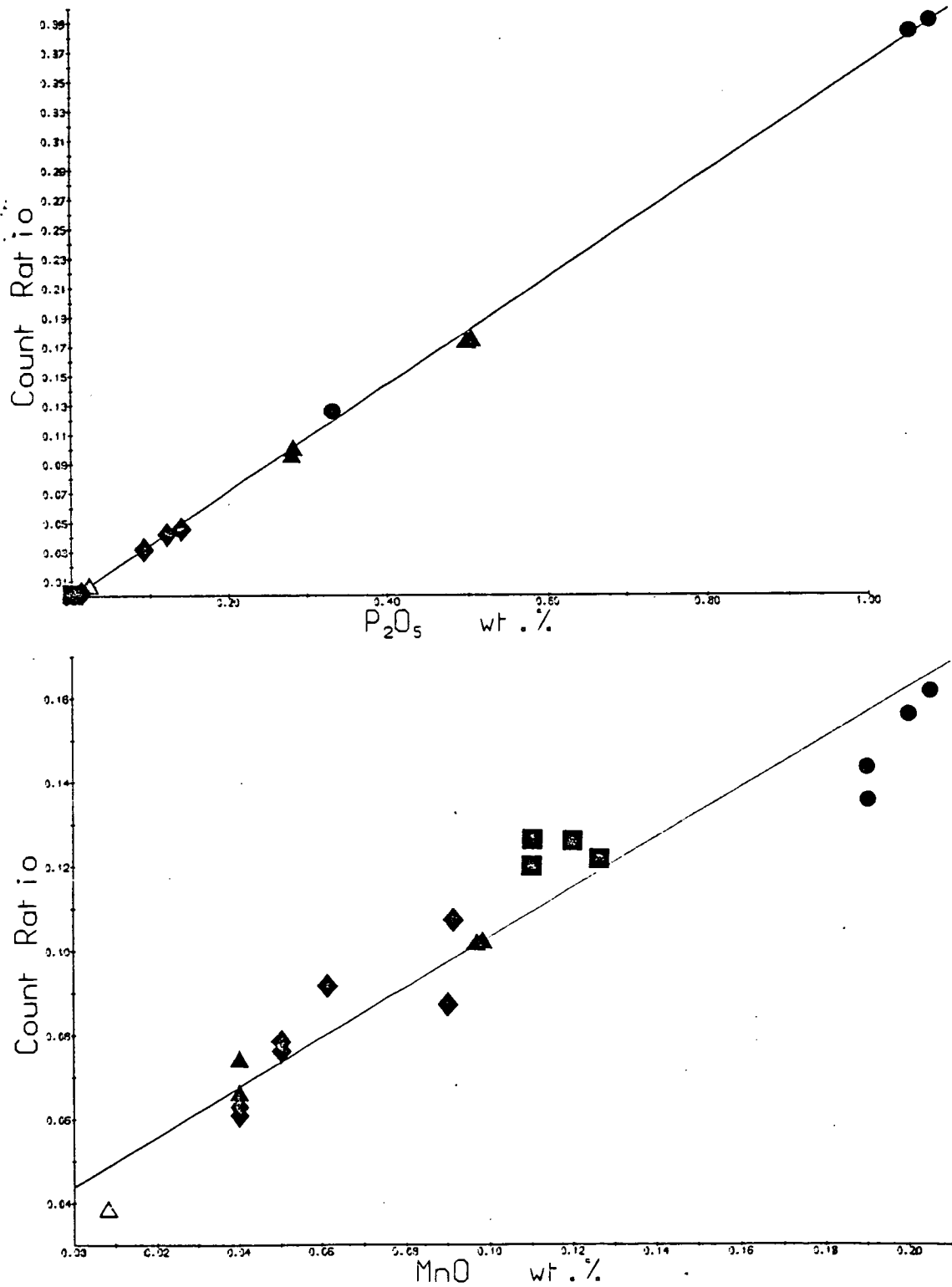


Fig. B1 i & j : Major element calibration graphs



in calibration. Scatter in the MnO calibration is caused by the values in Abbey (1977) being quoted to only two decimal places. It is believed that the high degree of linearity of the calibrations is justification for not making matrix corrections, providing that the rocks analysed are not extreme in composition. More extreme compositions e.g. limestones may be brought into the calibration range by fusion with a known weight of a specpure oxide.

A number of methods have been used by previous workers for matrix correction of trace element data. A common method involves ratio to background, used, for example, by Gandy (1973a), and based on Anderman and Kemp (1958). The latter authors state that their method should not be used for wavelengths longer than the FeK_α absorption edge, but this has not prevented a number of workers from using the correction for V and Cr. The method states that

$$\mu_i \propto 1/B_i$$

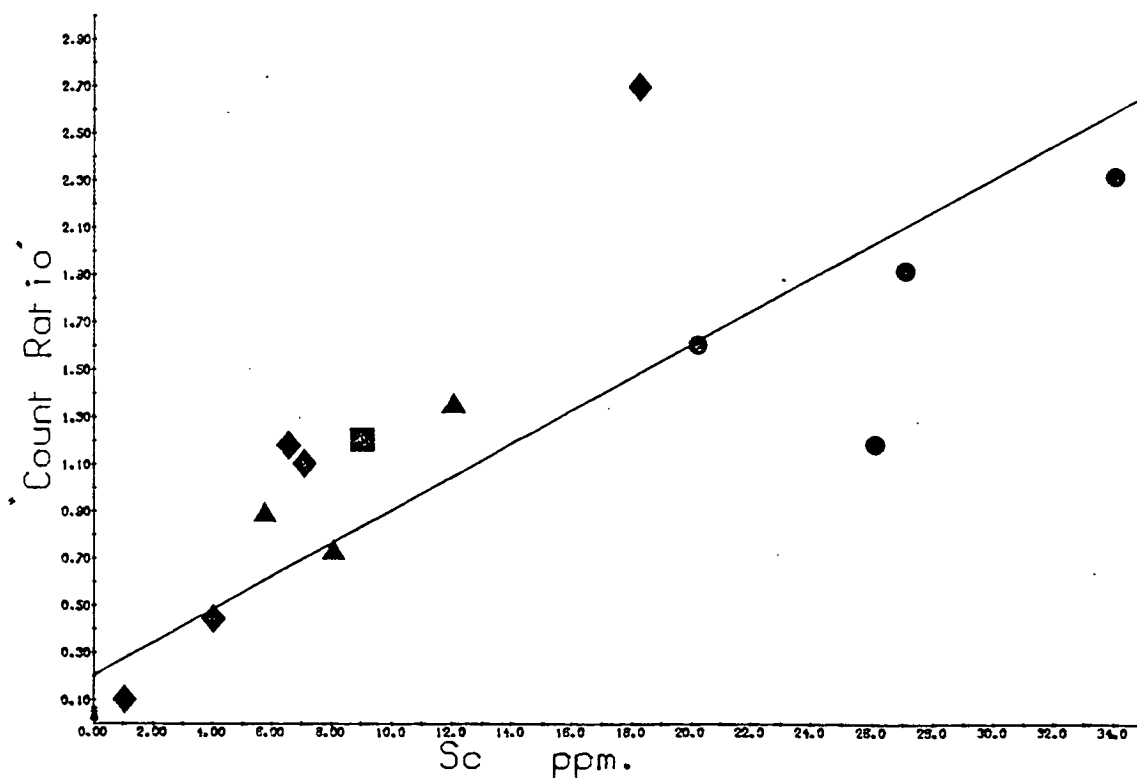
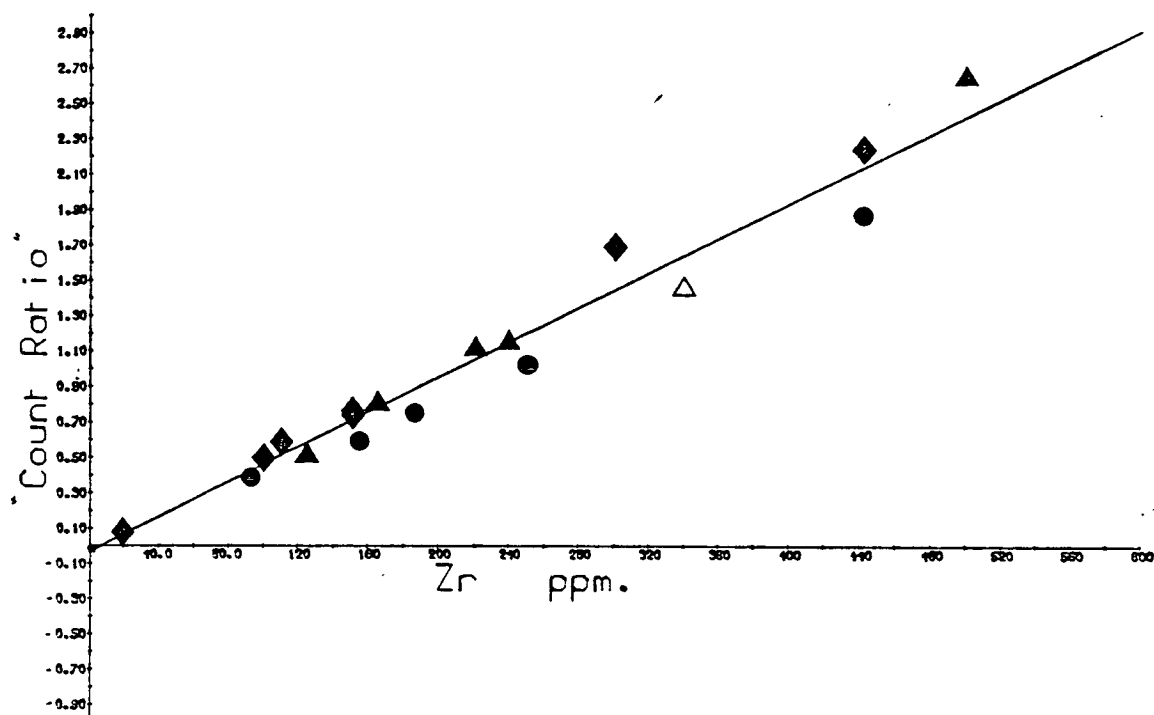
at the wavelength of the i analytical line. Mass absorption coefficients for a number of USGS standards have been calculated using the data of Theisen and Vollach (1967). At all wavelengths shorter than CaK_α the coefficients of basaltic rocks are higher than those of granites. Superimposed chart recorder spectra for these standards between the wavelengths of CaK_α and NbK_α demonstrate that, with increasing wavelength, the basaltic background intensity increases towards the level of the granitic background, until, at wavelengths longer than CrK_α , the basaltic background is higher than the granitic, and, approximately,

$$\mu_i \propto B_i$$

This is the inverse of the Anderman-Kemp relation. The reason for this inversion is not understood, and requires further work. It is clearly unwise to use the Anderman-Kemp correction method until more is known about the μ_i - B_i relationship. In Fig. B2 calibration graphs are presented for Sc (K_α with longer wavelength than the FeK_α absorption edge) and Zr (K_α shorter than the FeK_α absorption edge) with matrix correction made by ratio to background. It is clear that they are both inferior to the calibrations produced using the same data, but with the matrix correction method described below (Fig. B3).

Other correction methods involve extra determinations of matrix absorption: an example is the method of Reynolds (1963), where the reciprocal of the intensity of the MoK_α Compton scatter peak, measured using a Mo-tube, is used as a mass absorption coefficient. This is closely related to the Anderman-Kemp method, for the scatter peak is merely a particularly intense segment of the background. It has the advantage of being accurately measurable, but suffers from the same disadvantages as the Anderman-Kemp method, although an extension of its applicability to wavelengths longer than the FeK_α absorption edge has been reported by Nesbitt et al.

Fig. B2 : Calibration graphs for Zr and Sc using the Anderman-Kemp matrix correction procedure.
N.B. different calibration lines for acid and basic rocks. Symbols as Fig. B1..



N.B. These calibrations have not been used in the calculation of Zr and Sc concentrations.

(1976). In addition, the method involves an extra determination for each sample, and is only strictly applicable to one wavelength. Some direct determination methods for μ_s^i have been reported, but these are very time-consuming, for they involve determination at every analytical wavelength.

By definition:

$$\mu_s^i = \sum_{z=1}^{z=92} \mu_z^i x_s^z$$

where μ_z^i is the mass absorption coefficient of pure element atomic number z at the wavelength of the i analytical line,

x_s^z is the weight fraction of element atomic number z in sample s .

Since around 99.5% of most samples are composed of the ten major elements analysed on glass discs with oxygen, this may be simplified to:

$$\mu_s^i = \sum_z \mu_z^i x_s^z \quad \text{for } z=8, 11-15, 19, 20, 22, 25, 26$$

and, if z is taken to refer to the oxide, so that μ_z^i is the mass absorption coefficient of the pure element oxide at the i analytical wavelength, the value for $z=8$ may be omitted. Coefficients of μ_z^i have been taken from Theisen and Vollach (1967), and may be easily converted to oxide coefficients. The calculation may be further simplified by use of the relation $\mu \propto 1/\lambda^3$, and thus, providing analytical lines for i_1 and i_2 are between major element absorption edges,

$$\mu_{i_1}^s / \mu_{i_2}^s = \text{constant, for all samples } s$$

Analytical lines for Sc, V, La and TiK β lie between the CaK α and TiK α absorption edges, and oxide absorption coefficients calculated at TiK α have been used for these lines by means of the above relation. Similarly, coefficients calculated at CrK α have been used for analytical lines between the Ti and Mn K α absorption edges (Cr, Ba, Ce, Nd, Sm), and at SrK α for analytical lines with wavelengths shorter than the FeK α absorption edge.

Examination of the tables of Theisen and Vollach (1967) discloses that the relation $(\mu_{i_1}^s / \mu_{i_2}^s) = \text{constant}$, a subset of the previous relation, only holds true if elements z are in the same period, and, between elements in different periods, the discrepancy becomes greater the further separate i_1 and i_2 are. Lines relating to TiK α and CrK α are sufficiently close for this discrepancy to be very small, and no allowance has been made. For lines relating to SrK α , 4th period oxide concentrations are multiplied by a factor of

$$\frac{(\mu_{i_1}^s / \mu_{i_2}^s) - 4\text{th period}}{(\mu_{i_1}^s / \mu_{i_2}^s) - 3\text{rd period}}$$

This factor ranges from 0.908 (Ni) to 1.024 (Nb). Oxygen is

Fig. B3 a & b : Trace element calibration graphs

Symbols as Fig. B1.

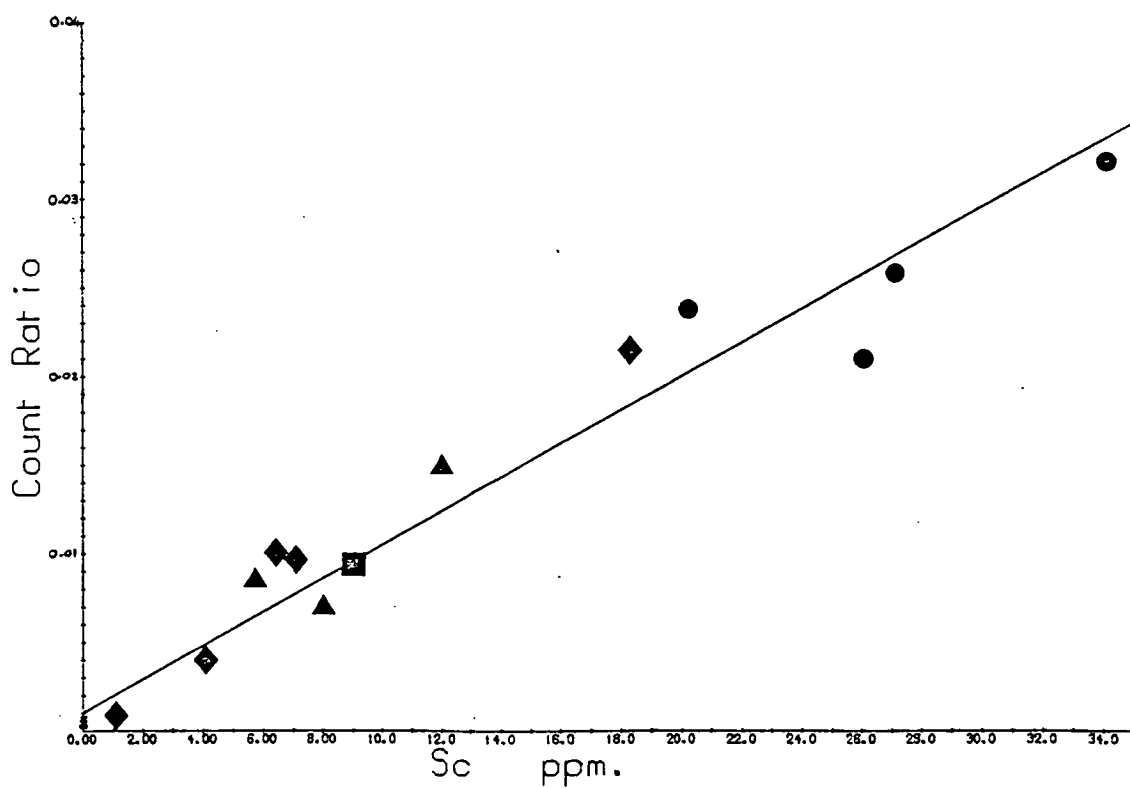
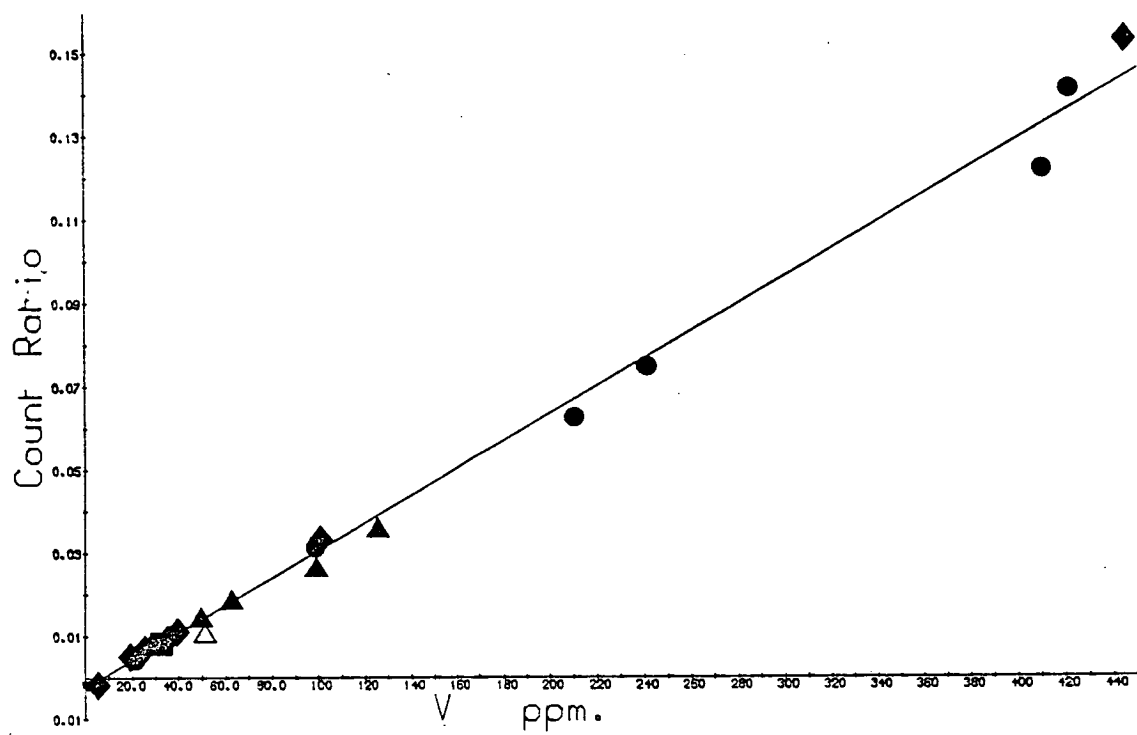


Fig. B3 c & d : Trace element calibration graphs

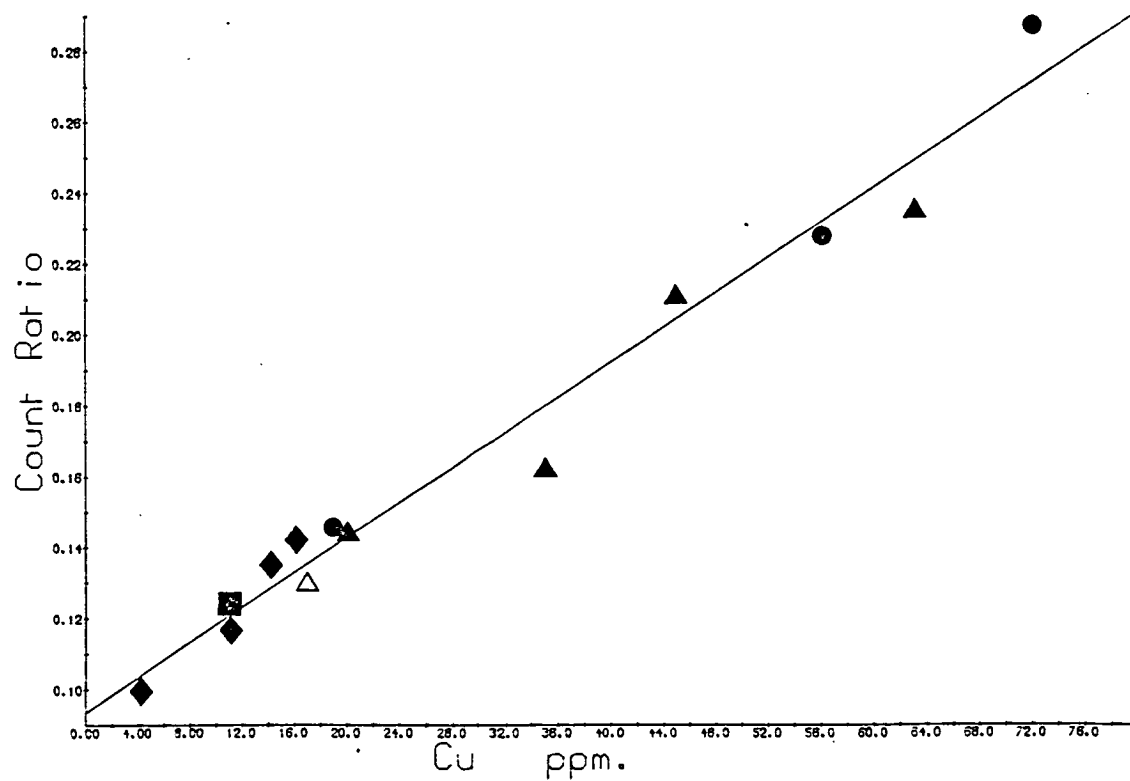
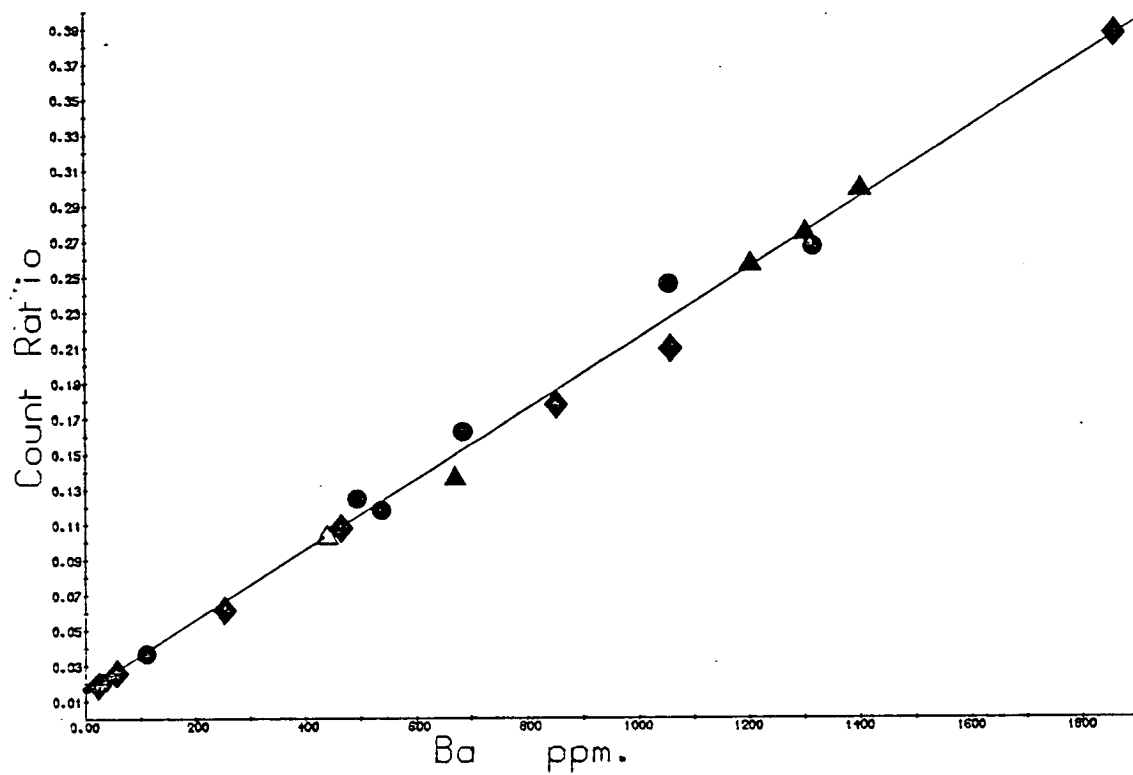


Fig. B3 e & f : Trace element calibration graphs

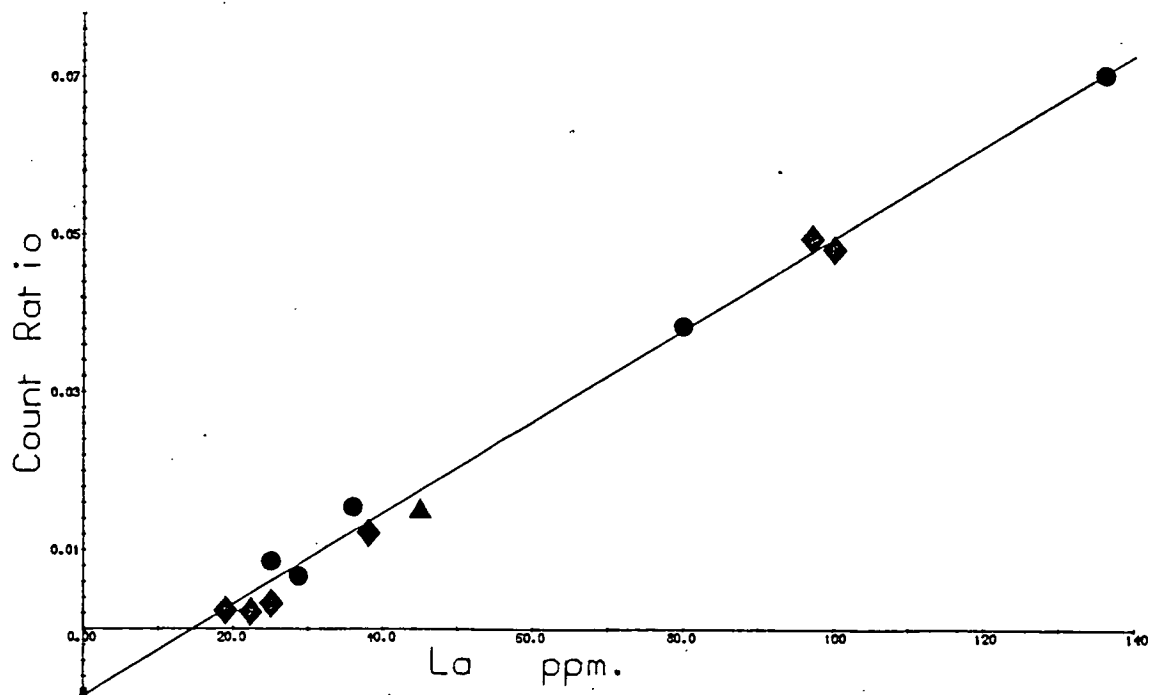
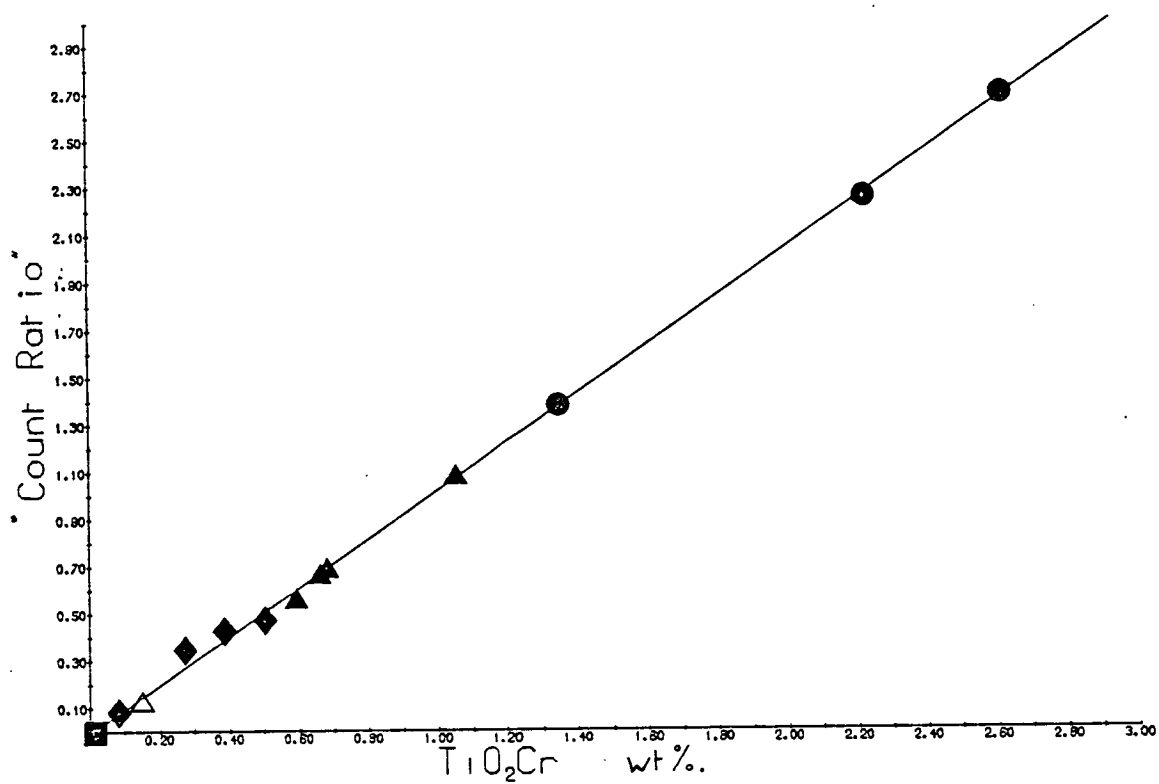


Fig. B3 g & h : Trace element calibration graphs

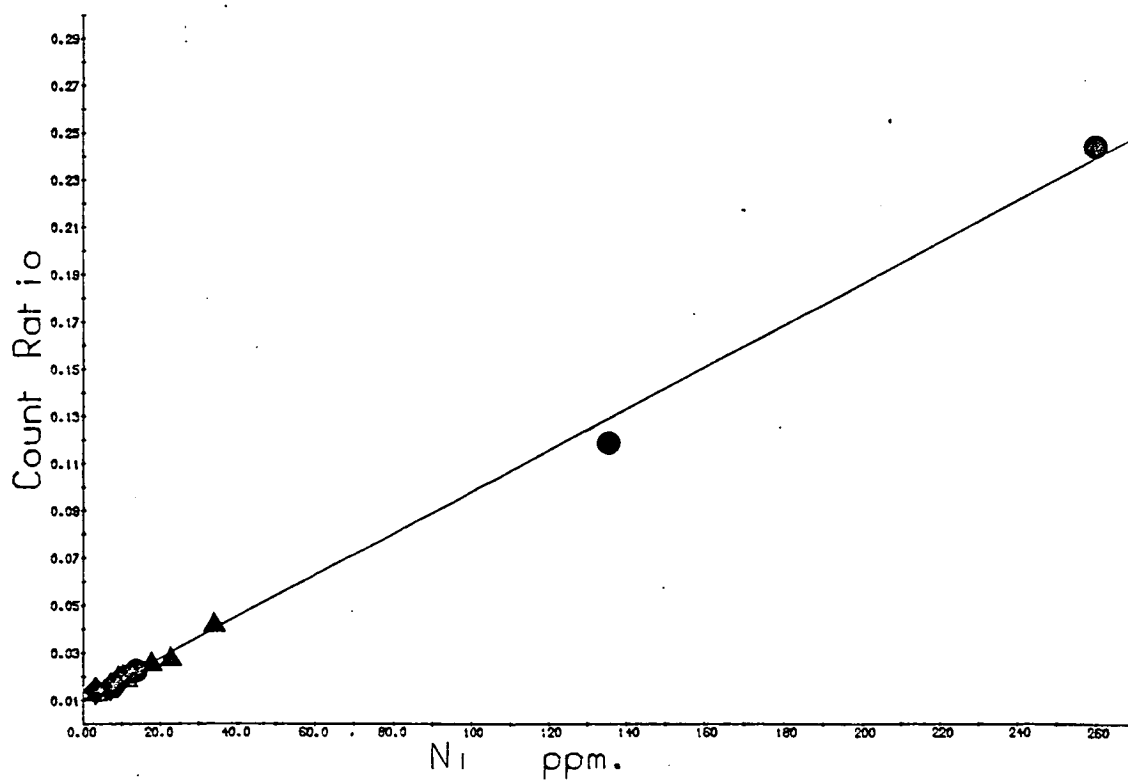
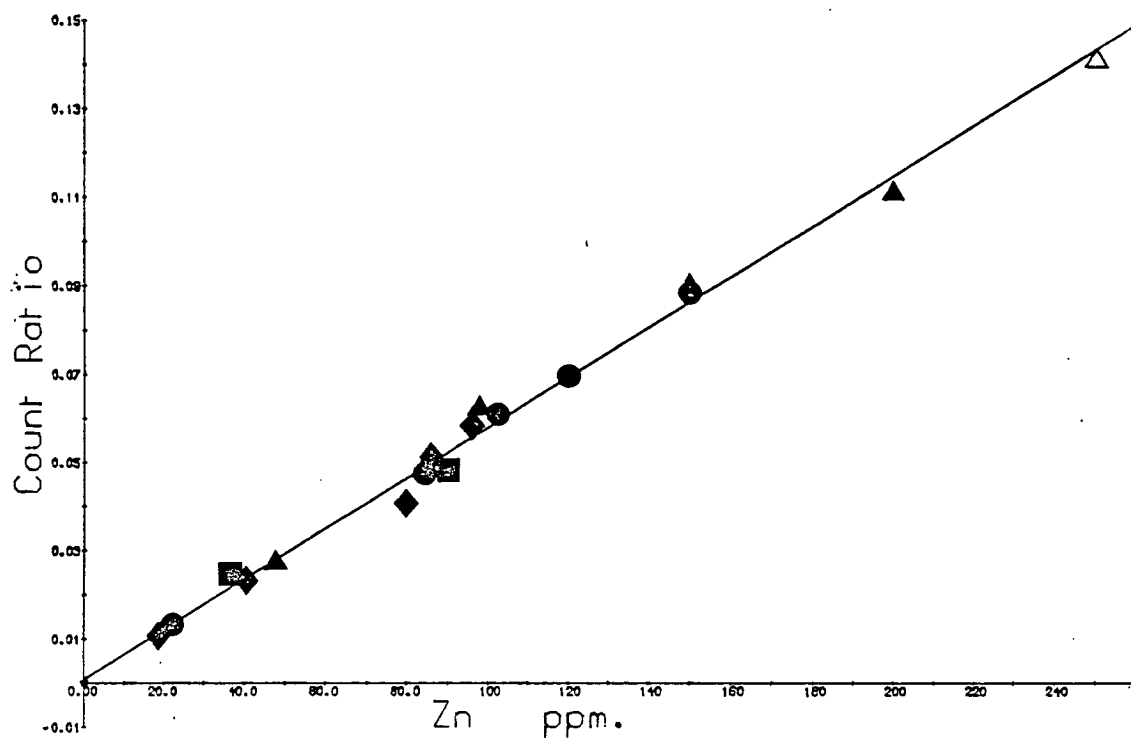


Fig. B3 i & j : Trace element calibration graphs

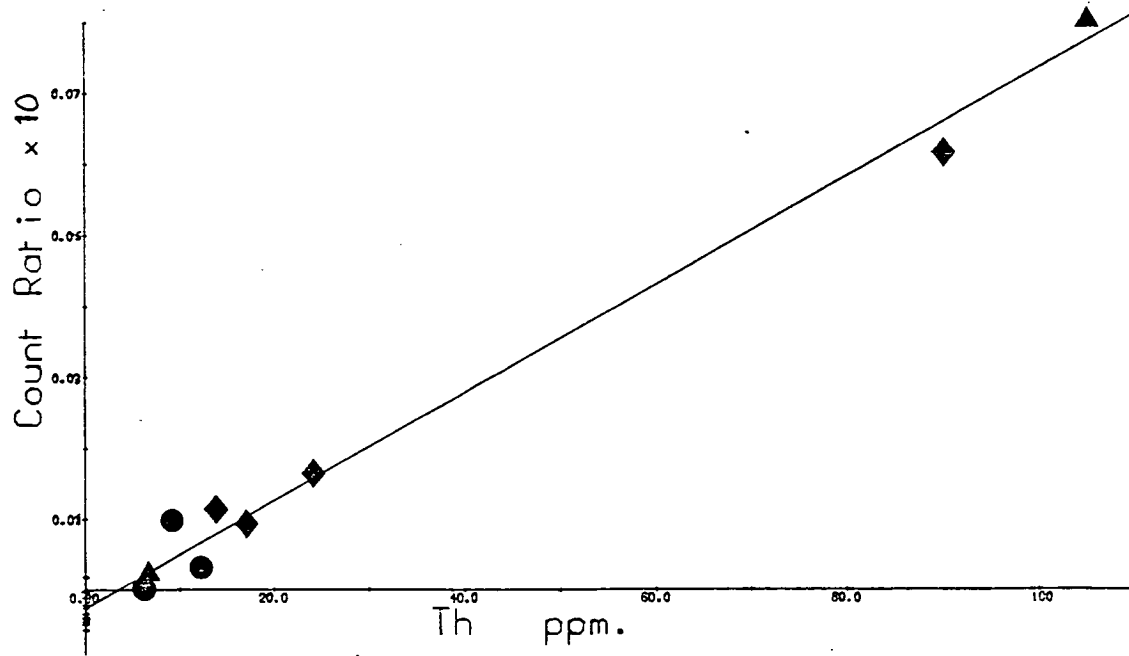
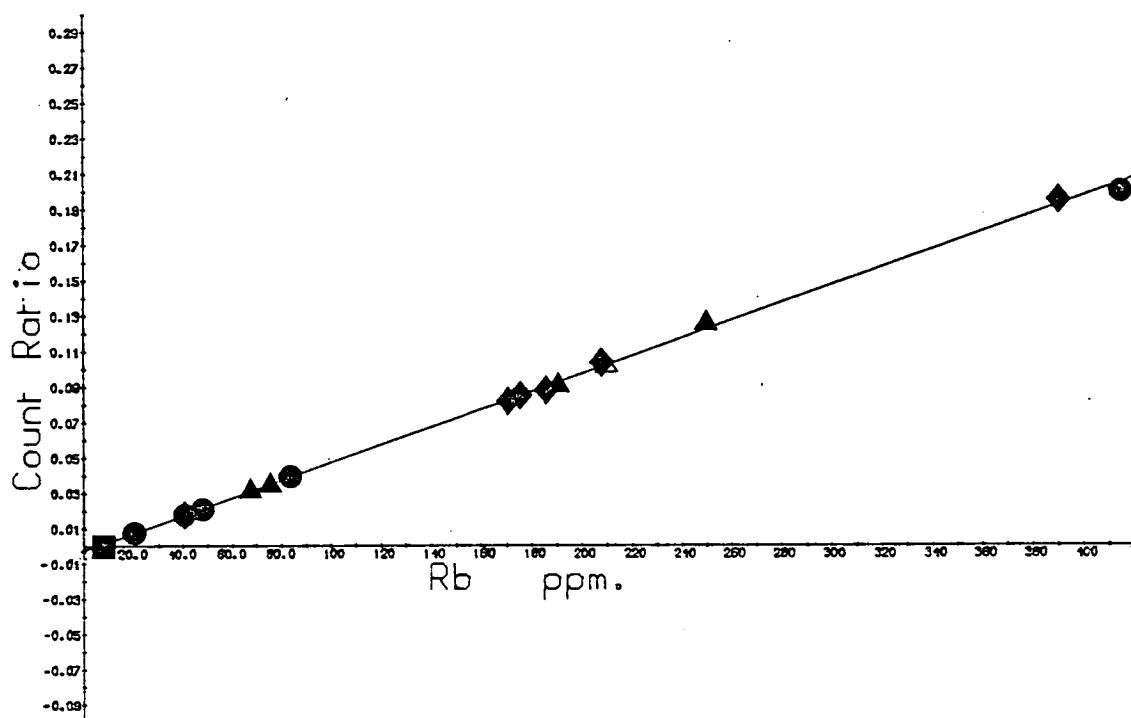


Fig. B3 k & l : Trace element calibration graphs

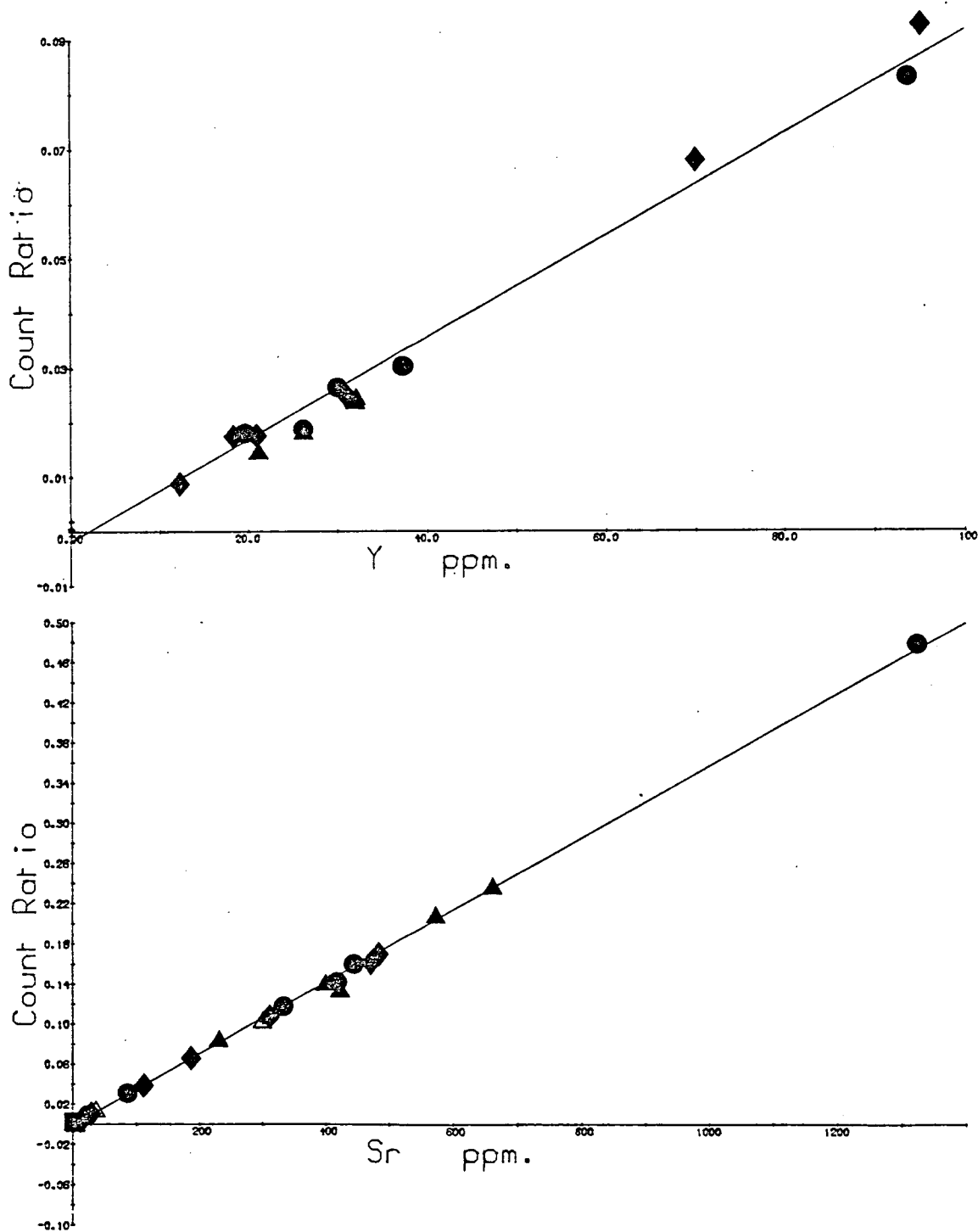


Fig. B3 m & n : Trace element calibration graphs

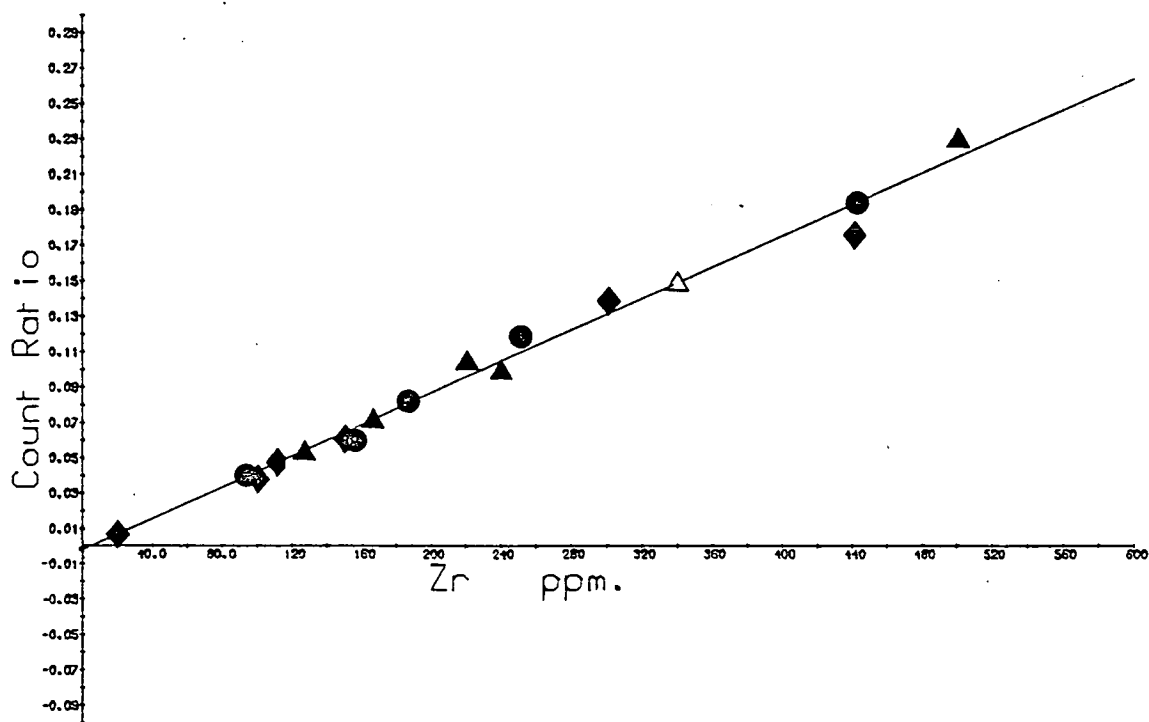
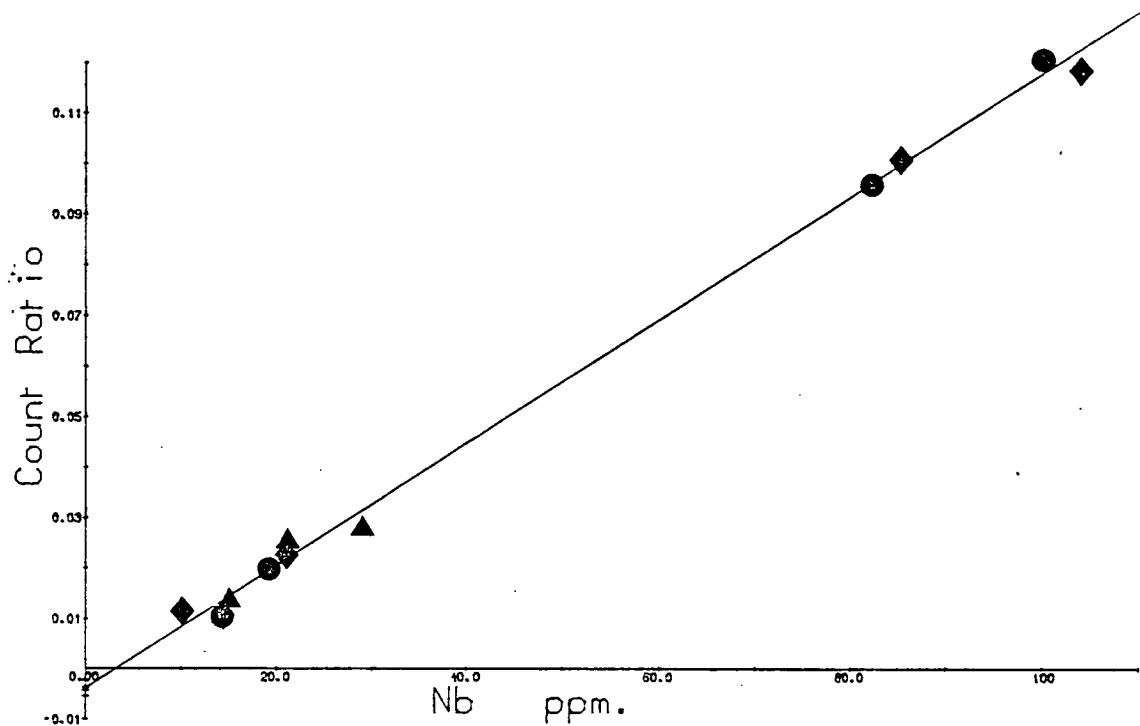


Fig. B3 o & p : Trace element calibration graphs

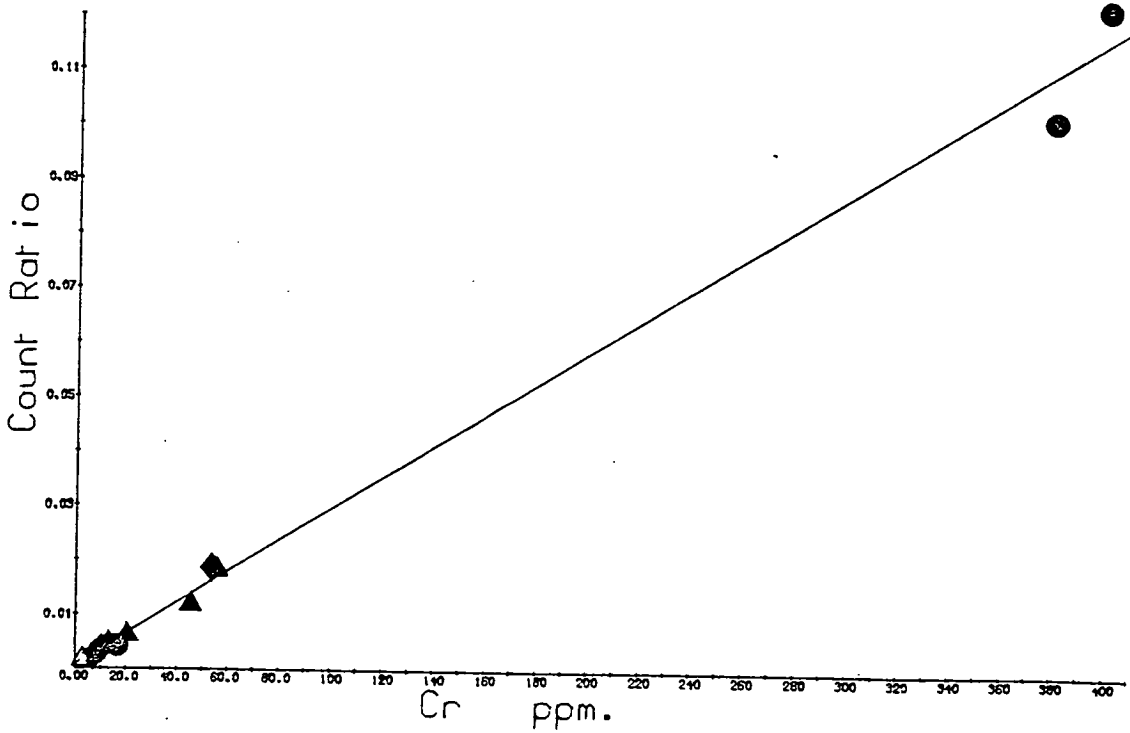
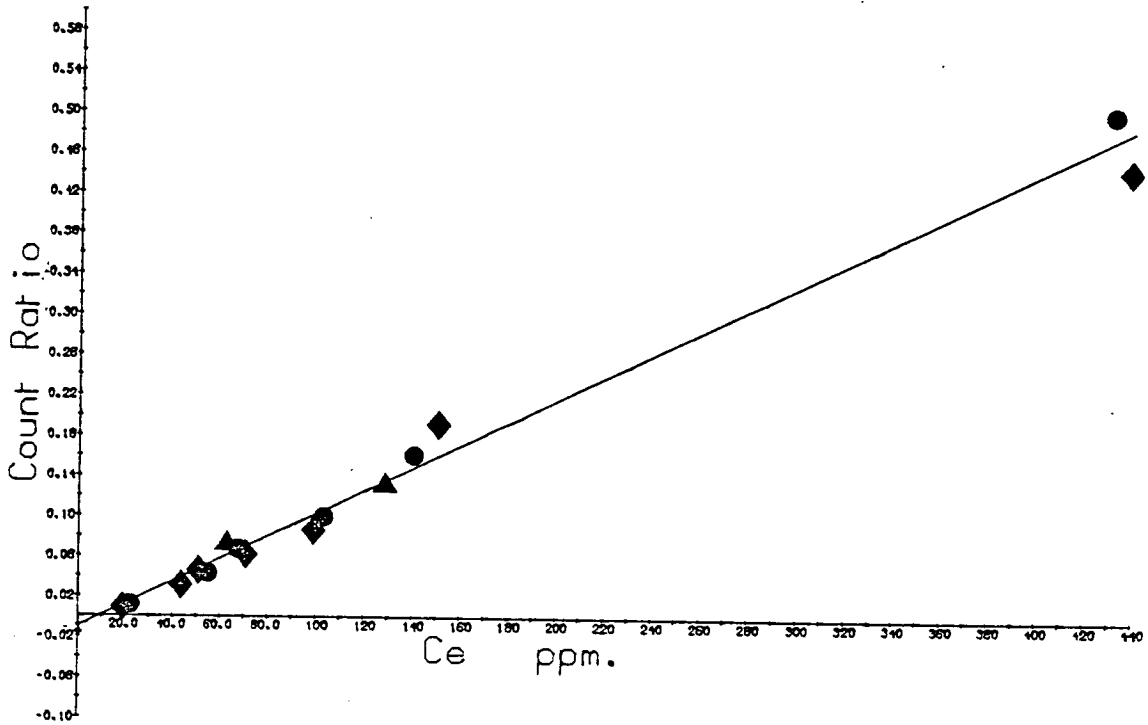


Fig. B3 q & r : Trace element calibration graphs

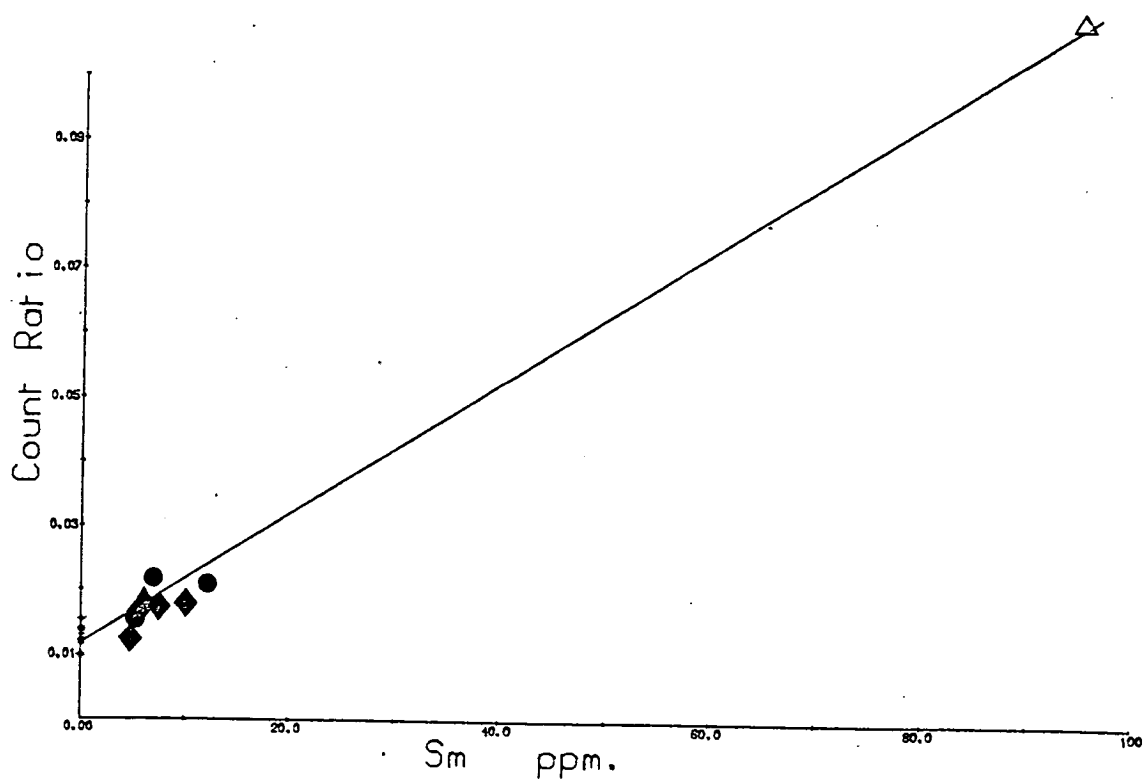
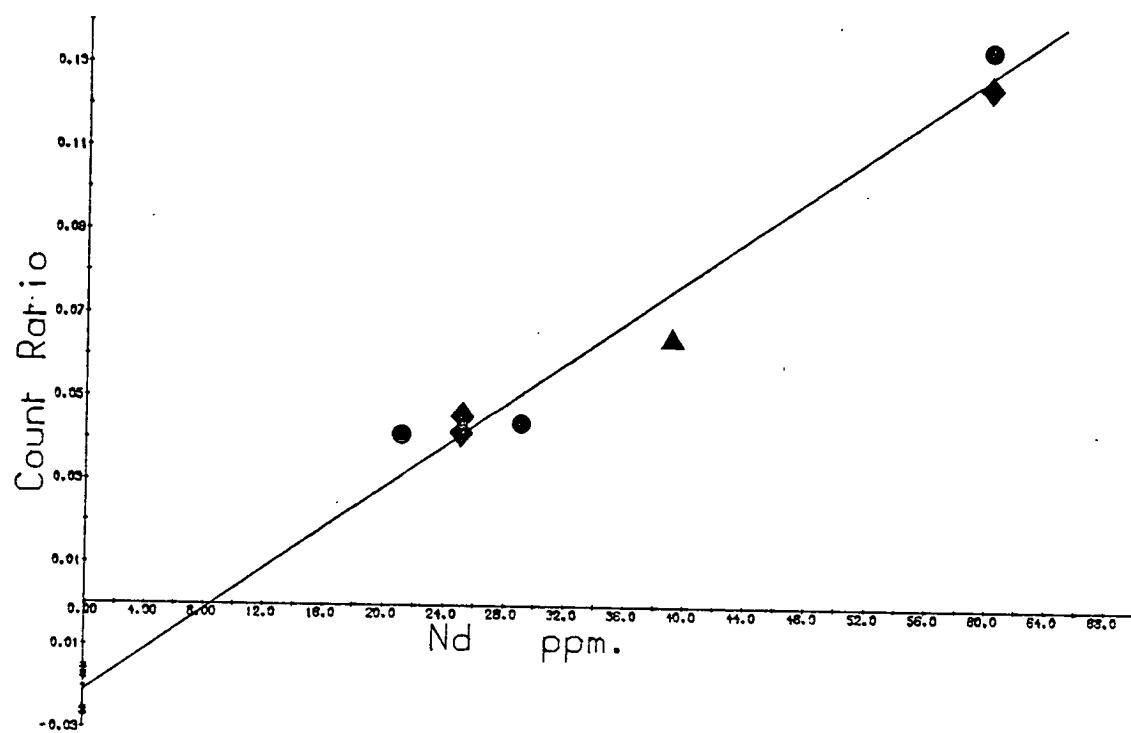


Fig. B3 s : Trace element calibration graphs

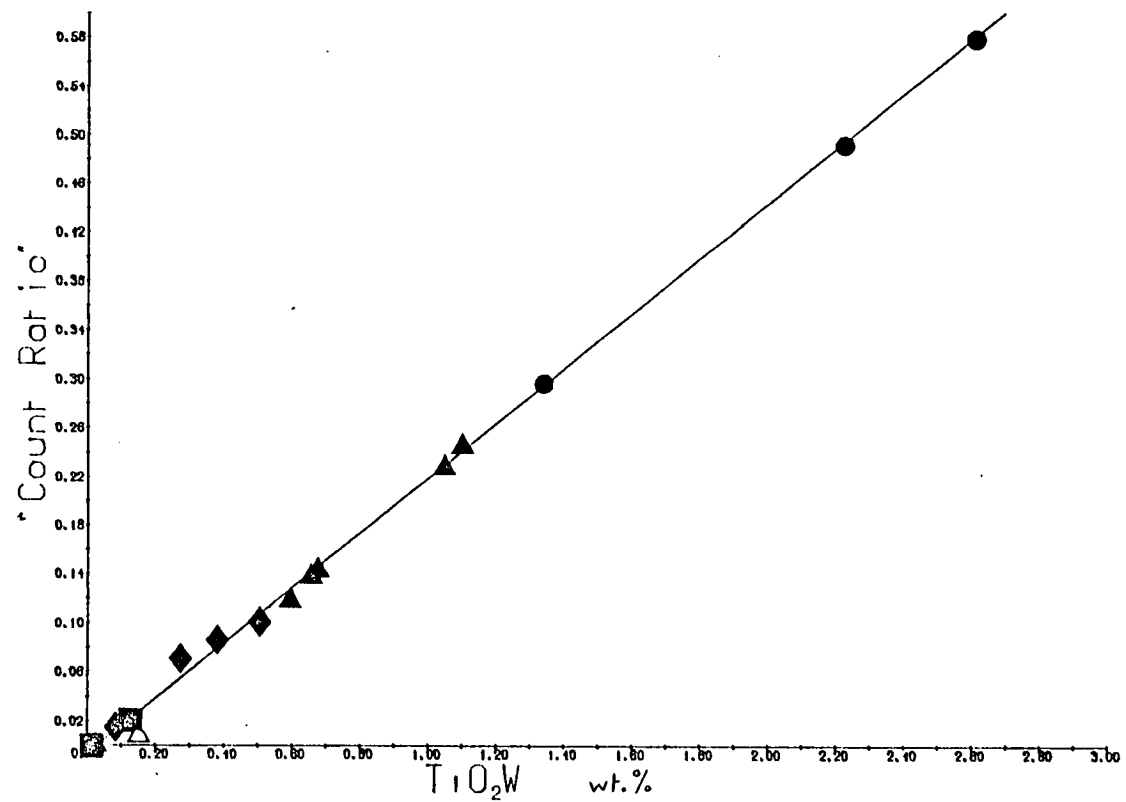


TABLE B15: Analytical Accuracy

Analyses of standard samples run as unknowns, not included in calibrations, compared with values from Abbey (1977).
Major elements in wt.%, trace elements in ppm.

Major elements: sample GS-N

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃ *	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅
XRF	66.09	14.81	3.82	2.30	2.45	3.60	4.687	0.662	0.060	0.269
Abbey (1977)	65.98	14.71	3.75	2.31	2.51	3.78	4.64	0.68	0.06	0.28

XRF							Abbey (1977)					
	DR-N	FK-N	UB-N	W1	SY2	TB	DR-N	FK-N	UB-N	W1	SY2	TB
Sc	34	0	14	37	6	21	-	-	-	?35	?7	13.5
V	224	2	68	264	50	121	220	-	75	240	50	105
Cu	44	4	20	102	3	32	52	?3	30	110	4	50
Ba	398	198	40	175	460	777	380	?210	?45	160	460	720
La	20	2	3	12	67	51	-	-	-	?12	?85	?56

		Ni	Zn	Th	Rb	Sr	Y	Zr	Nb	Cr	Ce	Sm	Nd
XRF	W1	74	84	2	22	196	24	107	9	128	19	3	11
	SY2	11	260	427	226	270	124	288	37	9	157	13	72
	TB	44	98	19	189	164	33	188	20	107	103	7	43
Abbey (1977)	W1	78	86	2	21	190	25	105	110	120	123	14	15
	SY2	10	250	370	220	270	130	270	25	10	210	16	70
	TB	40	95	19	180	155	39	175	-	80	115	9	-

in the second period, but its contribution to the total mass absorption is so small that the error of up to 5% introduced in treating it as third period is trivial.

The accuracy of this method of matrix correction may be judged by the high degree of calibration linearity (Fig. B3), in particular for Rb, Sr, TiO₂Cr and TiO₂W, where standard concentrations are best known. Departures from linearity are mainly attributable to inaccurately known standard concentrations, although a few difficulties remain, in particular a low Zn value for GH, and low REE values for GSP1. It seems unlikely that these discrepancies are due to poor matrix correction, for they only apply to single samples: they may possibly be explained by sample inhomogeneity. It is possible that negative values for Ce and Nd in PCC1 are the result of a fault in matrix correction procedure, for this is common to all highly magnesian samples. Since these are usually also Cr-rich, it is difficult to separate this possible matrix effect from the effect of overlap of CrK α onto the Ce, Nd background (section B5).

B9 : ANALYTICAL ACCURACY

Analytical accuracy is to a large extent measured by the linearity of the calibration graphs provided sufficient standards are used. In addition, a number of standards became available too late to be included in the calibration: these may be used as a measure of analytical accuracy (Table B15). Further confirmation of the accuracy of the trace element matrix correction procedure is provided by comparison (Table B16) with isotope dilution analyses of USGS standards for Rb and Sr, which is better than with the values of Abbey (1977).

Table B16 : Comparison of XRF and Isotope Dilution analyses (Pankhurst and O'Nions, 1973) for Rb and Sr.

Rb (ppm.)					
ID	XRF			Abbey (1977)	
	Jan. '79	Feb. '79	April '79		
BCR1	47.3	48.4	46.7	47.9	47
AGV1	67.1	68.1	67.3	68.0	67
GSP1	254.7	255.3	256.1	254.9	250
G2	169.3	170.2	169.5	169.0	170

Sr (ppm.)					
ID	XRF			Abbey (1977)	
	Jan. '79	Feb. '79	April '79		
BCR1	332.1	334.4	332.4	332.1	330
AGV1	662.0	661.1	659.4	657.6	660
GSP1	233.1	235.3	237.2	233.3	230
G2	476.3	476.4	476.9	474.7	480

In addition to the overall confirmation of accuracy, it is useful to have a check incorporated into each analysis made. For major elements, the total oxides forms such a check, for after ignition this should fall slightly less than 100%. The bulk of the analyses reported in Table B17 have totals between 99.2% and 100.2%, with the exception of a few rhyolites up to 100.8% (section B8). Discs giving totals outside this range were re-analysed.

The check chosen for trace element analyses was the analysis of TiO₂ in the trace element programs, giving the values of TiO₂Cr and TiO₂W in Table B17, analysed respectively with the Cr-tube and W-tube trace elements. The analytical check consists of comparison between these and the TiO₂ value determined on the glass disc. TiO₂ was chosen because of its relatively low concentration, the high precision and accuracy of the glass disc analyses, and the ability to use mass absorption coefficients previously calculated for TiK α . TiK β was chosen as the analytical line because of its low intensity, the need to count on it as an interference correction for V, and because of interference on it from VK α and BaL β ₃. This makes TiK β comparable with the more difficult trace element lines. The high degree of linearity of both the TiO₂Cr and the TiO₂W calibrations (Fig. B3) is evidence for the accuracy of the TiK α mass absorption coefficients: the difference in linearity between these and most trace element calibrations is presumably mainly due to the greater accuracy of the Ti standard values.

Comparison between TiO₂Cr, TiO₂W and glass disc TiO₂ is generally good, with the somewhat lower values of TiO₂Cr probably due to its not being run with a monitor. Future Cr-tube trace element runs will include monitoring of TiK. A number of highly discrepant values are present, however, although the discrepancy is usually smaller for TiO₂W. Particularly discrepant samples include OC93, OC94, S16, S17, S30 and S32. These pellets have been recycled, and remade, with no change, suggesting that the discrepancy is a sample effect, although samples that show it have little in common. The possibility that disc TiO₂ was incorrect was eliminated by use of plasma source spectrometry on a number of samples, by Dr. J.N. Walsh of University of London Kings College. It is possible that other elements are incorrect for samples with high TiO₂-TiO₂W, most probably V, although it is difficult to suggest which until the reason for the Ti discrepancy is understood. The very close similarity for all elements except V and Zn between S29 (no Ti discrepancy) and S32 (high Ti discrepancy) suggests that the cause may lie in the behaviour of opaque oxides on pelleting. V and Zn data should perhaps be treated with caution for Ti discrepant samples.

B10 : DATA PROCESSING

Averaging of count ratios, calibration regressions, interference and matrix corrections were carried out using programs written by the author in the high level language

IMP (ERCC, 1974). The work was rapidly performed using the twin ICL 4-75 computers of the Edinburgh Regional Computing Centre (ERCC); forming part of the Edinburgh Multi-Access System (EMAS, ERCC, 1976). The system has a number of interactive terminals on which a user may operate his process i.e. manipulate data stored as files by transferring these from a user-restricted disc storage to a portion of active computer core. Geology user numbers begin with the letters EGEO, and programs described in the following sections are preserved as text files on EGEO07, but may be run by other EGEO users.

XRF punched paper tape output is transferred to ERCC where it is read in as a file on an EGEO process. Such a file contains no information of sample names, which are inserted in order of analysis at the beginning with separating spaces. The number '999' is inserted at the end of the file to provide an end-marker, and any XRF printing mistakes are corrected by means of the EMAS EDIT command prior to use of the programs.

The flow diagram of Fig. B4 illustrates the general course of XRF data processing from the EMAS command level, and is followed by the program listings.

(i) RATMAJ (Fig. B5)

Source file: XRFS ; Object file: XRFY

Input data: file of XRF output of program 90, with initial sample names and terminal 999 (Table B8).

Output: file of count ratios for the ten major elements for each sample (Fig. B6).

Spurious counts for peaks are detected if any of the three subsequent counts differs from the first by more than a constant (DIFF(J)) multiplied by the square root of the first count (INITP(A)).

Spurious counts for backgrounds are detected if the second count differs from the first by more than a constant amount (DIFF(J+10)).

(ii) MAJORS (Fig. B7)

Source file: XRFS ; Object file: XRFY

Input data: EITHER

File of direct XRF output from pre-sample loader program

OR: Count ratio file from RATMAJ

OR: Major element analyses (Fig. B10)

AND, in the first two cases, EITHER:

Concentrations of standards in file ANAL (Fig. B8)

OR: Calibration gradients and intercepts in file STDATA (Fig. B9)

Output: One or more of:

(a) Count ratio file (if direct XRF output used as input)

(b) Analysis file (Fig. B10). This should have LOI values inserted if samples were ignited.

(c) Norminput file (Fig. B11). This is the only output possible if analysis file is used as input.

(d) File STDATA (Fig. B9). This is updated with each new calibration.

Figure B4: Flow diagram of computer processing of XRF data.

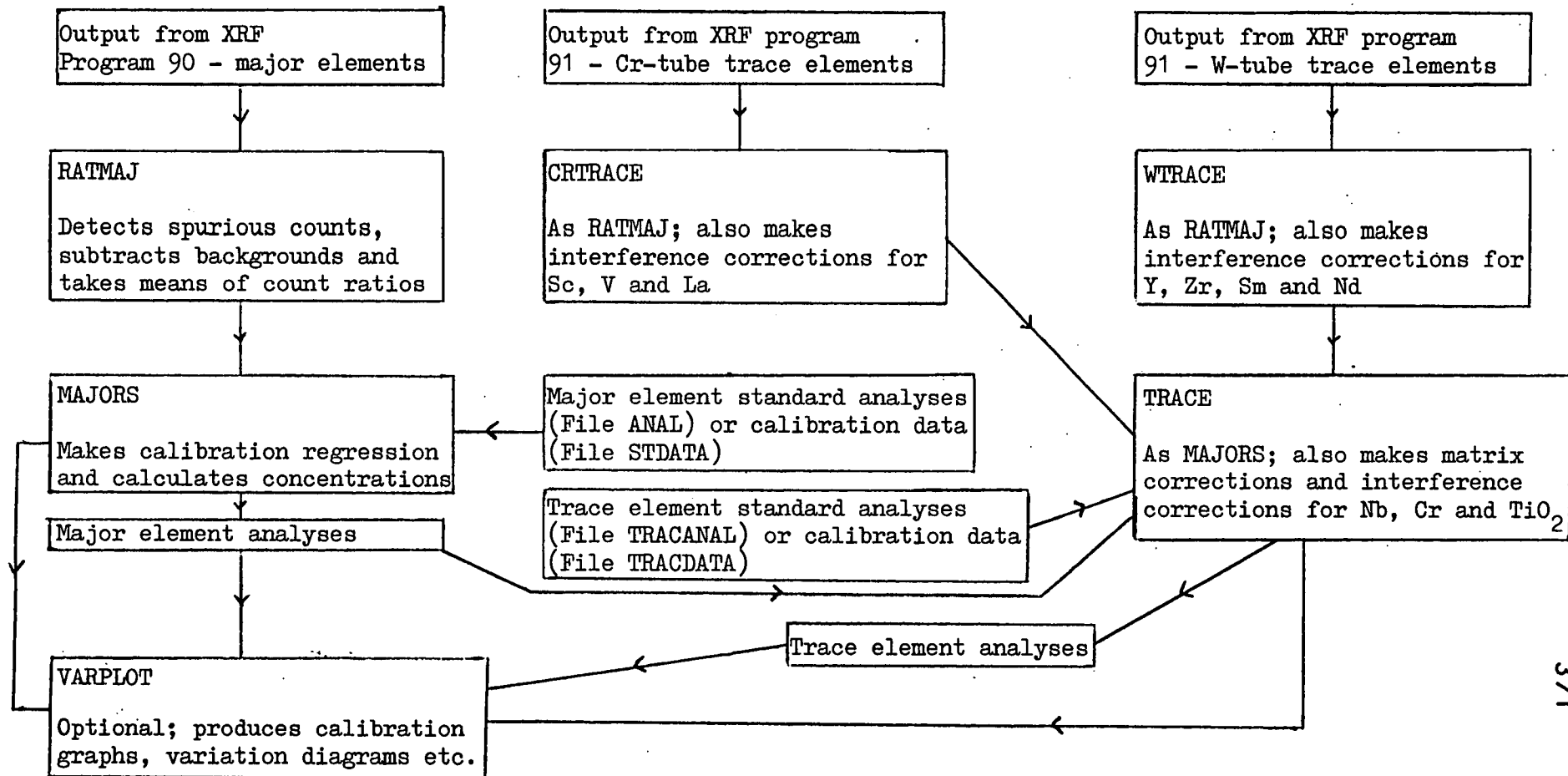


FIG. B5 : Compiled listing of program RATMAJ

```

1374 EXTERNAL ROUTINE RATMAJ
1375 DYNAMICROUTINESPEC RSTRG(STRINGNAME S)
1376 DYNAMICROUTINESPEC RTILLSP(STRINGNAME S)
1377 DYNAMICROUTINESPEC PROMPT(STRING(15) S)
1378 DYNAMICROUTINESPEC DEFINE(STRING(63) S)
1379 INTEGER NOSAMS,V,J,A,E,C,COUNT
1380 STRING(255) S,S1
1381 PROMPT('INPUT FILE: ');RSTRG(S)
1382 DEFINE('ST1','S)
1383 PROMPT('CTRATIOFILE: ');RSTRG(S1)
1384 DEFINE('ST2','S1)
1385 PROMPT('NO.OF SAMPLES: ');READ(NOSAMS)
1386 BEGIN
1387 REALARRAY CR(1:10,1:NOSAMS),RAT(1:3)
1388 CONSTREALARRAY DIFF(1:20)=1,1,3,1,1,7,8,3,2,8,6,5,3,5,10,10,
1389 20,3,100,3,5,250,40
1390 ! FACTORS USED IN DETECTION OF SPURIOUS COUNTS
1391 INTEGERARRAY Z(1:10),INITP,INITB(1:3)
1392 STRING(15) ARRAY NS(1:NOSAMS)
1393 SELECTINPUT(1)
1394 ! READS IN SAMPLE NAMES, SEPARATED BY SPACES.
1395 CYCLE V=1,1,NOSAMS
1396 RTILLSP(NS(V))
1397 REPEAT
1398 V=V+3
1399 1:CYCLE A=1,1,5
1400 RSTRG(S); IF S='999' THEN ->2
1401 ! END OF INPUT MARKER, OTHERWISE READS 5 LINES RUBBISH.
1402 REPEAT
1403 V=V+3
1404 CYCLE J=1,1,10
1405 ! 10 ELEMENTS
1406 CYCLE A=1,1,3
1407 RAT(A)=0
1408 REPEAT
1409 CYCLE C=1,1,3
1410 ! 3 PAIRS OF COUNTS FOR EACH ELEMENT.
1411 READ(Z(J))
1412 ! READS ATOMIC NUMBER OF EACH ELEMENT.
1413 CYCLE A=1,1,3
1414 READ(B)
1415 REPEAT
1416 CYCLE A=1,1,3
1417 ! 3 SAMPLES
1418 READ(COUNT); READ(B)
1419 IF C=1 THEN INITP(A)=COUNT ELSE START
1420 IF !COUNT-INITP(A)!>DIFF(J)*SQRT(INITP(A)) START
1421 ! SPURIOUS PEAK CHECK
1422 NEWLINE
1423 PRINTSTRING('SPURIOUS COUNT FOR ELEMENT ');PRINT(Z(J),2,0)
1424 PRINTSTRING(' SAMPLE ',NS(V+A))
1425 FINISH
1426 FINISH
1427 RAT(A)=RAT(A)+COUNT
1428 ! PEAK ADDED
1429 REPEAT
1430 READ(B); READ(B)
1431 IF C=1 THEN READ(B) AND READ(B)
1432 ! PEAK
1433 CYCLE A=1,1,3
1434 READ(COUNT); READ(B)
1435 IF C=1 THEN RAT(A)=RAT(A)+COUNT ELSE RAT(A)=RAT(A)-COUNT+2
1436 ! ADD PEAK OR SUBTRACT TWICE BACKGROUND
1437 IF C=1 START
1438 IF !COUNT-INITP(A)!>DIFF(J)*SQRT(INITP(A)) START
1439 NEWLINE
1440 PRINTSTRING('SPURIOUS COUNT FOR ELEMENT ');PRINT(Z(J),2,0)
1441 PRINTSTRING(' SAMPLE ',NS(V+A))
1442 FINISH
1443 FINISH
1444 IF C=2 THEN INITB(A)=COUNT
1445 IF C=3 START
1446 ! SPURIOUS BACKGROUND CHECK
1447 IF !COUNT-INITB(A)!>DIFF(J+10) START
1448 NEWLINE
1449 PRINTSTRING('SPURIOUS COUNT FOR BACKGROUND ');PRINT(Z(J),2,0)
1450 PRINTSTRING(' SAMPLE ',NS(V+A))
1451 FINISH
1452 FINISH
1453 REPEAT
1454 REPEAT
1455 CYCLE A=1,1,3
1456 RAT(A)=RAT(A)/40000
1457 CR(J,V+A)=RAT(A)
1458 REPEAT
1459 REPEAT
1460 ->1
1461 2:SELECTOUTPUT(2);SETHARGINS(2,1,130)
1462 SPACES(20)

```


FIG. B5 : continued. Program RATMAJ

```

1463      CYCLE J=1,1,10
1464      PRINT(Z(J),2,0);SPACES(8)
1465      REPEAT
1466      NEWLINES(2)
1467      CYCLE V=1,1,NOSAMS
1468      PRINTSTRING(NS(V)); SPACES(16-LENGTH(NS(V)))
1469      CYCLE J=1,1,10
1470      PRINT(CR(J,V),2,6); SPACE
1471      REPEAT
1472      NEWLINE
1473      REPEAT
1474      END
1475      END

```

FIG. B6 : Example of a major element count ratio file

	14	13	76	12	20	11	19	22	25	15
GA	1.094000	0.795325	0.138275	0.026375	0.161750	0.234650	0.474175	0.084000	0.087175	0.042225
SH	1.195800	0.681975	0.070450	0.003050	0.050025	0.258525	0.550700	0.026475	0.075900	0.003050
BR	0.587200	0.516350	0.636175	0.343075	0.910550	0.211725	0.167475	0.531375	0.155625	0.382825

```

70 ROUTINE INSTRG(STRINGNAME S)
71 SHORTROUTINE
72 INTEGER I
73 S=""
74 UNTIL I=NL CYCLE
75 READSYMBOL (I)
76 S=S.TOSTRING(I)
77 REPEAT
78 LENGTH(S)=LENGTH(S)-1
79 END

80 EXTERNALROUTINE RSTRG(STRINGNAME S)
81 INSTRG(S) UNTIL S=""
82 END

83 RECORDFORMAT MAJF(LONGREALARRAY STPC,STRAT(1:40),LONGREAL CALM,CALC)
84 EXTERNALRECORDARRAY CALIB(1:15) (MAJF)
85 EXTERNALSTRING(15) ARRAY ELNAME(1:15)
86 EXTERNALROUTINE MAJORS
87 DYNAMICINTEGERREFNSPEC INTEGSTR(STRINGNAME S)
88 DYNAMICROUTINESPEC PRELOAD(STRING(63)S)
89 DYNAMICROUTINESPEC DEFINE(STRING(63)S)
90 DYNAMICROUTINESPEC PROMPT(STRING(15)S)
91 DYNAMICROUTINESPEC RSTRG(STRINGNAME S)
92 INTEGER S,C,J,K,V,T,G,EG,SNO,NOSAMS,BLOCK,EXIT
93 STRING(200) STANSUSEC,OMIT,HT,PREL
94 STRING(200) S,S1,S2,S3,POCK,HEAD,TAIL,ANSWER
95 LONGREALARRAY CT(0:3,1:6),PK,BG(0:3,1:10)
96 INTEGERARRAY STAN,Z(1:10),STANINIT,STANFINAL(1:15)
97 PROMPT("INPUT FILE: ");RSTRG(S3)
98 IF S3="" NULL THEN ->60
99 ! .NULL IF INPUT IS FROM "RATMAJ" OUTPUT
100 DEFINE("ST1","S3")
101 60:PROMPT("CTRATIO FILE: ");RSTRG(S1)
102 IF S1="" NULL THEN ->25
103 DEFINE("ST2","S1")
104 25:PROMPT("ANALYSIS FILE: ");RSTRG(S2)
105 IF S2="" NULL THEN ->26
106 NEWLINE
107 PRINTSTRING("DO YOU REQUIRE LOSS ON IGNITION VALUES IN ANALYSIS")
108 PRINTSTRING(" FILE? (Y OR N)");NEWLINE
109 PROMPT("ANSWER: ");RSTRG(ANSWER)
110 DEFINE("ST3","S2")
111 26:PROMPT("NORMINPUTFILE: ");RSTRG(S)
112 IF S="" NULL THEN ->27
113 DEFINE("ST4","S")
114 27:PROMPT("NO. SAMPLES: ");READ(NOSAMS)
115 IF S3="" NULL AND S1="" NULL THEN ->35
116 NEWLINE
117 PRINTSTRING("STATE NO. OF GROUPS OF STANDARDS.")
118 ! NO. OF BATCHES OF STANDARDS IN INPUT SAMPLES
119 NEWLINE
120 PROMPT(" ");READ(BLOCK)
121 OMIT=""
122 IF BLOCK=0 THEN DEFINE("ST7","EGE007.STDATA") AND ->35
123 ! BLOCK=0 IMPLIES NO NEW CALIBRATION
124 PROMPT("PRELOAD? ");RSTRG(PREL)
125 CYCLE Q=1,1,BLOCK
126 PRINTSTRING("STATE POSITION IN SEQUENCE OF SPECIMENS OF FIRST ")
127 PRINTSTRING("STANDARD OF GROUP ")
128 PRINT(Q,1,0);NEWLINE
129 PROMPT(" ");READ(STANINIT(Q))
130 PRINTSTRING("STATE POSITION IN SEQUENCE OF SPECIMENS OF FINAL ")
131 PRINTSTRING("STANDARD OF GROUP ")
132 PRINT(Q,1,0);NEWLINE
133 PROMPT(" ");READ(STANFINAL(Q))
134 REPEAT
135 OMIT="BR 14:DTS1 26:PCC1 26:NBS99A 25:DTS11G 26:"
136 "DTS1BIG 26:PCC11G 26:PCC1BIG 26:"
137 NEWLINE
138 PRINTSTRING("OMIT="OMIT")
139 NEWLINE
140 PROMPT("CHANGE OMIT? ");RSTRG(HEAD)
141 DEFINE("ST7","STDATA")
142 IF HEAD="N" THEN ->35
143 PROMPT("TYPE OMIT: ");RSTRG(OMIT)
144 35:DEFINE("ST6","EGE007.ANAL")
145 CYCLE J=1,1,10; STAN(J)=0 ; REPEAT
146 BEGIN
147 STRING(15) COUNTSATS
148 STRING(10) ARRAY NS(1:3,1:(NOSAMS//3+2))
149 LONGREALARRAY CR(0:3,1:10,1:(NOSAMS//3+2))
150 STRING(17) ARRAY ELEM(1:10)
151 ELEM(1)="SI02"; ELEM(2)="AL203"; ELEM(3)="FE203"; ELEM(4)="PG0";
152 ELEM(5)="CA0"; ELEM(6)="NA20"; ELEM(7)="K20"; ELEM(8)="T102"
153 ELEM(9)="MNO"; ELEM(10)="P205"
154 IF S3="" NULL THEN EG=NOSAMS//3+1 AND ->03
155 ! S3="" NULL IMPLIES INPUT OF RATMAJ OUTPUT

```

FIG. B7 : continued. Program MAJORS

```

156      !
157      ! FOLLOWING LINES RELATE TO PRE-SAMPLE LOADER INPUT
158      SELECTINPUT(1)
159      IF S1='.NULL' THEN ->30
160      SELECTOUTPUT(2); SET MARGINS(2,1,120); SPACES(14)
161      30:EQ=0
162      01:EQ=EQ+1
163      CYCLE C=1,1,3
164      40:RSTRG(ROCK)
165      IF ROCK='999' THEN ->03
166      IF ROCK->HEAD.('<1>').TAIL THEN ->40
167      IF ROCK->HEAD.('') THEN TAIL THEN TAIL->HEAD.(' ').ROCK
168      WHILE ROCK->(' ').ROCK CYCLE:REPEAT
169      NS(C,EQ)<-ROCK
170      REPEAT
171      IF NEXTITEM='<' THEN RSTRG(ROCK)
172      READ(Q);RSTRG(HEAD); CYCLE J=1,1,10
173      READ(Z(J))
174      CYCLE B=1,1,6
175      IF B=1 THEN ->02
176      READ(K)
177      02:READ(SNC)
178      CYCLE C=0,1,3
179      READ(CT(C,B)); READ(T)
180      CT(C,B)=CT(C,B)/(T/1000)
181      REPEAT:REPEAT
182      CYCLE C=0,1,3
183      PK(C,J)=(CT(C,1)+CT(C,2)+CT(C,3))/3
184      BG(C,J)=(CT(C,4)+CT(C,5)+CT(C,6))/3
185      PK(C,J)=PK(C,J)-BG(C,J)
186      REPEAT
187      CYCLE C=1,1,3
188      CR(C,J,EG)=PK(C,J)/PK(C,J)
189      REPEAT
190      IF EQ=1 OR S1='.NULL' THEN ->09
191      PRINT(Z(J),2,0); SPACES(7)
192      09:REPEAT
193      IF S1='.NULL' THEN ->01
194      CYCLE C=1,1,3
195      NEWLINE: IF EQ=1 AND C=1 THEN NEWLINE
196      PRINTSTRING(NS(C,EG)); SPACES(10-LENGTH(NS(C,EG)))
197      CYCLE J=1,1,10
198      PRINT(CR(C,J,EG),2,6); REPEAT: REPEAT
199      ->01
200      !
201      !
202      03:NOSAMS=(EQ-1)*3
203      STANSUSED=''
204      BEGIN
205      STRING(7) TO
206      INTEGER BG
207      STRING(4) END
208      STRING(2) A
209      LONGREALARRAY P,R,ANALYSIS(1:10,1:NOSAMS)
210      LONGREALARRAY MA,CX,ERR,EP,ER,ERP(1:10),LOI,TOT(1:NOSAMS)
211      STRING(200) STNO
212      STRING(10) ARRAY NO(1:NOSAMS)
213      BG=-2
214      END='-1'; A='.'
215      IF S3='.NULL' AND S1='.NULL' THEN ->33
216      IF S3='.NULL' THEN ->61
217      CYCLE EQ=1,1,(NOSAMS//3)
218      CYCLE C=1,1,3
219      V=3*EQ+C-3
220      CYCLE J=1,1,10
221      R(J,V)=CR(C,J,EQ); NO(V)=NS(C,EQ)
222      REPEAT: REPEAT
223      REPEAT
224      !
225      ! START OF TREATMENT OF RATMAJ OUTPUT
226      61: IF S3='.NULL' THEN ->62
227      SELECTINPUT(2)
228      CYCLE J=1,1,10; READ(Z(J)); REPEAT
229      ! READS ATOMIC NUMBER
230      CYCLE V=1,1,NOSAMS
231      RTILLSP(NO(V))
232      ! READS SAMPLE NAME
233      CYCLE J=1,1,10
234      READ(R(J,V))
235      REPEAT:REPEAT
236      ! READS TEN COUNT RATIOS
237      62:CYCLE J=1,1,10
238      ERR(J)=0; EP(J)=0; ER(J)=0; ERP(J)=0
239      REPEAT
240      IF BLOCK=0 THEN ->11 ELSE ->12
241      11:SELECTINPUT(7)
242      ! NO RECALIBRATION, INPUT FROM STDATA
243      CYCLE J=1,1,10
244      RTILLSP(ELEM(J)); READ(MA(J)); READ(CX(J))
245      ! READS ATOMIC NUMBER, CALIBRATION GRADIENT AND INTERCEPT

```

FIG. B7 : continued. Program MAJORS

```

246 REPEAT: ->06
247 !
248 ! RECALIBRATION.
249 12: IF PREL='Y' THEN PRELOAD(**)
250 CYCLE J=1,1,10
251 ELNAME(J)=ELEM(J)
252 REPEAT
253 SELECTINPUT(6)
254 ! INPUT FROM ANAL
255 !
256 ! GOES THROUGH EACH STANDARD IN INPUT COUNT RATIO FILE, AND TRIES TO
257 ! FIND SAME NAME AMONG STANDARDS IN ANAL. STANDARD NAMES SHOULD BE
258 ! EXACTLY AS WRITTEN ON DISC LABEL
259 CYCLE Q=1,1,BLOCK
260 CYCLE V=STANINIT(Q),1,STANFINAL(Q)
261 05: RSTRG(STNO): IF STNO='STOP' THEN ->13
262 IF STNO#NO(V) THEN ->06 ELSE ->07
263 06: RSTRG(STNO): ->05
264 07: STANSUSED<-STANSUSED.' 'STNO
265 ! A CORRESPONDING NAME HAS BEEN FOUND, AND IS ADDED TO A LIST OF STANDARD
266 ! USED IN THE CALIBRATION
267 CYCLE J=1,1,10
268 READ(P(J,V))
269 ! READS 10 STANDARD PERCENT OXIDES, IN USUAL ORDER
270 IF OMIT->HEAD.(STNO.' ').TAIL START
271 B13: CYCLE EQ=1,1,LENGTH(TAIL)
272 EXIT=740
273 IF CHARNO(TAIL,EQ)='': OR CHARNO(TAIL,EQ)='.' START
274 HT=FROMSTRING(TAIL,1,EQ-1)
275 IF Z(J)=INTEGSTR(HT) THEN EXIT=750 G
276 C AND EXIT
277 IF CHARNO(TAIL,EQ)='.' THEN EXIT
278 TAIL->HEAD.(.' ').TAIL
279 EXIT=730: EXIT
280 FINISH
281 REPEAT
282 IF EXIT=750 THEN ->A13
283 IF EXIT=730 THEN ->E11
284 FINISH
285 ! LAST 15 LINES CAUSE EXCLUSION OF STANDARDS IN 'OMIT' FROM CALIBRATION
286 !
287 STAN(J)=STAN(J)+1
288 ! STAN(J)= NO. OF STANDARDS USED IN JTH CALIBRATION
289 CALIB(J)_STPC(STAN(J))=P(J,V)
290 CALIB(J)_STRAT(STAN(J))=R(J,V)
291 ! CORE STORE RECORDS SET TO STANDARD PERCENTS AND RATIOS
292 EP(J)=EP(J)+P(J,V): ER(J)=ER(J)+R(J,V)
293 ! EP= SUM OF PERCENTS, ER = SUM OF RATIOS
294 ERR(J)=ERR(J)+(R(J,V))**2
295 ERP(J)=ERP(J)+(R(J,V))*(P(J,V))
296 ! ERR = SUM OF SQUARES OF RATIOS, ERP = SUM OF PERCENT-RATIO PRODUCTS
297 A13: REPEAT
298 13: SELECTINPUT(98): CLOSESTREAM(6): SELECTINPUT(6)
299 REPEAT: REPEAT
300 SELECTOUTPUT(7)
301 CYCLE J=1,1,10
302 CYCLE BQ=1,1,24
303 IF CALIB(J)_STPC(BQ)=0 THEN CALIB(J)_STPC(BQ)=.00001
304 ! SETS ANY REMAINING ZERO VALUES TO .00001 PREVENTS PLOTTING
305 ! OF ZERO POINTS.
306 REPEAT
307 MA(J)=(STAN(J)*ERP(J)-(ER(J))*(EP(J)))/(STAN(J)*ERP(J)-(ER(J))**2)
308 CX(J)=(EP(J)*ERR(J)-ER(J)*ERP(J))/(STAN(J)*ERR(J)-(ER(J))**2)
309 CALIB(J)_CALM=MA(J)
310 CALIB(J)_CALC=CX(J)
311 ! OUTPUTTING OF NEW CALIBRATION DATA TO STDATAM4
312 PRINTSTRING(ELEM(J)): SPACES(12-LENGTH(ELEM(J)))
313 PRINT(MA(J),4,5): SPACES(2)
314 PRINT(CX(J),3,5): NEWLINE: REPEAT
315 NEWLINES(2): PRINTSTRING(STANSUSED)
316 ! PRINTS LIST OF STANDARDS USED IN CALIBRATION
317 !
318 08: IF S2='NULL' THEN ->33
319 IF ANSWER='N' THEN ->NOL
320 SELECTINPUT(98): SELECTOUTPUT(99)
321 ! RETURNS OUTPUT/INPUT TO INTERACTIVE TERMINAL
322 NEWLINE
323 PRINTSTRING('LIST LOSS ON IGNITION VALUE IN RESPONSE TO PROMPT')
324 PRINTSTRING(' OF SAMPLE NAME.')
325 NEWLINE
326 CYCLE V=1,1,NOSAMS
327 PROMPT(NO(V).'. '): READ(LOC(V))
328 REPEAT
329 !
330 ! PRINTING OF ANALYSIS FILE
331 NOL: SELECTOUTPUT(3): SET MARGINS(3,1,120)
332 ELEM(3)='FE2O3'
333 SPACES(11)
334 CYCLE J=1,1,10
335 PRINTSTRING(ELEM(J)): SPACES(9-LENGTH(ELEM(J))): IF J=3 THEN SPACE

```

FIG. B7 : continued. Program MAJORS

```

335      REPEAT
336      TO="TOTAL"
337      SPACE
338      PRINTSTRING(TO)
339      IF ANSWER="N" THEN->NL
340      SPACES(6)
341      PRINTSTRING('LOI')
342      NL:NEWLINE
343      CYCLE V=1,1,NOSAMS
344      NEWLINES(2)
345      TOT(V)=0
346      PRINTSTRING(NO(V)); SPACES(9-LENGTH(NO(V)))
347      CYCLE J=1,1,10
348      ANALYSIS(J,V)=MA(J)*R(J,V)+CX(J)
349      ! CALCULATES ANALYSIS AND SUMS TOTAL OXIDES
350      TOT(V)=TOT(V)+ANALYSIS(J,V)
351      REPEAT
352      CYCLE J=1,1,10
353      PRINT(ANALYSIS(J,V),3,3);SPACE
354      REPEAT
355      SPACES(2); PRINT(TOT(V),3,3)
356      IF ANSWER="Y" THEN SPACES(4) AND PRINT(LOI(V),1,2)
357      REPEAT
358      NEWLINES(4)
359      PRINTSTRING('STOP')
360      ! *STOP* FORMS ANALYSIS FILE TERMINATOR WHEN USED FOR MATRIX CORRECTIONS
361      NEWLINES(8)
362      CYCLE J=1,1,10
363      PRINT(Z(J),2,0);PRINT(MA(J),4,5);PRINT(CX(J),5,5)
364      NEWLINE
365      REPEAT
366      NEWLINES(2);PRINTSTRING(STANSUSED)
367      NEWLINES(2);PRINTSTRING(OMIT)
368      ! LAST SIX LINES PRINT COPY OF STDATA AT END OF ANALYSIS FILE
369      !
370      33:IF S="NULL" THEN ->23
371      SELECTOUTPUT(4)
372      IF S3="NULL" AND S1="NULL" START
373      ! TAKES ANALYSIS FILE INPUT AND PRODUCES NORMINPUT FILE
374      SELECTINPUT(3)
375      CYCLE J=1,1,10
376      RTILLSP(ELEM(J)); REPEAT
377      RSTRG(STNO)
378      CYCLE V=1,1,NOSAMS
379      RTILLSP(NO(V))
380      CYCLE J=1,1,10
381      READ(ANALYSIS(J,V))
382      REPEAT
383      RSTRG(STNO)
384      REPEAT
385      ->X23
386      FINISH
387      CYCLE V=1,1,NOSAMS; CYCLE J=1,1,10
388      ANALYSIS(J,V)=MA(J)*R(J,V)+CX(J)
389      REPEAT:REPEAT
390      ! PRINTING OF NORMINPUT FILE
391      X23:CYCLE V=1,1,NOSAMS
392      ELEM(3)="FE2O3"
393      PRINTSTRING(NO(V));
394      PRINTSTRING(A);NEWLINE
395      CYCLE J=1,1,10
396      ! ROUTINE TAKES STANDARD ANALYSIS AND PUTS IT INTO ARRAY MAJ
397      PRINTSTRING(ELEM(J));PRINT(ANALYSIS(J,V),3,3);SPACE
398      IF J=5 THEN NEWLINE
399      REPEAT
400      NEWLINE
401      IF V=NOSAMS THEN PRINTSTRING(END) ELSE PRINT(B0,2,0)
402      NEWLINE
403      REPEAT
404      23:END

435      29:END
?  UNUSED LABEL      29
?  UNUSED NAME COUNTPTS

406      END

```

AGV11G
 60.074 17.322 6.881 1.559 5.030 4.336 2.947 1.056 0.098 0.503
 BCR11G
 54.844 13.679 13.519 3.490 6.979 3.290 1.680 2.220 0.190 0.330
 OTS11G
 40.676 0.290 8.599 49.825 0.150 0.007 0.001 0.013 0.110 0.002

FIG. B8 : Part of file ANAL -
 major element standard data

14	59.72945	4.51928
13	18.47972	0.19681
26	20.68417	-0.10829
12	37.66466	0.00285
20	15.28127	-0.02784
11	15.96797	-0.26075
19	8.60696	-0.04338
22	4.97556	-0.05071
25	1.69021	-0.07403
15	2.75345	0.00403

FIG. B9 : Example of file STDATA -
 gradients and intercepts of
 major element calibrations

	SI02	AL203	FE203T	MGO	CAO	NA2O	K2O	TI02	MNO	P2O5	TOTAL	LOI
AY126	63.795	18.148	3.643	1.620	3.516	4.493	3.368	1.002	0.035	0.191	99.808	1.38
AY2213	60.810	18.150	5.642	2.275	3.605	3.838	3.587	0.992	0.036	0.190	99.124	1.75
AY3211	50.335	17.747	7.245	5.574	12.308	3.687	1.238	1.279	0.085	0.238	99.735	8.63

FIG. B10 : Example
 of major element
 analysis file

AY126
 SI02 63.795 AL203 18.148 FE203 3.643 MGO 1.620 CAO 3.516 NA2O 4.493
 K2O 3.368 TI02 1.002 MNO 0.035 P2O5 0.191 LOI 1.38
 NI 15.1 CR 11.5 V 133.1 SC 15.1 CU 14.9 ZN 142.6
 SR 300.1 RB 70.4 ZR 188.2 NB 9.9 BA 532.7 TH 12.3
 LA 20.9 CE 50.9 ND 23.1 SM 5.1 Y 18.9 TI02CR 1.078 TI02W 1.045
 -1

AY2213
 SI02 60.810 AL203 18.150 FE203 5.642 MGO 2.275 CAO 3.605 NA2O 3.838
 K2O 3.587 TI02 0.992 MNO 0.036 P2O5 0.190 LOI 1.75
 NI 14.6 CR 10.0 V 124.0 SC 15.5 CU 13.9 ZN 80.8
 SR 314.5 RB 78.4 ZR 187.2 NB 8.9 BA 676.3 TH 13.5
 LA 22.8 CE 49.5 ND 22.9 SM 3.2 Y 21.2 TI02CR 1.018 TI02W 1.014
 -1

FIG. B11 : Example of a
 norminput file, complete with
 major and trace element data.

(e) External records CALIB and ELNAME if option PRELOAD:Y is chosen. These records are held in core storage until log-off, and form the necessary input to program VARPLOT, if calibration graphs are to be plotted.

Calibration uses regression to solve for m^i and c^i in the equation

$$X_s^i = m^i R_s^i + c^i$$

Analogous variables in the program are $i=J$, $s=V$, $X_s^i = P(J,V)$, $R_s^i = R(J,V)$, $m^i = MA(J)$, $c^i = CX(J)$. It is assumed that precision errors on count ratios are substantially smaller than errors in the standard concentrations, and the regression has therefore been carried out by minimizing the sum of squares of errors in concentrations. This assumption is not strictly valid, but several regression procedures have been tested which have little difference in practice.

For a sample s , the error Δ_s is given by :

$$\Delta_s = mR_s + c - X_s \quad \text{for constant } i$$

so that sum of squares of errors is given by

$$\sum_1^N \Delta_s^2 = (mR_s + c - X_s)^2$$

where N = total number of standards used in i th calibration. At the minimum,

$$\frac{\partial \sum \Delta_s^2}{\partial m} = 0 \quad , \quad \text{and} \quad \frac{\partial \sum \Delta_s^2}{\partial c} = 0$$

Therefore $\sum_{s=1}^N 2R_s (mR_s + c - X_s) = 0$ and $\sum_{s=1}^N 2(mR_s + c - X_s) = 0$

$$m \sum R_s^2 + c \sum R_s - \sum R_s X_s = 0 \quad \text{and} \quad m \sum R_s + Nc - \sum X_s = 0$$

substituting into the first equation gives

$$Nm \sum R_s^2 + \sum X_s \sum R_s - m \sum R_s \sum R_s - N \sum R_s X_s = 0$$

and
$$m = \frac{N \sum R_s X_s - \sum X_s \sum R_s}{N \sum R_s^2 - \sum R_s \sum R_s}$$

Converting to the variable names in the program gives

$$MA(J) = \frac{STAN(J) \cdot ERP(J) - ER(J) \cdot EP(J)}{STAN(J) \cdot ERR(J) - ER(J) \cdot ER(J)}$$

and, substituting, the value of $CX(J)$.

(111) CRIRACE (Fig. B12)

Source file: XRFS ; Object file XRFY

Input data: file of XRF data from Cr-tube program 91 (Table B9) with initial sample names and terminal 999.

Output data: One or both of

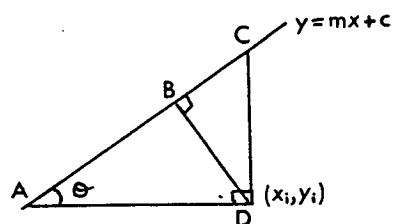
Count ratio file, comparable to Fig. B6, uncorrected for interferences,

Corrected file, of count ratios corrected for interference of Ca on Sc, Ti on V and La.

Spurious counts for both peak and background are detected if subsequent counts exceed the first by a constant amount (DIFF(J)).

The program is very similar to RATMAJ, but includes interference regressions. It was considered that the method of minimizing errors in one of the variables, as used for the major element calibration regression, was unsatisfactory when errors on the two variables were of the same order, and a method of regression which minimizes errors normal to the eventual line was derived as follows.

Consider a point (x_i, y_i) a short distance Δ_i away from the eventual line of equation $y=mx+c$,



Point A has co-ordinates $(\frac{y_i - c}{m}, y_i)$
 Point C has co-ordinates $(x_i, mx_i + c)$
 Therefore,

$$CD = mx_i + c - y_i$$

$$\text{and } AD = x_i + (c - y_i)/m$$

$$BD = \Delta_i = CD \cos \theta = AD \sin \theta$$

and since $\sin^2 \theta + \cos^2 \theta = 1$,

$$\frac{\Delta_i^2}{CD^2} + \frac{\Delta_i^2}{AD^2} = 1$$

and sum of squares of errors

$$\sum_i \Delta_i^2 = \sum_i \frac{CD^2 \cdot AD^2}{CD^2 + AD^2} = \sum_i \frac{(mx_i + c - y_i)^2 (x_i + \frac{c - y_i}{m})^2}{(mx_i + c - y_i)^2 + (x_i + \frac{c - y_i}{m})^2}$$

and multiplying through by m^2 ,

$$\sum_i \Delta_i^2 = \sum_i \frac{(mx_i + c - y_i)^2}{m^2 + 1}$$

For a stationary point, $\frac{\partial \Delta_i^2}{\partial m} = 0$ and $\frac{\partial \Delta_i^2}{\partial c} = 0$

$$\sum_{i=1}^N \Delta_i^2 = \frac{\sum y_i^2 - 2m \sum x_i y_i + 2cm \sum x_i - 2c \sum y_i + m^2 \sum x_i^2 + Nc^2}{m^2 + 1}$$

As before, two simultaneous equations are given

$$\textcircled{1} \quad \frac{\partial}{\partial c} \Delta_i^2 = \frac{2}{m^2 + 1} \sum_i (mx_i - y_i + c) = 0 \quad \Rightarrow \quad c = \frac{\sum y_i - m \sum x_i}{N}$$

$$\textcircled{2} \quad \frac{\partial}{\partial m} \Delta_i^2 = \frac{2}{m^2 + 1} \sum_i (cx_i - x_i y_i + mx_i^2) - \frac{2m}{(m^2 + 1)^2} \sum_i (y_i - mx_i - c)^2 = 0$$

$$\therefore (m^2 + 1) \sum_i (cx_i - x_i y_i + mx_i^2) = m \sum_i (y_i - mx_i - c)^2$$

$$\text{or } m \sum y_i^2 + (1 - m^2) \sum x_i y_i + c(m^2 - 1) \sum x_i - 2cm \sum y_i - m \sum x_i^2 + Nmc^2 = 0$$

Substituting for c and multiplying through by N ,

$$\begin{aligned}
 N \sum y_i^2 + N(1-m^2) \sum x_i y_i + (m^2-1)(\sum x_i \sum y_i - m \sum x_i \sum x_i) \\
 - 2m \sum y_i (\sum y_i - m \sum x_i) - mN \sum x_i^2 + m(\sum y_i - m \sum x_i)^2 = 0 \\
 \therefore m^2(\sum y_i \sum x_i - N \sum x_i y_i) + m[N \sum y_i^2 + \sum x_i \sum x_i - \sum y_i \sum y_i - N \sum x_i^2] \\
 + N \sum x_i y_i - \sum y_i \sum x_i = 0
 \end{aligned}$$

In the programs, $\sum y_i \sum x_i - N \sum x_i y_i = \text{REA}$ and

$N \sum y_i^2 - N \sum x_i^2 + (\sum x_i)^2 - (\sum y_i)^2 = \text{REB}$, so that

$$\text{REAM}^2 + \text{REBm} - \text{REA} = 0$$

Two values for m and c are produced, corresponding to a maximum and a minimum in the $\sum \Delta_i^2 - m - c$ relation. The values producing minimum sum of squares of errors are determined by substitution of the two pairs of m, c values into this relation. The method of regression has been used for interference corrections in CRTRACE and WTRACE, and for the trace element calibration regressions.

By replying 'Y' to the prompt P-B/B?, it is possible to obtain output of count ratios divided by background, i.e. the Anderman-Kemp matrix correction method. This may be run for comparison between the different methods of matrix correction.

(iii) WTRACE (Fig. B13)

Source_file: XRFS ; Object_file: XRFY

Input_data: file of XRF data from W-tube program 91 (Table B10), with initial sample names and terminal 999.

Output_data: comparable to CRTRACE.

The program is very similar to CRTRACE, but spurious counts are detected in the same manner as in RATMAJ. Backgrounds are interpolated assuming linearity between two background positions.

(iv) TRACE (Fig. B14)

Source_file: XRFS ; Object_file: XRFY

Input_data: a combination of

- (a) File of direct XRF output from pre-sample loader program
- (b) Count ratio file (corrected) from CRTRACE or WTRACE or an analogous program, e.g. ODDTRACE
- (c) Mass absorption corrected count ratio file, previously output by TRACE
- (d) Concentrations of standards in file TRACANAL (Fig. B15)
- (e) Calibration gradients and intercepts in file TRACDATA (similar to STDATA)
- (f) Major element compositions of samples analysed (and any others) in analysis file format (Fig. B10)
- (g) Major element compositions as (f) with LOI
- (h) Major element compositions as norminput file (Fig. B11)
- (i) As (h) with LOI
- (j) Major and trace element compositions in norminput

```

1476 EXTERNAL ROUTINE CRTRACE
1477 DYNAMIC ROUTINESPEC $STRG($STRINGNAME $)
1478 DYNAMIC ROUTINESPEC $TILLSP($STRINGNAME $)
1479 DYNAMIC ROUTINESPEC $DEFINE($STRING($3) $)
1480 DYNAMIC ROUTINESPEC $PROMPT($STRING($15) $)
1481 INTEGER NOSAMS,V,J,A,B,C,D
1482 STRING(200) S,S1,REGRESS
1483 PROMPT('INPUT FILE: ');RSTRG(S)
1484 DEFINE('ST1','S)
1485 PROMPT('CTRATIO FILE: ');RSTRG(S1)
1486 IF S1='NULL' THEN->1
1487 DEFINE('ST2','S1)
1488 3:PROMPT('CORRECTED FILE: ');RSTRG(S)
1489 DEFINE('ST3','S)
1490 PRINTSTRING('REGRESSION FOR INTERFERENCE CORRECTION? (Y OR N)')
1491 NEWLINE:PROMPT('ANSWER: ');RSTRG(REGRESS)
1492 ! THIS REGRESSION ONLY FEASIBLE IF SAMPLES IN FILE INCLUDE
1493 ! INTSG, INTSE, INTSA, INTSBT1, INTSAT1.
1494 PROMPT('NO. OF SAMPLES: ');READ(NOSAMS)
1495 BEGIN
1496 STRING(20) ARRAY NS(1:NOSAMS)
1497 REALARRAY CA,TI(1:NOSAMS),CR(1:5,1:NOSAMS),BG(1:6,1:NOSAMS)
1498 CONST SHORT INTEGERARRAY DIFF(1:10)=30,60,200,100,50,25,30,160,30,40
1499 ! FACTORS USED IN DETECTION OF SPURIOUS COUNTS
1500 INTEGERARRAY Z(1:5),INITP,INITB,RAT(1:3)
1501 D=0
1502 SELECT INPUT(1)
1503 CYCLE V=1,1,NOSAMS
1504 RTILLSP(NS(V));CA(V)=0;TI(V)=0
1505 ! READS IN SAMPLE NAMES
1506 CYCLE B=1,1,5;BG(B,V)=0;REPEAT
1507 REPEATIV=-3
1508 1:CYCLE B=1,1,4
1509 RSTRG(S);IF S='999' THEN->2;REPEAT
1510 ! END OF FILE MARKER
1511 V=V+3
1512 CYCLE J=1,1,5
1513 CYCLE A=1,1,3;RAT(A)=0;REPEAT
1514 IF J=1 OR J=2 START
1515 ! READS IN PRESET TIME CA AND TI - NEEDS CHANGING
1516 9: CYCLE A=1,1,3
1517 READ(B);READ(B)
1518 CYCLE B=1,1,3
1519 READ(C);RAT(B)=RAT(B)+C;READ(C)
1520 REPEAT:REPEAT
1521 IF D=999 THEN->10
1522 CYCLE A=1,1,3
1523 IF J=1 THEN CA(V+A)=RAT(A)/2000000 ELSE TI(V+A)=RAT(A)
1524 REPEAT
1525 CYCLE A=1,1,3;RAT(A)=0;REPEAT
1526 IF J=1 THEN->8
1527 D=999
1528 ->9
1529 10: CYCLE B=1,1,3
1530 TI(V+B)=(TI(V+B)-2.5+RAT(B))/200000 ; !UNITS COUNTS/MILLISEC//10
1531 BG(6,V+B)=RAT(B)/5000
1532 RAT(B)=0
1533 REPEAT
1534 D=0
1535 8: FINISH
1536 CYCLE A=1,1,4
1537 READ(Z(J));READ(B);READ(B);READ(B)
1538 CYCLE B=1,1,3
1539 READ(C);RAT(B)=RAT(B)+C
1540 IF A=1 THEN INITP(B)=RAT(B) ELSE START
1541 IF !C=INITP(B)!>DIFF(J) START
1542 NEWLINE
1543 PRINTSTRING('SPURIOUS COUNT FOR ELEMENT ');PRINT(Z(J),2,0)
1544 PRINTSTRING(' SAMPLE *.NS(V+B))
1545 FINISH
1546 FINISH
1547 READ(C)
1548 REPEAT:READ(B);READ(B)
1549 CYCLE B=1,1,3
1550 READ(C);RAT(B)=RAT(B)+C
1551 IF A=1 THEN INITB(B)=C ELSE START
1552 IF !C=INITB(B)!>DIFF(J+5) START
1553 NEWLINE
1554 PRINTSTRING('SPURIOUS COUNT FOR BACKGROUND ');PRINT(Z(J),2,0)
1555 PRINTSTRING(' SAMPLE *.NS(V+B))
1556 FINISH
1557 FINISH
1558 BG(J,V+B)=BG(J,V+B)+C
1559 READ(C)
1560 REPEAT:REPEAT
1561 CYCLE A=1,1,3
1562 CR(J,V+A)=RAT(A)/40000
1563 BG(J,V+A)=BG(J,V+A)/40000
1564 REPEAT:REPEAT->21

```

FIG. B12 : continued. Program CRTRACE

```

1565      2: IF S1='NULL' THEN=>4
1566      SELECTOUTPUT(2); SETMARGINS(2,1,130)
1567      SPACES(20)
1568      CYCLE J=1,1,5
1569      PRINT(Z(J),2,0); SPACES(8)
1570      REPEAT
1571      PRINTSTRING('CAKB      TIME')
1572      NEWLINES(2)
1573      CYCLE V=1,1,NOSAMS
1574      PRINTSTRING(NS(V)); SPACES(16-LENGTH(NS(V)))
1575      CYCLE J=1,1,5
1576      PRINT(CR(J,V),2,6); SPACE
1577      REPEAT
1578      SPACES(6); PRINT(CA(V),4,6); SPACE; PRINT(TI(V),4,6)
1579      NEWLINE; REPEAT
1580      4: BEGIN
1581      LONGREAL ARRAY MA,CX(1:6),EYY,EX,EY,EXY,EXX(1:3)
1582      INTEGER NOPPOINTS; REAL REB,REA,REC
1583      IF REGRESS='N' START
1584      SELECTOUTPUT(99); SELECTINPUT(98)
1585      MA(1)=.084735; MA(2)=.116606; MA(3)=.007956
1586      ! INTERFERENCE CORRECTION GRADIENTS DERIVED BY EARLIER
1587      ! REGRESSION (1=SC, 2=V, 3=LA)
1588      ->5
1589      FINISH
1590      ! REGRESSION AS IN WTRACE
1591      NOPPOINTS=0
1592      CYCLE C=1,1,3
1593      EYY(C)=0; EX(C)=0; EY(C)=0; EXY(C)=0; EXX(C)=0
1594      REPEAT
1595      CYCLE V=1,1,NOSAMS
1596      UNLESS NS(V)->('INT') S THEN=>6
1597      IF CHARNO(NS(V),6)='R' THEN=>6
1598      EX(1)=EX(1)+CA(V)
1599      EX(2)=EX(2)+TI(V)
1600      EX(3)=EX(3)+TI(V)
1601      EXX(1)=EXX(1)+CA(V)**2
1602      EXX(2)=EXX(2)+TI(V)**2
1603      EXX(3)=EXX(3)+TI(V)**2
1604      EXY(1)=EY(1)+CA(V)*CR(1,V)
1605      EXY(2)=EY(2)+TI(V)*CR(2,V)
1606      EXY(3)=EY(3)+TI(V)*CR(5,V)
1607      CYCLE C=1,1,3
1608      IF C=3 THEN A=5 ELSE A=C
1609      EY(C)=EY(C)+CR(A,V)
1610      EYY(C)=EYY(C)+CR(A,V)**2
1611      REPEAT
1612      NOPPOINTS=NOPPOINTS+1
1613      6: REPEAT
1614      CYCLE C=1,1,3
1615      REB=NOPPOINTS*EYY(C)-NOPPOINTS*EXX(C)+EX(C)**2-EY(C)**2
1616      REA=EY(C)+EX(C)-NOPPOINTS*EXY(C)
1617      MA(C)=(-REB+SQRT(REB**2+4*REA**2))/(2*REA)
1618      MA(C+3)=(-REB-SQRT(REB**2+4*REA**2))/(2*REA)
1619      CX(C)=(EY(C)-MA(C)*EX(C))/NOPPOINTS
1620      CX(C+3)=(EY(C)-MA(C+3)*EX(C))/NOPPOINTS
1621      REPEAT
1622      SELECTOUTPUT(99); SELECTINPUT(98)
1623      CYCLE C=1,1,3
1624      CYCLE B=0,1,1
1625      REC='A(C+3)**2+1
1626      REC=(EY(C)-2*MA(C+3)*RE)*EXY(C)+2*CX(C+3)*B*MA(C+3)*EY(C) C
1627      -2*CX(C+3)*B*EY(C) C
1628      +EXX(C)+MA(C+3)*B**2+NOPPOINTS*CX(C+3)*B**2)/REC
1629      IF B=0 THEN REA=REC
1630      REPEAT
1631      IF REC<REA THEN MA(C)=MA(C+3) AND CX(C)=CX(C+3)
1632      IF C=1 THEN S='SC'; IF C=2 THEN S='V'; IF C=3 THEN S='LA'
1633      PRINTSTRING('INTERFERENCE CORRECTION FOR *.S.* IS')
1634      PRINT(MA(C),2,6)
1635      PRINTSTRING('COUNT RATIO *.S.* PER UNIT INTERFERING ELEMENT')
1636      NEWLINE
1637      PRINTSTRING('INTERCEPT OF CORRECTION IS AT COUNT RATIO ')
1638      PRINT(CX(C),2,6)
1639      NEWLINE
1640      REPEAT
1641      5: NEWLINE; PRINTSTRING('LA CORRECTION? (Y OR N)')
1642      ! LA CORRECTION PERHAPS NOT NEEDED IF FINE COLLIMATOR USED.
1643      NEWLINE; PROMPT(' '); RSTRG(REGRESS)
1644      PROMPT('P-B/9? '); RSTRG(S1)
1645      ! *Y* FOR ANDERMAN-KEMP CORRECTION
1646      SELECTOUTPUT(3); SETMARGINS(3,1,130); SPACES(20)
1647      CYCLE J=1,1,5; PRINT(Z(J),2,3); SPACES(8); REPEAT
1648      PRINTSTRING('17')
1649      NEWLINES(2)
1650      CYCLE V=1,1,NOSAMS
1651      CR(1,V)=CR(1,V)-MA(1)*CA(V)
1652      CR(2,V)=CR(2,V)-MA(2)*TI(V)
1653      IF REGRESS='N' THEN=>7
1654      CR(5,V)=CR(5,V)-MA(3)*TI(V)

```

FIG. B12 : continued. Program CRTRACE

```

1653      7:PRINTSTRING(NS(V));SPACES(16-LENGTH(NS(V)))
1654      IF S1='Y' THEN TI(V)=TI(V)/B6(6,V)
1655      CYCLE J=1,1.5
1656      IF S1='Y' THEN CR(J,V)=CR(J,V)/B6(J,V)
1657      ! ANDERMAN-KEMP CORRECTION
1658      PRINT(CR(J,V),2,6);SPACE
1659      REPEAT
1660      PRINT(TI(V),4,6)
1661      NEWLINE
1662      REPEAT
1663      END
1664      END
1665      END

```

FIG. B13 : Compiled listing of program WTRACE

```

1666 EXTERNAL ROUTINE WTRACE
1667 DYNAMIC ROUTINE SPEC RSTRG (STRINGNAME S)
1668 DYNAMIC ROUTINE SPEC RTILLSP (STRINGNAME S)
1669 DYNAMIC ROUTINE SPEC DEFINE (STRING (63) S)
1670 DYNAMIC ROUTINE SPEC PROMPT (STRING (13) S)
1671 INTEGER NOSAMS,V,J,A,B,C,EUNG,INDTIME,THMON
1672 LONGREAL RE1,RE2
1673 STRING(20) S,S1,REGRESS,PB
1674 PROMPT ('INPUT FILE: ');RSTRG(S)
1675 DEFINE ('ST1','S')
1676 PROMPT ('CTRATIO FILE: ');RSTRG(S1)
1677 IF S1='NULL' THEN-23
1678 DEFINE ('ST2','S1')
1679 3: PROMPT ('CORRECTED FILE: ');RSTRG(S)
1680 DEFINE ('ST3','S')
1681 PRINTSTRING ('REGRESSION FOR INTERFERENCE CORRECTION? (Y OR N)')
1682 NEWLINE; PROMPT ('ANSWER: ');RSTRG(REGRESS)
1683 ! REGRESSION ONLY POSSIBLE IF WIDE RANGE OF INTERFERENCE STANDARDS
1684 ! INCLUDED
1685 PROMPT ('NO. OF SAMPLES: '); READ (NOSAMS)
1686 BEGIN
1687 STRING(20) ARRAY NS(1:NOSAMS)
1688 REALARRAY CR(1:13,1:NOSAMS),INITP,INIB,RAT(1:3),TIME(1:13) C
1689 ! SG(1:13,1:NOSAMS)
1690 CONSTREALARRAY DIFF(1:26)=1.3,1.3,.5,.8,1..8..8,1..7,2.3,1.7,2.5,
1691 ! 15,15.8,20.0,70.0,70.0,0,120,100,35
1692 ! FACTORS USED IN DETECTION OF SPURIOUS COUNTS
1693 INTEGERARRAY Z,MONCOUNT(1:13),THB(1:3)
1694 SELECTINPUT (1)
1695 CYCLE V=1,1,NOSAMS
1696 CYCLE J=1,1,13
1697 BG (J,V)=0
1698 REPEAT
1699 RTILLSP (NS(V))
1700 DEFERAT V=-3
1701 BUNG =3
1702 !
1703 B1 =V+BUNG
1704 BUNG =0
1705 1: PSTRG (S)
1706 WHILE S->(' ') S CYCLE; REPEAT
1707 IF S='999' THEN-22
1708 ! END OF FILE MARKER
1709 IF S='91' THEN-21
1710 ! 91 - BEGINNING OF CYCLE MARKER
1711 BUNG =BUNG+1
1712 ! LAST 5 LINES COUNT NUMBER OF SAMPLES (BUNG) IN NEW CYCLE
1713 ->1
1714 A1: CYCLE J=1,1,13
1715 TIME (J)=0
1716 REPEAT
1717 !
1718 CYCLE J=1,1,13
1719 ! 13 ELEMENTS
1720 IF J=3 OR J=9 THEN RSTRG(S)
1721 CYCLE A=1,1,BUNG
1722 RAT (A)=0
1723 REPEAT
1724 IF J=1 OR J=2 OR J=9 OR J=11 OR J=13 START
1725 CYCLE A=1,1,4
1726 ! 4 PEAK-BACKGROUND PAIRS: NI, ZN, CR, SM, TIO2W
1727 READ (Z(J)); READ (B); READ (B); READ (B)
1728 CYCLE B=1,1,BUNG
1729 ! BUNG SAMPLES
1730 READ (C); RAT (B)=RAT(B)+C
1731 IF A=1 THEN INITP(B)=C ELSE START
1732 ! INITIAL PEAK SET ON FIRST PK/BG PAIR, OTHERWISE SPURIOUS COUNT CHECK
1733 IF !C-INITP(B)!>DIFF(J)+SORT(INITP(B)) START
1734 NEWLINE
1735 PRINTSTRING ('SPURIOUS COUNT FOR ELEMENT '); PRINT (Z(J),2,0)
1736 PRINTSTRING (' SAMPLE ',NS(V+B))
1737 FINISH
1738 READ (C)
1739 REPEAT
1740 READ (B); READ (B)
1741 CYCLE B=1,1,BUNG
1742 IF J=9 START
1743 ! CR
1744 READ (C)
1745 IF A=1 OR A=2 START
1746 BG (9,V+B)=BG(9,V+B)+2*(6924-6850)*C/(7068-6850)
1747 ! CR- 2 BACKGROUND POSITIONS
1748 RAT (B)=RAT(B)-2*(6924-6850)*C/(7068-6850)
1749 IF A=1 THEN INIB(B)=C ELSE START
1750 IF !C-INIB(B)!>5 START
1751 NEWLINE
1752 PRINTSTRING ('SPURIOUS COUNT FOR BACKGROUND 24.')
1753 PRINTSTRING ('SAMPLE ',NS(V+B))

```

FIG. B13 : continued. Program WTRACE

```

1754      FINISH
1755      FINISH
1756      FINISH
1757      IF A=3 OR A=4 START
1758      RAT(B)=RAT(B)-2*(7068-6924)*C/(7068-6850)
1759      BG(J,V+B)=BG(J,V+B)+2*(6924-6850)*C/(7068-6850)
1760      IF A=3 THEN INITB(B)=C ELSE START
1761      IF !C-INITB(B)!>6 START
1762      NEWLINE
1763      PRINTSTRING('SPURIOUS COUNT FOR BACKGROUND 24,')
1764      PRINTSTRING('SAMPLE *.NS(V+B)')
1765      FINISH
1766      FINISH
1767      FINISH
1768      ->C1
1769      FINISH
1770      ! IF J ISN'T 0 THEN NEXT 9 LINES EXECUTED
1771      READ(C);RAT(B)=RAT(B)-C
1772      BG(J,V+B)=BG(J,V+B)+C
1773      IF A=1 THEN INITB(B)=C ELSE START
1774      IF !C-INITB(B)!>DIFF(J+13) START
1775      NEWLINE
1776      PRINTSTRING('SPURIOUS COUNT FOR BACKGROUND ')
1777      PRINT(Z(J),2,0);PRINTSTRING(' SAMPLE *.NS(V+B)')
1778      FINISH
1779      FINISH
1780      C1: READ(C)
1781      REPEAT:REPEAT
1782      CYCLE B=1,1,BUNG
1783      CR(J,V+B)=RAT(B)/40000
1784      BG(J,V+B)=BG(J,V+B)/40000
1785      REPEAT
1786      FINISH
1787      IF J=5 OR J=6 OR J=7 OR J=10 START
1788      ! TH, SR, ZR, CE - ALL HAVE NO BACKGROUNDS
1789      CYCLE A=1,1,4
1790      READ(Z(J));READ(C);READ(MONCOUNT(J));READ(INDTIME)
1791      TIME(J)=TIME(J)+INDTIME/4
1792      ! TIME COUNTED FOR EACH ELEMENT AND MONITOR COUNT READ IN.
1793      CYCLE B=1,1,BUNG
1794      READ(C);RAT(B)=RAT(B)+C
1795      IF A=1 THEN INITP(B)=C ELSE START
1796      IF !C-INITP(B)!>DIFF(J)*SQRT(INITP(B)) START
1797      NEWLINE
1798      PRINTSTRING('SPURIOUS COUNT FOR ELEMENT ');PRINT(Z(J),2,0)
1799      PRINTSTRING(' SAMPLE *.NS(V+B)')
1800      FINISH
1801      FINISH
1802      READ(C)
1803      REPEAT:REPEAT
1804      CYCLE B=1,1,BUNG
1805      CR(J,V+B)=RAT(B)/40000
1806      REPEAT
1807      FINISH
1808      IF J=4 START
1809      ! RB, FIRSTLY A SET OF EXTRA BACKGROUNDS (THB) FOR TH IS READ IN
1810      READ(C);READ(C)
1811      CYCLE B=1,1,BUNG
1812      READ(THB(B))
1813      READ(THMON)
1814      ! TIME ON TH BACKGROUND
1815      REPEAT
1816      FINISH
1817      IF J=4 OR J=6 OR J=8 OR J=12 START
1818      ! RB, Y, NB, ND: 4PK, 496 WHICH MUST BE USED FOR OTHER ELEMENTS
1819      CYCLE A=1,1,4
1820      READ(Z(J));READ(C);READ(MONCOUNT(J));READ(INDTIME)
1821      TIME(J)=TIME(J)+INDTIME/4
1822      ! MONITOR COUNTS AND TIME
1823      CYCLE B=1,1,BUNG
1824      READ(C);RAT(B)=RAT(B)+C
1825      IF A=1 THEN INITP(B)=C ELSE START
1826      IF !C-INITP(B)!>DIFF(J)*SQRT(INITP(B)) START
1827      NEWLINE
1828      PRINTSTRING('SPURIOUS COUNT FOR ELEMENT ');PRINT(Z(J),2,0)
1829      PRINTSTRING(' SAMPLE *.NS(V+B)')
1830      FINISH
1831      FINISH
1832      READ(C)
1833      REPEAT
1834      READ(C);READ(C)
1835      CYCLE B=1,1,BUNG
1836      READ(C);BG(J,V+B)=BG(J,V+B)+C
1837      IF A=1 THEN INITB(B)=C ELSE START
1838      IF !C-INITB(B)!>DIFF(J+13) START
1839      NEWLINE
1840      PRINTSTRING('SPURIOUS COUNT FOR BACKGROUND ')
1841      PRINT(Z(J),2,0);PRINTSTRING(' SAMPLE *.NS(V+B)')
1842      FINISH
1843      FINISH

```

FIG. B13 : continued. Program WTRACE

```

1844      READ(C)
1845      REPEAT
1846      CYCLE R=1,1,BUNG
1847      CR(J,V+B)=PAT(B)/40000
1848      BG(J,V+B)=BG(J,V+B)/40000
1849      REPEAT
1850      FINISH
1851      REPEAT
1852      CYCLE R=1,1,BUNG
1853      ! CALCULATIONS OF BACKGROUNDS FOR 3=TH, 4=RB, 5=SR, 6=Y, 7=ZR, 8=NB
1854      ! 10=CE, USING PEAK AND BACKGROUND ANGLES AND BACKGROUND
1855      ! COUNTS, TIMES AND MONITOR COUNTS.
1856      BG(3,V+B)=((.00005*THB(B)+.5*(BG(4,V+B)+MONCOUNT(4)*TIME(3)/(TIME(4)
1857      C      *MONCOUNT(3))))*(2737-2416)+(2860-2737)*(BG(6,V+B)+TIME(3)
1858      C      *MONCOUNT(6))/(TIME(6)+MONCOUNT(3)))/(2860-2416)
1859      RE1=(BG(4,V+B)*(2651-2416)+(2860-2651)*(BG(6,V+B)
1860      C      *MONCOUNT(6)+TIME(4)/(TIME(6)+MONCOUNT(4)))/(2860-2416)
1861      C      BG(5,V+B)=((BG(4,V+B)+MONCOUNT(4)*TIME(5)/(TIME(4)
1862      C      *MONCOUNT(5)))+(2504-2416)+(2860-2504)*(BG(6,V+B)+TIME(5)
1863      C      *MONCOUNT(6))/(TIME(6)+MONCOUNT(5)))/(2860-2416)
1864      RE2=(BG(6,V+B)*(2368-2090)+(2416-2368)*(BG(8,V+B)
1865      C      *MONCOUNT(8)+TIME(6)/(TIME(8)+MONCOUNT(6)))/(2416-2090)
1866      C      BG(7,V+B)=((BG(6,V+B)+MONCOUNT(6)*TIME(7)/(TIME(6)
1867      C      *MONCOUNT(7)))+(2245-2090)+(2416-2245)*(BG(8,V+B)+TIME(7)
1868      C      *MONCOUNT(8))/(TIME(8)+MONCOUNT(7)))/(2416-2090)
1869      PG(8,V+B)=((BG(6,V+B)+MONCOUNT(6)*TIME(8)/(TIME(6)
1870      C      *MONCOUNT(8)))+(2130-2090)+(2416-2130)*(BG(8,V+B))/(2416-2090)
1871      C      BG(10,V+B)=BG(12,V+B)+MONCOUNT(12)*TIME(10)/(TIME(12)
1872      C      *MONCOUNT(10))
1873      BG(4,V+B)=RE1;BG(6,V+B)=RE2
1874      ! NEXT 5 LINES SUBTRACT BACKGROUNDS
1875      CYCLE J=3,1,8
1876      CR(J,V+B)=CR(J,V+B)-BG(J,V+B)
1877      REPEAT
1878      CR(10,V+B)=CR(10,V+B)-BG(10,V+B)
1879      CR(12,V+B)=CR(12,V+B)-BG(12,V+B)
1880      REPEAT
1881      ->B1
1882      2:IF S1="NULL" THEN->4
1883      ! NEXT 13 LINES PRINT FILE OF UNCORRECTED COUNT RATIOS.
1884      SELECTOUTPUT(2);SETMARGINS(2,1,130)
1885      SPACES(16)
1886      CYCLE J=1,1,13
1887      IF Z(J)=25 THEN Z(J)=17
1888      PRINT(Z(J),2,0);SPACES(8)
1889      REPEAT
1890      NEWLINES(2)
1891      CYCLE V=1,1,NOSAMS
1892      PRINTSTRING(NS(V));SPACES(12-LENGTH(NS(V)))
1893      CYCLE J=1,1,13
1894      PRINT(CR(J,V),2,6);SPACE
1895      REPEAT
1896      NEWLINE;REPEAT
1897      4:BEGIN
1898      LONGREALARRAY MA,CX(6:13),EYY,EX,EY,EXY,EXX(6:9)
1899      INTEGERARRAY NOP(6:9)
1900      REAL REB,REA,REC
1901      IF REGRESS="N" START
1902      MA(6)=.359550;MA(7)=.093729
1903      MA(8)=.024535;MA(9)=.032563
1904      ! INTERFERENCE CORRECTION GRADIENTS DETERMINED IN A PREVIOUS
1905      ! REGRESSION: 6=RB ON Y, 7=SR ON ZR, 8=CE ON SM, 9=CE ON ND.
1906      SELECTOUTPUT(99);SELECTINPUT(98)
1907      ->5
1908      FINISH
1909      CYCLE C=5,1,9
1910      EYY(C)=0;EX(C)=0;EY(C)=0;EXY(C)=0;EXX(C)=0;NOP(C)=0
1911      REPEAT
1912      CYCLE V=1,1,NOSAMS
1913      ! CYCLE THROUGH TOTAL NUMBER OF SAMPLES
1914      UNLESS NS(V)->('INT').S THEN->6
1915      ! IF SAMPLE NAME DOESN'T START WITH 'INT' THEN EXCLUDE FROM REGRESSION
1916      IF LENGTH(NS(V))<6 THEN->6
1917      ! IF ONLY 5 OR LESS CHARACTERS IN SAMPLE NAME EXCLUDE FROM REGRESSION
1918      IF CHARNO(NS(V),6)='T' THEN->6
1919      IF CHARNO(NS(V),6)='B' THEN->6
1920      ! USE 'A' SERIES INTERFERENCE STANDARDS FOR Y, ZR.
1921      CYCLE C=6,1,7
1922      EX(C)=EX(C)+CR(C-2,V)
1923      ! X=RB,SR
1924      EY(C)=EY(C)+CP(C,V)
1925      ! Y=Y, ZR
1926      EXX(C)=EXX(C)+CR(C-2,V)**2
1927      EYY(C)=EYY(C)+CR(C,V)**2
1928      EXY(C)=EYY(C)+CR(C,V)+CR(C-2,V)
1929      NOP(C)=NOP(C)+1
1930      REPEAT
1931      ->6
1932      6:CYCLE C=6,1,9
1933      ! USE E SERIES INTERFERENCE STANDARDS FOR SM, ND

```

FIG. B13 : continued. Program WTRACE

```

1924      EX(C)=EX(C)+CR(10,V)
1925      ! X=CE
1926      EY(C)=EY(C)+CR(C+3,V)
1927      ! Y=SM, VD
1928      EXX(C)=EXX(C)+CR(10,V)**2
1929      EYY(C)=EYY(C)+CR(C+3,V)**2
1930      EXY(C)=EXY(C)+CR(10,V)*CR(C+3,V)
1931      NOP(C)=NOP(C)+1
1932      REPEAT
1933  6: REPEAT
1934      CYCLE C=6,1,9
1935      REB=NOP(C)*EY(C)-NOP(C)*EXX(C)+EX(C)**2-EY(C)**2
1936      REA=EY(C)*EX(C)-NOP(C)*EXY(C)
1937      MA(C)=(-REB+SQRT(REB**2+4*REA**2))/(2*REA)
1938      MA(C+4)=(-REB-SQRT(REB**2+4*REA**2))/(2*REA)
1939      CX(C)=(EY(C)-MA(C)*EX(C))/NOP(C)
1940      CX(C+4)=(EY(C)-MA(C+4)*EX(C))/NOP(C)
1941      ! LAST 6 LINES - CALCULATION OF 2 GRADIENT-INTERCEPT PAIRS
1942      REPEAT
1943      SELECTOUTPUT(99);SELECTINPUT(98)
1944      CYCLE C=6,1,9
1945      CYCLE B=1,1,1
1946      REC=MA(C+4*B)**2+1
1947      REC=(EYY(C)-2*MA(C+4*B)*EY(C)+2*CX(C+4*B)*MA(C+4*B)+EX(C)
C      -2*CX(C+4*B)*EY(C)
C      +EXX(C)+MA(C+4*B)**2+NOP(C)*CX(C+4*B)**2)/REC
1948      IF B=0 THEN REA=REC
1949      REPEAT
1950      IF REC<REA THEN MA(C)=MA(C+4) AND CX(C)=CX(C+4)
1951      ! LAST 9 LINES - SELECTION OF M/C PAIR GIVING MINIMUM
1952      IF C=6 THEN S='Y';IF C=7 THEN S='Z';IF C=8 THEN S='SM'
1953      IF C=9 THEN S='NO'
1954      PRINTSTRING('INTERFERENCE CORRECTION FOR '.S.' IS')
1955      PRINT(MA(C),2,6)
1956      PRINTSTRING(' COUNT RATIO '.S.' PER UNIT INTERFERING ELEMENT')
1957      NEWLINE
1958      PRINTSTRING('INTERCEPT OF CORRECTION IS AT COUNT RATIO ')
1959      PRINT(CX(C),2,6)
1960      NEWLINE
1961      REPEAT
1962  5: PROMPT('P-B/E? ');RSTRG(PB)
1963      ! ANDERMAN-KEMP CORRECTION
1964      SELECTOUTPUT(3);SETMARGINS(3,1,130);SPACES(13)
1965      ! PRINTING OF FILE OF CORRECTED COUNT RATIOS.
1966      CYCLE J=1,1,13;PRINT(Z(J),2,0);SPACES(5);REPEAT
1967      IF Z(J)=25 THEN Z(J)=17
1968      NEWLINES(2)
1969      CYCLE V=1,1,NOSAMS
1970      CYCLE C=6,1,7
1971      CR(C,V)=CR(C,V)-MA(C)*CR(C-2,V)
1972      REPEAT
1973      CYCLE C=8,1,9
1974      CR(C+3,V)=CR(C+3,V)-MA(C)*CR(10,V)
1975      REPEAT
1976      ! LAST 6 LINES MAKE INTERFERENCE CORRECTIONS
1977      PRINTSTRING(NS(V));SPACES(9-LENGTH(NS(V)))
1978      CYCLE J=1,1,13
1979      IF PB='Y' THEN CR(J,V)=CR(J,V)/BG(J,V)
1980      ! ANDERMAN-KEMP CORRECTION MADE IF REQUIRED
1981      PRINT(CR(J,V),2,6)
1982      REPEAT
1983      NEWLINE
1984      REPEAT
1985      END
1986      END
1987      END
1988      ENDOFFILE

```


FIG. B14 : Compiled listing of program TRACE

```

437 EXTERNAL REALSTR (STRINGNAME S)
438 REAL RE: INTEGER A,B
439 RE=0
440
441 1: CYCLE A=1,1,LENGTH(S)
442 IF CHARNO(S,A)=0 THEN EXIT
443 REPEAT
444 IF A=LENGTH(S) AND CHARNO(S,A)=0 THEN S=S..0 AND=21
445 IF A=1 THEN S=0.S AND=21
446 CYCLE B=1,1,A-1
447 RE=RE+(CHARNO(S,B)-48)*(10**(A-1-B))
448 REPEAT
449 CYCLE B=A+1,1,LENGTH(S)
450 RE=RE+(CHARNO(S,B)-48)*(10**(A-B))
451 REPEAT
452 RESULT=RE
453 END
454
455 EXTERNAL ROUTINE TRACE
456 ROUTINE ANALY (STRING(255)S, LONGREAL ARPAYNAME MAJ, INTEGER V)
457 INTEGER I
458 STRING(4)S1
459 CYCLE I=1,1,4
460 S->S1.(*)S
461 IF I>=11 THEN MAJ(I+1,V)=REALSTR(S1) ELSE MAJ(I,V)=REALSTR(S1)
462 REPEAT
463 END
464
465 DYNAMIC INTEGER ENSPEC INTEGSTR (STRINGNAME S)
466 DYNAMIC ROUTINESPEC PRELOAD (STRING(63) S)
467 DYNAMIC ROUTINESPEC DEFINE (STRING(63)S)
468 DYNAMIC ROUTINESPEC PROMPT (STRING(121)S)
469 DYNAMIC ROUTINESPEC RSTRG (STRINGNAME S)
470 INTEGER NOSAMS,BLOCK,EG,A,ZBG,ZBPNS,NOELS,B,V,NOEL,ZBP,COUNT,T,Y,K
471 INTEGER ANALF,FG
472 INTEGER ARRAY STAN(1:20)
473 INTEGER ECOUNTS,ZA
474 LONGREAL ARRAY ECC,EP,EC,ECP,EPP(1:20),MA,CX(1:2,1:20),REC(1:2)
475 LONGREAL PA,REA,RES
476 INTEGER ARRAY STANINIT,STANFINAL(0:20),Z,THETAP,THETA1,THETA2(1:20)
477 STRING(255) CPS,STANSUSED,STNO,CMIT,HEAD,TAIL,MT,STANSRES,LT
478 STRING(255) S1,S2,S3,S4,ROCK,NSZB,ANSWER,S5,PREL,S6
479 ANALF=0;COUNT=0
480 STANSUSED=0;STANSRES=0
481 PROMPT('INPUT FILE: ');RSTRG(S1)
482 IF S1=0.NULL THEN=21
483 DEFINE('ST1',S1)
484 1: PROMPT('CRATIO FILE: ');RSTRG(S2)
485 ! INPUT FROM WTRACE OR CRTRACE
486 IF S2=0.NULL THEN=22
487 DEFINE('ST2',S2)
488 2: PROMPT('CORRECTED FILE: ');RSTRG(S6)
489 ! MASS ABSORPTION CORRECTED COUNT RATIOS (INPUT OR OUTPUT)
490 IF S6=0.NULL THEN=22
491 DEFINE('ST4',S6)
492 A2: PROMPT('ANALYSIS FILE: ');RSTRG(S3)
493 IF S3=0.NULL THEN=23
494 DEFINE('ST3',S3)
495 3: PROMPT('NORM INPUT FILE: ');RSTRG(S5)
496 IF S5=0.NULL THEN=23
497 DEFINE('ST9',S5)
498 33: DEFINE('ST5','EGEO07.TRACANAL')
499 ! ATOMIC NUMBERS FOR WHICH NAMED STANDARD IS NOT TO BE USED IN CALIBRATION
500 CMIT=SY3 21,57,39;GSN 57,60,62;PCO1 56,57,28,24;UBN 28,24;J51 41;C
501 ! TAN21 21,57,39;J61 41,60;GSP1 57,58,60,62;C
502 ! INTSEA2 24,60,58;FKN 33,39;GH 30;INTSGA2 60,58;C
503 ! INTSEB2 57,21;INTSGB2 57,21;INTSEB3 21;INTSGB3 21;C
504 DEFINE('ST7','EMP')
505 IF S2=0.NULL AND S6=0.NULL THEN ANSWER='N' AND=212
506 ! REFERS TO INPUT FROM MU-CORRECTED FILE
507 NEWLINE
508 PRINTSTRING('DO YOU REQUIRE MASS ABSORPTION CORRECTIONS? (Y OR N)')
509 NEWLINE
510 PROMPT('ANSWER: ');RSTRG(ANSWER)
511 IF ANSWER='N' THEN=212
512 NEWLINE
513 PRINTSTRING('STATE MAJOR ELEMENT ANALYSIS FILE FOR M.A. CORRECTIONS.')
514 NEWLINE
515 PROMPT(' ');RSTRG(S4)
516 DEFINE('ST8',S4)
517 12: PROMPT('NO. SAMPLES: ');READ(NOSAMS)
518 NEWLINE
519 PRINTSTRING('STATE NO. OF GROUPS OF STANDARDS')
520 NEWLINE
521 PROMPT(' ');READ(BLOCK)
522 IF BLOCK=0 THEN DEFINE('ST6','EGEO07.TRACDATA') AND=24
523 PROMPT('PRELOAD? ');RSTRG(PREL)
524 DEFINE('ST6','TRACDATA')
525 CYCLE A=1,1,BLOCK
526 PRINTSTRING('STATE POSITION IN SEQUENCE OF SPECIMENS OF FIRST')

```

FIG. B14 : continued. Program TRACE

```

491 PRINTSTRING('STANDARD OF GROUP ')
492 PRINT(A,1,0):NEWLINE
493 PROMPT('': '):READ(STANINIT(A))
494 PRINTSTRING('STATE POSITION IN SEQUENCE OF SPECIMENS OF FINAL ')
495 PRINTSTRING('STANDARD OF GROUP ')
496 PRINT(A,1,0):NEWLINE
497 PROMPT('': '):READ(STANFINAL(A))
498 REPEAT
499 PRINTSTRING('OMIT=? OMIT):NEWLINE
500 PROMPT('CHANGE OMIT? '):RSTRG(NSZB)
501 IF NSZB='Y' THEN PROMPT('TYPE OMIT: ') AND RSTRG(OMIT)
502 4:EQ=0:ZBPNS=0:Y=0
503 35:BEGIN
504 STRING(10)APRAY NS(1:(NOSAMS+4)),ELEM(1:20),MAJEL(1:18)
505 CONSTREALARRAY MUFUDGE(1:9)=.908,.528,.987,.992,1.1,608,1.016,
506 1.024,.918
507 ! FACTORS RELATING TO NON-LINEARITY OF MU WITH WAVELENGTH-CUBED
508 ! THESE RELATE TO NI, ZN, TH, RB, SR, Y, ZR, NB, CU IN ORDER
509 LONGREAL MU2,MU3
510 LONGREALARRAY ECOUNT(1:4),BG1,BG2,P,PK(1:(NOSAMS+4),1:20), C
511 LOI(1:(NOSAMS+4)),MAJ(1:18,1:NOSAMS),MU1(1:9)
512 CONSTREALARRAY COEF1(1:10)=7.08,6.5,48.7,5.88,26.3,5.43,26.7,
513 25.1,48.8,7.9
514 ! OXIDE MU-COEFFICIENTS AT SR KA: ! MAJOR ELEMENT ORDER AS USUAL
515 CONSTREALARRAY COEF2(1:10)=105.6,97.9,5.87,6.34,0.1,80.5,343.7,
516 364.5,86.9,117.7
517 ! OXIDE COEFFICIENTS AT CRKA
518 CONSTREALARRAY COEF3(1:10)=176.6,162.1,148.9,146.4,553.3,134.3,
519 558.8,93.4,142.8,196.8
520 ! OXIDE COEFFICIENTS AT TIKA
521 CYCLE V=1,1,NOSAMS
522 LOI(V)=0
523 CYCLE NOEL=1,1,18
524 MAJ(NOEL,V)=C
525 REPEAT:REPEAT
526 MAJEL(1)='SiO2':MAJEL(2)='AL2O3':MAJEL(3)='Fe2O3'
527 MAJEL(4)='MgO':MAJEL(5)='CaO':MAJEL(6)='Na2O':MAJEL(7)='K2O'
528 MAJEL(8)='TiO2':MAJEL(9)='MnO':MAJEL(10)='P2O5':MAJEL(11)='
529 MAJEL(12)='LOI':MAJEL(13)='V':MAJEL(14)='LA':MAJEL(15)='BA'
530 MAJEL(16)='SC':MAJEL(17)='CU':MAJEL(18)='TI02CR'
531 ! MAJEL(11) IS TOTAL OXIDES
532 IF S1='NULL' THEN->224
533 ! UNTIL LABEL 24 REFERS TO PRE-SAMPLE LOADER RUNS
534 CYCLE V=1,1,(NOSAMS+4)
535 CYCLE A=1,1,20
536 BG1(V,A)=0
537 REPEAT:REPEAT
538 SELECTINPUT(1):->5
539 14:Z(NOEL)=ZBG
540 CYCLE B=1,1,4
541 V=(EQ-1)+B
542 PK(V,NOEL)=ECOUNT(B)/ECOUNTS
543 REPEAT
544 5:EQ=EQ+1
545 ZBG=C
546 CYCLE B=1,1,4
547 IF Y=1 THEN ROCK=NSZB AND Y=0 ELSE RSTRG(ROCK)
548 WHILE ROCK->(' ') ROCK CYCLE:REPEAT
549 IF ROCK='999' THEN->215
550 V=(EQ-1)+B
551 NS(V)<-ROCK
552 REPEAT
553 NSZB='0'
554 READ(B):NOEL=C
555 ->92
556 6:IF NEXTSYMBOL=NL THEN SKIPSYMBOL
557 WHILE NEXTSYMBOL=' ' THEN SKIPSYMBOL
558 IF NEXTTITE<='/' OR NEXTTITE=':' THEN->214
559 92:READ(ZBP)
560 IF NEXTSYMBOL=' ' OR ZBP>99 THEN->210 ELSE->211
561 10:UNLESS NEXTSYMBOL=10 THEN RSTRG(NSZB)
562 SELECTOUTPUT(7):WRITE(ZBP,1)
563 PRINTSTRING(NSZB) UNLESS NSZB='0'
564 SELECTOUTPUT(99):CLOSESTREAM(7):SELECTINPUT(7)
565 RSTRG(NSZB):Y=1
566 SELECTINPUT(98):CLOSESTREAM(7):SELECTINPUT(1):->14
567 11:READ(K)
568 IF ZBP=ZBG THEN->7
569 IF ZBG=0 THEN->28
570 CYCLE B=1,1,4
571 ECOUNT(B)=ECOUNT(E)/ECOUNTS
572 REPEAT
573 IF ZBG<10 OR ZBG>70 THEN->29
574 Z(NOEL)=ZBG
575 CYCLE B=1,1,4
576 V=(EQ-1)+B
577 PK(V,NOEL)=ECOUNT(B)
578 REPEAT
579 #NOEL=NOEL+1
580 ->13

```

FIG. B14 : continued. Program TRACE

```

581      9:CYCLE B=1,1,4
582      V=(EG-1)*4*F
583      IF ZBP<10 OR ZBP>70 THEN BG1(V,NOEL)=ECOUNT(B) AND->9E
584      BG2(V,NOEL)=ECOUNT(B)
585      9:REPEAT
586      13:ECOUNTS=0
587      CYCLE B=1,1,4
588      ECOUNT(B)=0
589      REPEAT
590      7:ZSG=ZBP
591      CYCLE B=1,1,4
592      READ(COUNT):READ(T)
593      ECOUNT(B)=COUNT/(T/1000)*ECOUNT(B)
594      REPEAT
595      ECOUNTS=ECOUNTS+1
596      ->6
597      15:NOELS=NOEL:NOSAMS=(EG-1)*4
598      SELECTINPUT(98)
599      NEWLINE
600      PRINTSTRING('LIST PEAK ANGLES USED (WITHOUT DECIMAL POINT)')
601      PRINTSTRING(' IN RESPONSE TO PROMPT OF ELEMENT NAME')
602      NEWLINE
603      CYCLE NOEL=1,1,NOELS
604      IF Z(NOEL)#37 THEN->16
605      ELEM(NOEL)='RE'
606      THETA1(NOEL)=2720
607      THETA2(NOEL)=2600
608      PROMPT('RB: ');READ(THETA1(NOEL))
609      ->17
610      16:IF Z(NOEL)#38 THEN->18
611      ELEM(NOEL)='SF'
612      THETA1(NOEL)=2600
613      THETA2(NOEL)=2450
614      PROMPT('SR: ');READ(THETA1(NOEL))
615      ->17
616      18:NEWLINE
617      PRINTSTRING('ATOMIC NUMBER (IE. E-SET ADDRESS) ')
618      WRITE(Z(NOEL),1);PRINTSTRING(' NOT RECOGNIZED. PLEASE IDENTIFY')
619      NEWLINE
620      PROMPT('ELEMENT: ');RSTRG(ELEM(NOEL))
621      PROMPT('PEAK ANGLE: ');READ(THETA1(NOEL))
622      IF BG1(1,NOEL)=0 THEN->20
623      PROMPT('1ST BG ANGLE: ');READ(THETA1(NOEL))
624      PROMPT('2ND BG ANGLE: ');READ(THETA2(NOEL))
625      ->17
626      20:PROMPT('BG ANGLE: ');READ(THETA2(NOEL))
627      17:REPEAT
628      CYCLE V=1,1,NOSAMS
629      CYCLE NOEL=1,1,NOELS
630      IF BG1(V,NOEL)=0 THEN->21
631      BG1(V,NOEL)=(THETA1(NOEL)-THETA2(NOEL))*(BG1(V,NOEL)-BG2(V,NOEL))
632      BG2(V,NOEL)=BG1(V,NOEL)/(THETA1(NOEL)-THETA2(NOEL))*BG2(V,NOEL)
633      21:PK(V,NOEL)=PK(V,NOEL)-BG2(V,NOEL)
634      REPEAT
635      REPEAT
636      24:IF S1='NULL' OR S2='NULL' START
637      IF S2='NULL' THEN SELECTINPUT(4) AND SETMARGINS(4,1,160) C
638      ELSE SELECTINPUT(2) AND SETMARGINS(2,1,160)
639      ! NEXT 6 LINES READ IN ATOMIC NUMBERS FROM COUNT RATIO FILE INPUT
640      ! AND COUNT THEM. NOELS= NO.OF ELEMENTS ANALYSED
641      NOELS=0
642      21: NOELS=NOELS+1
643      WHILE NEXTSYMBOL=' ' THEN SKIPSYMBOL
644      IF NEXTSYMBOL=NL THEN->A21
645      READ(Z(NOELS)):->E21
646      A21: NOELS=NOELS-1
647      CYCLE V=1,1,NOSAMS
648      PTILLSP(NS(V))
649      CYCLE NOEL=1,1,NOELS
650      READ(PK(V,NOEL))
651      REPEAT:REPEAT
652      IF Z(1)=2? START
653      ! W-TYPE TRACES INPUT
654      ELEM(1)='NI';ELEM(2)='ZN';ELEM(3)='TH'
655      ELEM(4)='RB';ELEM(5)='SR';ELEM(6)='Y'
656      ELEM(7)='ZR';ELEM(8)='Nb';ELEM(9)='CR';ELEM(10)='CE'
657      ELEM(11)='SM';ELEM(12)='ND';ELEM(13)='TI02N'
658      ->F41
659      FINISH
660      IF Z(1)=21 START
661      ! CR-TYPE TRACES INPUT
662      ELEM(1)='SC';ELEM(2)='V';ELEM(3)='CU';ELEM(4)='BA';ELEM(5)='LA'
663      ELEM(6)='TI02CP'
664      CYCLE V=1,1,NOSAMS
665      PK(V,6)=PK(V,6)-.185*PK(V,2)
666      ! TI02CR CORRECTED FOR BALB3 AND VKA INTERFERENCE
667      PK(V,2)=PK(V,2)*(1+.1166*.185)
668      ! V. CORRECTED FOR V INTERFERENCE ON TI OR V (THIS LINE COULD
669      ! BE OMITTED)
670      PK(V,5)=PK(V,5)+.007956*.185*PK(V,2)

```


FIG. B14 : continued. Program TRACE

```

716 COUNT=1
717 IF ANALF=1 THEN->A1
718 ! ANALF=1 => COMPOSITIONS FILE IS IN ANALYSIS FILE FORMAT
719 ! NEXT 8 LINES IDENTIFY FORMAT OF ANALYSIS FILE
720 E41:WHILE NEXTSYMBOL=' ' THEN SKIPSYMBOL
721 IF NEXTSYMBOL='S' START
722 ! FIRST NON-SPACE CHARACTER IN FILE IS 'S' - COULD BE ANALYSIS FILE
723 ! (SIO2) OF SAMPLE NAME BEGINNING WITH S
724 CYCLE NOEL=1,1,12
725 RTILLSP(MAJEL(NOEL))
726 IF NOEL=1 AND MAJEL(NOEL)='SIO2' THEN EXIT
727 REPEAT
728 IF MAJEL(1)='SIO2' THEN ROCK=MAJEL(1) AND C
729 MAJEL(1)='SIO2' AND ->A4 ELSE ANALF=1
730 ! ANALF=1 IF FIRST ITEM IN FILE IS SIO2
731 ! NEXT 14 LINES READ IN DATA FROM ANALYSIS FILE INTO ARRAY MAJ
732 41: RTILLSP(ROCK)
733 IF ROCK='STOP' START
734 IF COUNT=0 THEN COUNT=4
735 ->A4
736 FINISH
737 IF ROCK=NS(V) START
738 IF ROCK->(NS(V)'.S').HT THEN NS(V)=ROCK AND->A6
739 RSTRG(ROCK)
740 ->A1
741 FINISH
742 46: CYCLE NOEL=1,1,12
743 READ(MAJ(NOEL,V));REPEAT
744 ->B41
745 FINISH
746 !
747 ! NEXT 29 LINES TAKE DATA FROM NORMINPUT FILE
748 ! PROGRAM OPERATES FASTEST IF SAMPLE ORDER IN NORMINPUT FILE IS
749 ! SAME AS ORDER OF COUNT RATIOS.
750 C41:RSTRG(ROCK)
751 IF ROCK->ROCK.( ' ') OR ROCK->ROCK.( ' ') THEN->A41
752 A41:IF ROCK=NS(V) START
753 IF ROCK->(NS(V)'.S').HT THEN NS(V)=ROCK AND->D41
754 ! IF 8 SYMBOLS USED IN COMPOSITIONS FILE, THEY WILL TRANSFER TO
755 ! OUTPUT DATA. THEY NEED NOT APPEAR IN COUNT RATIO FILE
756 CYCLE; RTILLSP(ROCK)
757 IF ROCK='-1' OR ROCK='END' OR ROCK='-2' THENEXIT
758 READ(PA)
759 REPEAT
760 IF ROCK='-1' OR ROCK='END' THEN->C41
761 IF ROCK='-2' START
762 IF COUNT=0 THEN COUNT=4
763 ->A4
764 FINISH
765 FINISH
766 D41:RTILLSP(ROCK)
767 IF ROCK='-1' THEN->D41
768 IF ROCK='-2' START
769 SELECTINPUT(58);CLOSESTREAM(8);SELECTINPUT(6)
770 ->B41
771 FINISH
772 READ(PA)
773 CYCLE NOEL=1,1,18
774 IF ROCK=MAJEL(NOEL) START
775 MAJ(NOEL,V)=PA
776 IF NOEL<11 THEN MAJ(11,V)=MAJ(11,V)+PA
777 ! TOTAL OXIDES CREATED
778 EXIT
779 FINISH
780 REPEAT
781 ->D41
782 B41:IF NS(V)='INTSBB1' THEN MAJ(13,V)=1020 AND MAJ(14,V)=1402
783 IF NS(V)='INTSBB1' THEN MAJ(13,V)=1050 AND MAJ(14,V)=1017
784 IF NS(V)='INTSBB2' THEN MAJ(13,V)=420 AND MAJ(14,V)=577
785 IF NS(V)='INTSBB2' THEN MAJ(13,V)=444 AND MAJ(14,V)=430
786 IF NS(V)='INTSBB3' THEN MAJ(13,V)=99 AND MAJ(14,V)=136
787 IF NS(V)='INTSBB3' THEN MAJ(13,V)=180 AND MAJ(14,V)=97
788 IF NS(V)='INTSBB4' THEN MAJ(13,V)=23.7 AND MAJ(14,V)=28.5
789 IF NS(V)='INTSBB4' THEN MAJ(13,V)=19.2 AND MAJ(14,V)=18.6
790 IF NS(V)='INTSBA1' THEN MAJ(15,V)=1313
791 IF NS(V)='INTSBA1' THEN MAJ(15,V)=2534
792 IF NS(V)='INTSBA2' THEN MAJ(15,V)=535
793 IF NS(V)='INTSBA2' THEN MAJ(15,V)=1054
794 IF NS(V)='INTSBA3' THEN MAJ(15,V)=107
795 IF NS(V)='INTSBA3' THEN MAJ(15,V)=250
796 IF NS(V)='INTSBA4' THEN MAJ(15,V)=25
797 IF NS(V)='INTSBA4' THEN MAJ(15,V)=55.1
798 ! V, LA AND SA DATA FOR INTERFERENCE STANDARDS
799 CYCLE FG=1,1,9
800 MU1(FG)=0
801 REPEAT
802 MU2=0;MU3=0
803 CYCLE NOEL=1,1,10
804 CYCLE FG=1,1,9
805 IF NOEL=1 OR NOEL=5 OR 6<NOEL<10 THEN PA=MUFUDGE(FG) ELSE PA=1

```

FIG. B14 : continued. Program TRACE

```

805      ! 4TH PERIOD OXIDES MULTIPLIED BY MUFUDGE, OTHERS BY 1
806      MU1(FG)=MU1(FG)+MAJ(NOEL,V)*COEF1(NOEL)*FA
807      REPEAT
808      MU2=MU2+MAJ(NOEL,V)*COEF2(NOEL)
809      MU3=MU3+MAJ(NOEL,V)*COEF3(NOEL)
810      ! 12 MASS ABSORPTION COEFFICIENTS CALCULATED PER SAMPLE
811      REPEAT
812      IF MAJ(12,V)=C START
813      ! IF NO LOI DATA INPUT PROGRAM ASSUMES UNIGNITED SAMPLES
814      ! NEXT 5 LINES ASSUME 100-TOTAL OXIDES FOR UNIGNITED SAMPLES IS
815      ! 50 H2O - 50 CO2
816      CYCLE FG=1,1,9
817      MU1(FG)=(MU1(FG)+(100-MAJ(11,V))*1.86)/1000
818      REPEAT
819      MU2=(MU2+(100-MAJ(11,V))*30.9)/1000
820      MU3=(MU3+(100-MAJ(11,V))*52.7)/1000
821      ->43
822      FINISH
823      LOI(V)=MAJ(12,V)
824      IF STANSPRES->HT.(NS(V)).LT START
825      ! IF SAMPLE IS STANDARD THEN LOI QUOTED IS H2O+CO2
826      CYCLE FG=1,1,9
827      MU1(FG)=(MU1(FG)+LOI(V)*1.86)/1000
828      REPEAT
829      MU2=(MU2+LOI(V)*30.9)/1000
830      MU3=(MU3+LOI(V)*52.7)/1000
831      ->43
832      FINISH
833      ! NEXT 5 LINES APPLY TO IGNITED SAMPLES: TOTAL MU IS REDUCED BY
834      ! (100-LOI)/100 AND THEN LOI (H2O+CO2) CONTRIBUTION ADDED.
835      CYCLE FG=1,1,9
836      MU1(FG)=(MU1(FG)*(100-LOI(V))/100+LOI(V)*1.86)/1000
837      REPEAT
838      MU2=(MU2*(100-LOI(V))/100+LOI(V)*30.9)/1000
839      MU3=(MU3*(100-LOI(V))/100+LOI(V)*52.7)/1000
840      43:->40
841      44:SELECTINPUT(98)
842      UNLESS COUNT=4 THEN CLOSESTREAM(8) AND SELECTINPUT(8) C
843      AND COUNT=0 AND->441
844      COUNT=1
845      SELECTOUTPUT(99)
846      NEWLINE
847      PRINTSTRING('ANALYSIS OF ' NS(V) ' NOT PRESENT IN FILE ' S4)
848      NEWLINE
849      PRINTSTRING('DO YOU REQUIRE MATRIX CORRECTION TO THIS SAMPLE? (Y OR N)')
850      PRINTSTRING(' N)')
851      NEWLINE
852      PROMPT('ANSWER: ');RSTRG(ROCK)
853      IF ROCK='N' START
854      CYCLE FG=1,1,9
855      MU1(FG)=1
856      REPEAT
857      MU2=10;MU3=20
858      ->45
859      FINISH
860      PRINTSTRING('TYPE IN MAJOR ELEMENT ANALYSIS IN STANDARD ORDER')
861      NEWLINE
862      PRINTSTRING(' ', INCLUDING TOTAL OXIDES AND LOSS ON IGNITION (IF '))
863      NEWLINE
864      PRINTSTRING('USED). IN RESPONSE TO PROMPT OF "DATA".)')
865      PROMPT('DATA: ')
866      NEWLINE;->46
867      45:IF ROCK='Y' OR ROCK='N' THEN SELECTINPUT(8)
868      SELECTINPUT(98);CLOSESTREAM(8);SELECTINPUT(8)
869      40:CYCLE NOEL=1,1,NOELS
870      ! SELECTS CORRECT COEFFICIENT FOR EACH ELEMENT ANALYSED, AND
871      ! MULTIPLIES THE COUNT RATIO BY IT
872      IF ELEM(NOEL)='TH' THEN PK(V,NOEL)=PK(V,NOEL)*MU1(3) AND->44F
873      IF ELEM(NOEL)='DY' THEN PK(V,NOEL)=PK(V,NOEL)*MU1(1) AND->44F
874      IF ELEM(NOEL)='HF' THEN PK(V,NOEL)=PK(V,NOEL)*(MU1(1)+MU1(9))C
875      /2 AND->44F
876      IF ELEM(NOEL)='SC' OR ELEM(NOEL)='V' OR ELEM(NOEL)='LA' OR C
877      ELEM(NOEL)='TIO2CR' OR ELEM(NOEL)='TIO2W' C
878      THEN PK(V,NOEL)=PK(V,NOEL)*MU3/20 AND->44F
879      IF ELEM(NOEL)='CR' OR ELEM(NOEL)='BA' OR ELEM(NOEL)='CE' C
880      OR ELEM(NOEL)='ND' OR ELEM(NOEL)='SM' THEN C
881      PK(V,NOEL)=PK(V,NOEL)*MU2/10 AND->44F
882      IF ELEM(NOEL)='CU' THEN PK(V,NOEL)=PK(V,NOEL)*MU1(9) AND->44F
883      PK(V,NOEL)=PK(V,NOEL)*MU1(NOEL)
884      48:REPEAT
885      REPEAT
886      IF S6='NULL' THEN->22
887      ! PRINTED OF MU-CORRECTED COUNT RATIOS (NB. NOT CORRECTED FOR V/CR, LA/NB)
888      SELECTOUTPUT(4);SETMARGINS(4,1,130);SPACES(13)
889      CYCLE NOEL=1,1,NOELS;PRINT(2(NOEL),2,0);SPACES(7);REPEAT
890      NEWLINES(2)
891      CYCLE V=1,1,NOEAMS
892      PRINTSTRING(NS(V));SPACES(9-LENGTH(NS(V)))
893      CYCLE NOEL=1,1,NOELS
894      PRINT(PK(V,NOEL),2,6)

```

FIG. B14 : continued. Program TRACE

```

889      REPEAT
890      NEWLINE
891      REPEAT
892      22:CYCLE NOEL=1,1,NOELS
893      ECC(NOEL)=0;ECP(NOEL)=0;EC(NOEL)=0;ECP(NOEL)=0;STAN(NOEL)=0;EPP(NOEL)=0
894      REPEAT
895      IF ELEM(1)='H' THEN->2422
896      ! INPUT DATA FROM TRACE SHOULD BE CORRECTED FOR V/CR, LA/NE
897      SELECT OUTPUT(99);SELECT INPUT(98)
898      ! INPUT/OUTPUT REVERTS TO INTERACTIVE TERMINAL
899      BEGIN
900      LONGREAL ARRAY MA,CX(8:11),EX,EY,EXY,EXX,EYY(8:9)
901      REAL REA,PB,REC
902      INTEGER NOPPOINTS,J,P
903      NEWLINE
904      PRINTSTRING('REGRESSION FOR NB AND CR CORRECTIONS? (Y OR N)')
905      NEWLINE
906      PROMPT('ANSWER: ');RSTRG(HT)
907      ! REGRESSION ONLY POSSIBLE IF 'B' SERIES INTERFERENCE STANDARDS PRESENT
908      IF HT='Y' START
909      MA(8)=-.00001461;MA(9)=-.00001407
910      ->C22
911      ! CORRECTION GRADIENTS FROM PREVIOUS REGRESSION - P=NB, 9=CR
912      FINISH
913      CYCLE J=8,1,9
914      EX(J)=0;EY(J)=0;EXY(J)=0;EXX(J)=0;EYY(J)=0
915      REPEAT
916      ! REGRESSION PROCEDURE AS IN WTRACE
917      NOPPOINTS=0
918      CYCLE V=1,1,NOSAMS
919      UNLESS NS(V)->('INTS').HT THEN->2222
920      IF LENGTH(NS(V))<6 THEN->2222
921      UNLESS CHARNO(NS(V),6)='B' THEN->2222
922      CYCLE J=8,1,9
923      EX(J)=EX(J)+MAJ(22-J,V)
924      EY(J)=EY(J)+PK(V,J)
925      EXY(J)=EXY(J)+PK(V,J)+MAJ(22-J,V)
926      EXX(J)=EXX(J)+MAJ(22-J,V)**2
927      EYY(J)=EYY(J)+PK(V,J)**2
928      REPEAT
929      NOPPOINTS=NOPPOINTS+1
930      22:REPEAT
931      CYCLE J=8,1,9
932      REB=NOPPOINTS+EYY(J)-NOPPOINTS+EXX(J)+EX(J)**2-EY(J)**2
933      REA=EY(J)+EX(J)-NOPPOINTS+EXY(J)
934      MA(J)=(-REB+SQRT(REB**2+4*REA**2))/(2*REA)
935      MA(J+2)=(-REB-SQRT(REB**2+4*REA**2))/(2*REA)
936      CX(J)=(EY(J)-MA(J)+EX(J))/NOPPOINTS
937      CX(J+2)=(EY(J)-MA(J+2)+EX(J))/NOPPOINTS
938      REPEAT
939      CYCLE J=8,1,9
940      CYCLE B=0,1,1
941      REC=MA(J+2*B)**2+1
942      REC=(EYY(J)-2*MA(J+2*B)+EXY(J)+2*CX(J+2*B)+MA(J+2*B)+EX(J)
943      -2*CX(J+2*B)+EY(J)
944      +EXX(J)+MA(J+2*B)**2+NOPPOINTS*CX(J+2*B)**2)/REC
945      IF B=0 THEN REA=REC
946      REPEAT
947      IF REA<0 THEN MA(J)=MA(J+2) AND CX(J)=CX(J+2)
948      NEWLINE
949      PRINTSTRING('INTERFERENCE CORRECTION FOR 'ELEM(J) IS')
950      PRINT(MA(J),1,8);PRINTSTRING(' COUNT RATIO 'ELEM(J))
951      NEWLINE;PRINTSTRING('PER UNIT INTERFERING ELEMENT')
952      NEWLINE
953      PRINTSTRING('INTERCEPT OF CORRECTION IS AT COUNT RATIO ')
954      PRINT(CX(J),1,8)
955      NEWLINE
956      REPEAT
957      22:CYCLE V=1,1,NOSAMS
958      CYCLE J=8,1,9
959      PK(V,J)=PK(V,J)-MA(J)+MAJ(22-J,V)*(100-LOI(V))/100
960      ! CORRECTION FOR CR AND NB REDUCED BECAUSE V AND LA REFER TO DRY
961      ! SAMPLE
962      REPEAT
963      PK(V,13)=PK(V,13)-.000082*MAJ(13,V)-.000088*MAJ(15,V)
964      ! TIO2W CORRECTED FOR V (13) AND BA (15) INTERFERENCE
965      REPEAT
966      END
967
968      26:IF BLOCK=0 THEN->226 ELSE->227
969      26:SELECT INPUT(6)
970      ! NO STANDARDS. CALIBRATION TAKEN FROM TRACDATA.
971      CYCLE NOEL=1,1,NOELS
972      READ(Z(NOEL));READ(MA(1,NOEL));READ(CX(1,NOEL))
973      REPEAT
974      ->26
975      27:IF PREL='Y' THEN PRELOAD('')
976      ! NEW CALIBRATION. PROCEDURE AS IN MAJORS
977      CYCLE NOEL=1,1,NOELS
978      ELNAME(NOEL)=ELEM(NOEL)

```

FIG B14 : continued. Program TRACE

```

976 REPEAT
977 SELECT INPUT(5);SET MARGINS(5,1,150)
978 ! INPUT FROM TRACANAL
979 STANSUSED=0
980 CYCLE A=1,1,BLOCK
981 CYCLE V=STANINIT(A),1,STANFINAL(A)
982 29:RSTRG(STNO)
983 IF STNO='STOP' THEN->230
984 IF STNO=NS(V) THEN->231
985 RSTRG(STNO):->29
986 31:STANSUSED<STANSUSED.' '.STNO
987 CYCLE B=1,1,18
988 READ(ZA);READ(PA)
989 ! 19 ATOMIC NUMBER-CONCENTRATION PAIRS PER STANDARD
990 CYCLE NOEL=1,1,NOELS
991 IF Z(NOEL)=ZA THEN P(V,NOEL)=PA AND EXII
992 REPEAT:REPEAT
993 ! NEXT 38 LINES PROVIDE EXTRA OMISSIONS FROM CALIBRATIONS
994 CYCLE NOEL=1,1,NOELS
995 IF Z(NOEL)=29 OR Z(NOEL)=17 START
996 IF STNO->('INTS').TAIL THEN->A30
997 FINISH
998 IF STNO='SY3' AND Z(NOEL)=62 THEN->C30
999 IF STNO->('INTS').HT START
1000 IF Z(NOEL)=24 OR Z(NOEL)=28 THEN->A30
1001 IF HT='B' OR HT='G' START
1002 IF Z(NOEL)=41 OR Z(NOEL)=62 THEN->A30
1003 FINISH
1004 FINISH
1005 IF STNO='PCC1' OR STNO='UBN' OR STAO='TANZ1' OR STNO='FKN' C
1006 OR STNO='DRN' OR STNO='SY3' START
1007 IF Z(NOEL)=41 OR Z(NOEL)=58 OR Z(NOEL)=60 OR Z(NOEL)=62 C
1008 THEN->A30
1009 FINISH
1010 IF STNO='PCC1' OR STNO='UBN' START
1011 IF Z(NOEL)=39 OR Z(NOEL)=40 THEN->A30
1012 FINISH
1013 IF STNO='PCC1' OR STNO='UBN' OR STNO='GSN' OR STNO='FKN' C
1014 OR STNO='TANZ1' OR STNO='DRN' OR STNO='SY3' THEN->A30
1015 FINISH
1016 IF Z(NOEL)=37 START
1017 IF STNO='TANZ1' OR STNO='FKN' OR STNO='INTSGA2' THEN->A30
1018 FINISH
1019 IF STNO->('INTS').HT.('A2') START
1020 IF Z(NOEL)=28 OR Z(NOEL)=41 THEN->A30
1021 FINISH
1022 IF STNO->('INTS').HT.('B2') START
1023 IF Z(NOEL)=30 OR Z(NOEL)=39 THEN->A30
1024 FINISH
1025 IF Z(NOEL)=40 START
1026 IF STNO='FKN' OR STNO='INTSBE2' THEN->A30
1027 FINISH
1028 IF STNO->('INTS').HT.('1') START
1029 UNLESS Z(NOEL)=56 THEN->A30
1030 FINISH
1031 C30:IF OMIT->HEAD.(STNO.' ').TAIL START
1032 B30:CYCLE ZA=1,1,LENGTH(TAIL)
1033 ZBP=740
1034 IF CHARNO(TAIL,ZA)='.' OR CHARNO(TAIL,ZA)='.' START
1035 HT=FROMSTRING(TAIL,1,ZA-1)
1036 IF Z(NOEL)=INTEGRAL(HT) THEN ZBP=750 AND EXII
1037 IF CHARNO(TAIL,ZA)='.' THEN EXII
1038 TAIL->HEAD.(' ').TAIL
1039 ZBP=730:EXII
1040 FINISH
1041 REPEAT
1042 IF ZBP=750 THEN->A30
1043 IF ZBP=730 THEN->B30
1044 FINISH
1045 ! REGRESSION COMPARABLE TO WTRACE
1046 STAN(NOEL)=STAN(NOEL)+1
1047 CALIB(NOEL)_STPC(STAN(NOEL))=P(V,NOEL)
1048 CALIB(NOEL)_STRAT(STAN(NOEL))=PK(V,NOEL)
1049 EP(NOEL)=EP(NOEL)+P(V,NOEL)
1050 EC(NOEL)=EC(NOEL)+PK(V,NOEL)
1051 ECC(NOEL)=ECC(NOEL)+PK(V,NOEL)**2
1052 ECP(NOEL)=ECP(NOEL)+PK(V,NOEL)*P(V,NOEL)
1053 EPP(NOEL)=EPP(NOEL)+P(V,NOEL)**2
1054 A30:REPEAT
1055 30:SELECT INPUT(98);CLOSESTREAM(5);SELECT INPUT(5)
1056 REPEAT:REPEAT
1057 SELECT OUTPUT(6)
1058 CYCLE NOEL=1,1,NOELS
1059 REB=STAN(NOEL)*EPP(NOEL)-STAN(NOEL)*ECC(NOEL)+EC(NOEL)**2-EP(NOEL)**2
1060 REA=EC(NOEL)*EP(NOEL)-STAN(NOEL)*ECP(NOEL)
1061 MA(1,NOEL)=(-REB+SQRT(REB**2+4*REA**2))/(2*REA)
1062 MA(2,NOEL)=(-REB-SQRT(REB**2+4*REA**2))/(2*REA)
1063 CY(1,NOEL)=(EP(NOEL)-MA(1,NOEL)*EC(NOEL))/STAN(NOEL)
1064 CY(2,NOEL)=(EP(NOEL)-MA(2,NOEL)*EC(NOEL))/STAN(NOEL)

```


FIG. B14 : continued. Program TRACE

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1063       CYCLE ZBP=1,1,2
1064       REC(ZBP)=MA(ZBP,NOEL)**2+1
1065       REC(ZBP)=(EPP(NOEL)-2*MA(ZBP,NOEL)*ECP(NOEL)+2*CX(ZBP,NOEL)*MA C
C         (ZBP,NOEL)*EC(NOEL)-2*CX(ZBP,NOEL)*EP(NOEL)+ECC(NOEL)*MA(ZBP,NOEL)C
C         **2+STAN(NOEL)*CX(ZBP,NOEL)**2)/REC(ZBP)
1066       REPEAT
1067       IF REC(2)<REC(1) THEN MA(1,NOEL)=MA(2,NOEL) AND CX(1,NOEL)=CX(2,NOEL)
1068       CYCLE ZBP=1,1,40
1069       IF CALIB(NOEL)_STPC(ZBP)=0 AND CALIB(NOEL)_STPAT(ZBP)=0 C
C         THEN CALIS(NOEL)_STPC(ZBP)=.00001
1070       REPEAT
1071       CALIB(NOEL)_CALM=MA(1,NOEL)
1072       CALIB(NOEL)_CALC=CX(1,NOEL)
1073       PRINT(Z(NOEL),2,0)
1074       ! UPDATING TRACDATA
1075       PRINT(MA(1,NOEL),5,7);SPACES(2)
1076       PRINT(CX(1,NOEL),5,7);NEWLINE
1077       REPEAT
1078       NEWLINES(2)
1079       PRINTSTRING(STANSUSED)
1080       28:IF S3="*.NULL" THEN-256
1081       SELECTOUTPUT(3);SET MARGINS(3,1,130)
1082       ! PRINTS ANALYSIS FILE, WITH COPY OF TRACDATA AT START
1083       CYCLE NOEL=1,1,NOELS
1084       PRINT(Z(NOEL),2,0);PRINT(MA(1,NOEL),5,7);SPACES(2)
1085       PRINT(CX(1,NOEL),5,7);NEWLINE
1086       REPEAT
1087       NEWLINES(2)
1088       PRINTSTRING(STANSUSED)
1089       NEWLINE; PRINTSTRING(OMIT)
1090       NEWLINES(3)
1091       SPACES(14)
1092       CYCLE NOEL=1,1,NOELS
1093       PRINTSTRING(ELEM(NOEL));SPACES(8-LENGTH(ELEM(NOEL)))
1094       REPEAT
1095       PRINTSTRING('T102M')
1096       NEWLINE
1097       CYCLE V=1,1,NOSAMS
1098       NEWLINES(2)
1099       PRINTSTRING(NS(V));SPACES(9-LENGTH(NS(V)))
1100       CYCLE NOEL=1,1,NOELS
1101       IF STANSPRES->HT.(NS(V)).LT START
1102       PA=MA(1,NOEL)*PK(V,NOEL)+CX(1,NOEL)
1103       ! CALCULATES ANALYSES OF STANDARDS (WET)
1104       ->928
1105       FINISH
1106       PA=(MA(1,NOEL)*PK(V,NOEL)+CX(1,NOEL))*100/(100-LOI(V))
1107       ! CALCULATES ANALYSES; ! IF LOI NON-ZERO RECALCULATES TO DRY BASIS
1108       28:IF ELEM(NOEL)->('T102').HT THEN PRINT(PA,3,3) AND-2426
1109       PRINT(PA,5,1)
1110       A28:REPEAT
1111       PRINT(MAJ(8,V),3,3) UNLESS MAJ(8,V)=0
1112       REPEAT
1113       50:IF S5="*.NULL" THEN-232
1114       IF S1="*.NULL" OR S2="*.NULL" THEN-234
1115       ! CREATES NPMINPUT FILE FROM ANALYSIS FILE
1116       NEWLINE
1117       PROMPT('NO.OF ELEMENTS:');READ(NOELS)
1118       SELECTINPUT(3)
1119       RSTRG(CPS)
1120       CYCLE NOEL=1,1,NOELS
1121       WHILE CPS->(' ').CPS CYCLE;REPEAT
1122       IF NOEL=NOELS THEN ELEM(NOEL)=CPS AND-237
1123       CPS->ELEM(NOEL).(' ').CPS
1124       37:REPEAT
1125       CYCLE V=1,1,NOSAMS
1126       RSTRG(CPS)
1127       CPS->NS(V).(' ').CPS
1128       SELECTOUTPUT(7)
1129       PRINTSTRING(CPS);NEWLINE
1130       SELECTOUTPUT(99);CLOSESTREAM(7);SELECTINPUT(7)
1131       CYCLE NOEL=1,1,NOELS
1132       READ(BG1(V,NOEL))
1133       REPEAT
1134       SELECTINPUT(3);CLOSESTREAM(7)
1135       REPEAT;-236
1136       34:CYCLE V=1,1,NOSAMS
1137       CYCLE NOEL=1,1,NOELS
1138       BG1(V,NOEL)=(PK(V,NOEL)*MA(1,NOEL)+OX(1,NOEL))*100/(100-LOI(V))
1139       REPEAT;REPEAT
1140       36:SELECTOUTPUT(9);SET MARGINS(9,1,110)
1141       ! PRINTS NPMINPUT FILE, OMITTING STANDARDS
1142       CYCLE V=1,1,NOSAMS
1143       IF STANSPRES->HT.(NS(V)).LT THEN-2426
1144       PRINTSTRING(NS(V));PRINTSTRING(' ')
1145       NEWLINE
1146       CYCLE NOEL=1,1,10
1147       PRINTSTRING(MAJ(ELEM(NOEL))); PRINT(MAJ(NOEL,V),4,3)
1148       SPACE; IF NOEL=5 THEN NEWLINE
1149       REPEAT

```

FIG. B14 : continued. Program TRACE

```

1150      NEWLINE
1151      IF MAJ(12,V)=0 THEN=2036
1152      PRINTSTRING('LOI');PRINT(MAJ(12,V),3,2);SPACE
1153      B36:IF Z(1)=21 THEN=2036
1154      CYCLE NOEL=13,1,17
1155      PRINTSTRING(MAJEL(NOEL));PRINT(MAJ(NOEL,V),5,1);SPACE
1156      REPEAT
1157      NEWLINE
1158      PRINTSTRING(MAJEL(18));PRINT(MAJ(18,V),2,3);SPACE
1159      C36:CYCLE NOEL=1,1,NOELS
1160      IF NOEL=4 OR NOEL=9 THEN NEWLINE
1161      IF ELEM(NOEL)->('TIO2').TAIL THEN PRINTSTRING(ELEM(NOEL)) AND C
1162      PRINT(BG1(V,NOEL),1,3) AND=2036
1163      PRINTSTRING(ELEM(NOEL));PRINT(BG1(V,NOEL),5,1);SPACE
1164      D36:REPEAT
1165      NEWLINE
1166      IF V=NOSAMS THEN PRINTSTRING('*-2') ELSE PRINTSTRING('*-1')
1167      NEWLINE
1168      A36:REPEAT
1169      32:END
1170      END
?  UNUSED LABEL 35

```

FIG. B15 : Part of file TRACANAL - trace element standard data

```

G2
56 1850 29 11 57 100 21 4 23 34 58 150 24 9 41 14 28 6 37 170 38 480 39 12 30 85 40 300 17 .5 90 24 60 60 62 7.3
GSP1
56 1300 29 35 57 200 21 8 23 49 58 390 24 13 41 29 28 9 37 250 38 230 39 32 30 98 40 500 17 .66 90 105 60 190 62 27
AGV1
56 1200 29 63 57 45 21 12 23 125 58 63 24 12 41 15 28 17 37 67 38 660 39 26 30 84 40 220 17 1.05 90 6.4 60 39 62 5.9
STOP

```

file previously output by TRACE.

Output data: a combination of

- (A) Count ratio file (only possible if (a) above chosen)
- (B) Mass absorption corrected count ratio file, as (c) above
- (C) Trace element analysis file, comparable to Fig. B10, with only the elements present as atomic numbers in the input count ratios. If (g), (i) or (j) with LOI are used for matrix correction, then all trace element analyses will be multiplied by $100/(100-LOI)$, i.e. they will be quoted volatile-free. In these cases, the ignited major element analyses (and V and La, if correction to Cr and Nb is required) are reduced by $(100-LOI)/100$ prior to matrix correction, and the LOI is assumed to be 50% CO₂, 50% H₂O for its contribution to matrix correction. If input data from WTRACE is to be processed, and the file used for matrix correction does not contain V, La or Ba values, then no correction will be made to the Cr, Nb and TiO₂W concentrations, respectively.
- (D) Norminput file, similar to Fig. B11, and containing the newly processed trace element data, together with major and Cr-tube trace data, if such were present in the file used for matrix correction.
- (E) File TRACDATA, similar to Fig. B9, updated with each new calibration.
- (F) External records CALIB and ELNAME, as for MAJORS (ii)(e).

The program is not dissimilar to MAJORS, but is considerably more complex. If input data from WTRACE is used, then interference corrections for V on Cr and La on Nb are made by regressing matrix-corrected count ratios against ppm V and La present in the file used for matrix correction. All regressions carried out in TRACE are by the perpendicular-to-line method.

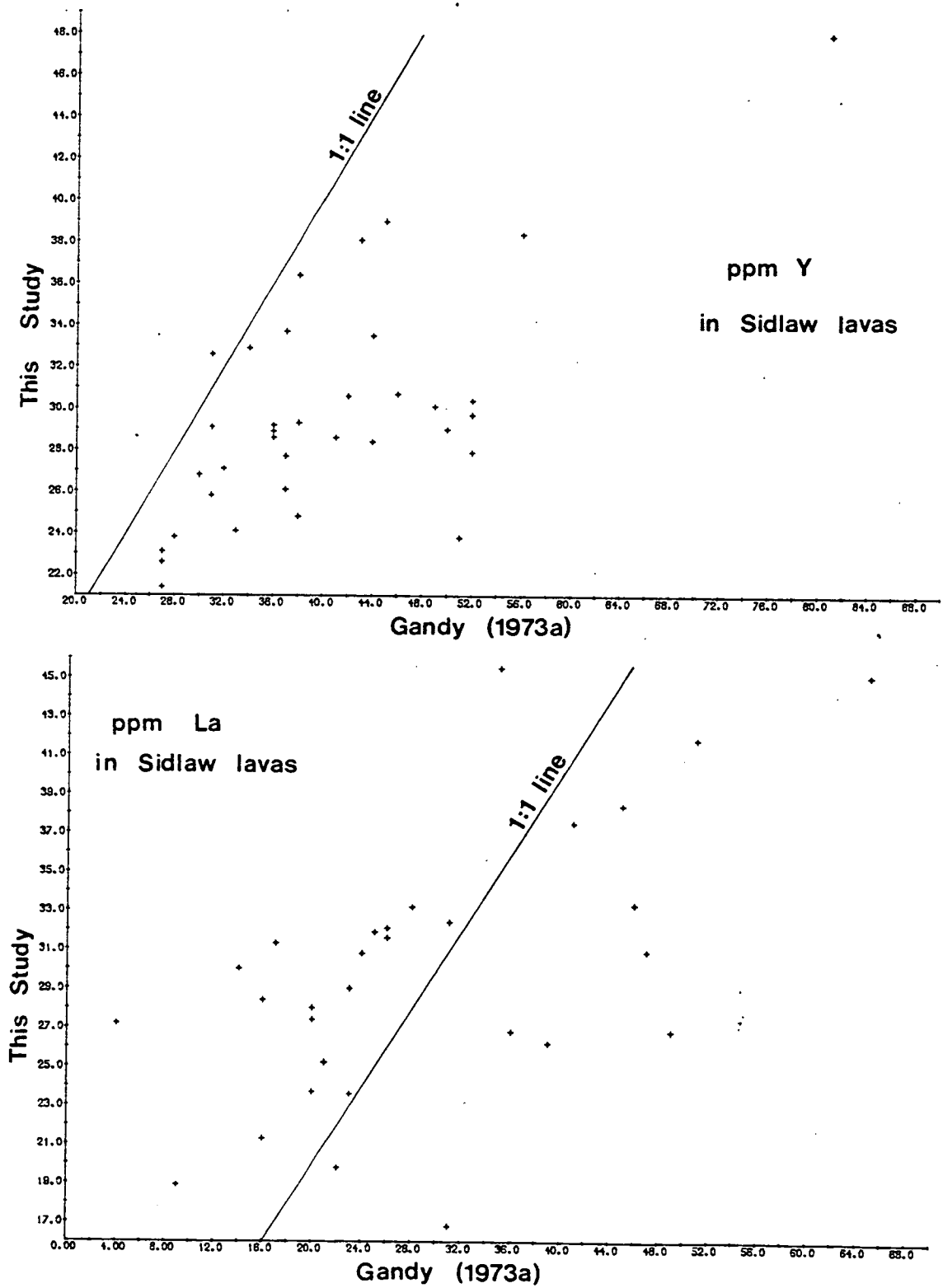
While there is a large number of possible routes by which data may be run using these programs, for ignited samples the most convenient way to obtain a full analysis is as follows:

- (1) RATMAJ and MAJORS, leading to Analysis file with LOI values
- (2) CRTRACE and TRACE, leading to norminput file with major elements, LOI and Cr-tube trace elements.
- (3) WTRACE and TRACE, leading to a norminput file containing the full analysis, all recalculated volatile-free.

B11 : COMPARISON WITH OTHER XRF METHODS

During the course of this study 35 samples with analyses quoted in Gandy (1973a) were re-analysed using the techniques previously described. Prior to comparison of results, the data of Gandy (1973a) were recalculated to 100%, to provide volatile-free analyses directly comparable with those of the author. Plots of the two values for each sample should ideally yield a 1:1 straight line, but only values for K₂O are a reasonable approximation to this. It will be seen that REE and Y compare particularly badly

**Fig. B16 : Comparison of analyses of S18-S52
from Table B17 and Gandy (1973a)**



(Fig. B16). It is difficult to suggest reasons for the large discrepancies in many elements, for a comprehensive account of the techniques used is not given in Gandy (1973a). It is suspected that some of the discrepancies in trace elements are caused by use of the Anderman-Kemp method of matrix correction, and the analysis of elements such as Ba, La and Ce on the highly energetic K_{α} lines. The strong evidence presented in Figs. B1, B3, Tables B15, B16 for the accuracy of the present techniques suggests that the analyses in Gandy (1973a) should be used with extreme caution.

Graham (in preparation) has re-analysed samples from Grenada, West Indies, previously analysed by Arculus (1973) at the University of Durham, and reports very large differences for several major elements. The differences are thought to be at least in part due to the use of an iterative correction procedure for counts made on pressed powder pellets (Holland and Brindle, 1966).

B12 : FUTURE IMPROVEMENTS IN METHOD

A number of modifications may possibly be made to improve the reported techniques in the future.

- (i) The use of a monitor in counting for TiK_{β} and CaK_{β} in the Cr-tube trace element program.
- (ii) Improvements in mass absorption coefficients, and possibly the extension of the calculation to give a coefficient for each analytical wavelength.
- (iii) The use of matrix correction for major elements.
- (iv) Improvements in knowledge of standard concentrations or in homogeneity of standards.
- (v) Use of improved knowledge of the relationship between background intensity and mass absorption coefficient to remove any problems caused by residual background B^* (section B5iii).
- (vi) Improvements in spectrometer resolution, reducing the magnitude of interference corrections.
- (vii) An understanding of the origin of the $TiO2W-TiO2$ discrepancy (section B9) may lead to changes in the techniques.
- (viii) Use of an interference correction for NdL_{α} on CeL_{β} , and possibly the use of an interference correction for CrK_{α} on the Nd and Ce backgrounds.
- (ix) Change in position of Cu background to avoid interference by HfL_{α} and 2nd order ZrK_{α} .

Precision and detection limits may easily be improved for all elements by increasing the total counting time. This may be done either by increasing the number of counts which the monitor is required to accumulate, or by increasing the number of peak-background pairs. The former method does not require modification of the computer programs, but if the interval between successive references to the monitor becomes too great then medium term machine drift can become important. It is thought that the low analytical precision quoted for Sm results from this effect, for the time between references to the monitor was here as

long as 18 min. It is believed that this time should be kept to less than about 6 min, and it has been shown that, by increasing substantially the number of peak-background pairs and counting for about 30 min per sample, Hf may be analysed to a precision of ± 0.5 ppm. Precision for Sm, Th and also Ba could therefore be improved by increasing the number of peak-background pairs. Analysis of a number of low concentration elements has been attempted using this method: it is believed that analysis of at least Hf, U, Pr, Cs and possibly Eu may be feasible.

Table B17 : Analyses of samples listed in Table A1 for 10 major and 17 trace elements.

FE203 is total iron as Fe2O₃, LOI is loss on ignition. TiO₂CR and TiO₂W are TiO₂ determined on trace element pellets as in section B9.

* = negative concentration; this has only occurred for Th (minimum -5 ppm), Sm (-2 ppm), Sc (-0.6 ppm) and Na₂O (-0.06 %). With the exception of Th, these are within the precision limits of zero concentration. The negative Th values do not appear to be the result of interference on background, and may have the same origin as the differences in Th content between the samples quoted in Table A2, and between MT45 run for precision (Table B7) and reproducibility (Table B3) data.

n.d. = not determined.

TABLE B17

	L1324	L321	L421	L5214	L821	L927	L1028	L1128	L1221
SI02	64.04	52.86	51.65	64.26	54.57	55.07	59.88	59.36	53.53
AL203	16.28	16.40	16.26	16.57	15.67	15.73	17.02	16.95	16.79
FE203	4.81	8.65	9.44	4.96	8.58	7.96	5.67	6.93	8.21
MGO	2.62	6.88	4.04	2.21	3.92	4.44	3.62	4.46	4.30
CAO	2.84	7.14	10.75	3.72	6.54	7.11	4.88	1.67	9.36
NA2O	4.50	3.72	3.65	4.20	3.75	3.90	4.83	5.84	3.70
K2O	3.669	2.212	1.901	3.123	2.973	1.948	2.584	2.905	1.987
TiO2	0.739	1.443	1.540	0.706	1.238	1.271	0.941	1.002	1.336
MNO	0.066	0.116	0.128	0.052	0.156	0.083	0.078	0.096	0.120
P2O5	0.233	0.460	0.465	0.208	0.523	0.363	0.340	0.344	0.432
TOTAL	99.82	99.89	99.93	100.00	99.92	99.87	99.83	99.55	99.77
LOI	3.82	2.17	4.55	3.40	1.60	1.71	1.34	2.22	6.17
NI	44.0	164.0	175.5	42.8	100.3	133.7	60.5	73.2	160.1
CR	73.0	370.8	312.6	87.7	275.4	250.3	143.7	160.3	295.3
V	86.1	165.6	168.9	84.4	139.9	153.8	115.6	125.0	168.1
SC	12.2	22.9	24.6	12.5	17.5	20.5	14.6	14.8	23.0
CU	17.9	18.4	23.5	20.4	12.6	44.8	31.6	14.2	32.8
ZN	62.4	85.5	89.2	56.3	89.6	77.3	65.6	77.1	93.7
SR	655.2	1251.4	1064.6	624.4	1333.6	926.3	1065.1	1427.6	961.4
RB	79.2	36.8	25.9	66.8	63.8	36.9	41.0	47.2	22.4
ZR	205.2	193.5	229.9	176.9	211.9	197.6	162.1	161.1	231.1
NB	10.6	15.3	15.8	9.3	13.6	14.3	9.9	10.4	15.4
BA	1913.4	1079.2	804.0	1316.0	1418.1	744.6	1106.1	1430.3	697.4
TH	4.6	5.0	5.8	3.9	7.3	6.1	3.2	2.8	7.5
LA	31.5	34.8	33.3	27.8	44.7	32.3	30.4	33.1	38.7
CE	73.0	79.7	77.9	62.1	99.5	56.5	56.7	69.2	87.7
NO	31.9	37.1	36.9	28.4	43.5	29.8	30.2	31.6	40.8
SM	4.4	5.6	7.8	6.2	9.4	8.4	4.3	7.2	12.8
Y	18.3	21.0	23.3	16.1	17.4	20.8	15.5	15.7	23.1
TiO2CR	0.722	1.517	1.716	0.676	1.167	1.229	1.004	1.044	1.443
TiO2W	0.730	1.531	1.727	0.692	1.196	1.286	0.988	1.042	1.446
	L1321	L1428	L1821	L1921	L2127	L22220	L2321	L2427	L2521
SI02	57.62	61.05	56.78	51.91	59.55	64.56	48.90	54.27	55.01
AL203	16.57	16.70	16.62	16.98	16.31	15.69	17.47	16.10	16.89
FE203	7.39	5.92	8.05	7.62	6.23	4.97	9.87	7.58	7.42
MGO	3.63	3.06	3.33	4.62	3.69	1.31	7.19	5.72	4.56
CAO	6.82	4.48	6.79	11.22	5.62	2.74	10.57	7.98	8.47
NA2O	3.68	4.74	3.35	3.39	4.14	5.42	2.70	3.70	3.48
K2O	2.285	2.587	2.624	1.693	2.517	3.019	1.095	2.493	1.958
TiO2	1.345	0.787	1.376	1.692	1.026	0.728	1.535	1.331	1.317
MNO	0.091	0.051	0.088	0.134	0.087	0.053	0.135	0.101	0.081
P2O5	0.430	0.339	0.464	0.491	0.389	0.287	0.395	0.453	0.436
TOTAL	99.86	99.74	99.48	99.75	99.56	99.78	99.85	99.73	99.63
LOI	3.83	1.64	4.16	6.52	1.56	3.09	2.90	3.45	5.89
NI	161.1	48.6	154.3	177.7	76.9	33.6	91.9	164.9	158.3
CR	297.2	90.9	314.1	405.4	158.6	26.2	148.8	304.7	301.3
V	147.6	91.3	153.7	201.5	125.2	58.3	205.0	144.4	152.4
SC	23.4	11.8	24.2	30.7	15.9	10.9	29.6	21.8	22.0
CU	15.8	19.9	24.8	23.4	20.9	10.3	45.5	14.4	18.6
ZN	75.7	61.0	61.4	76.2	62.8	34.7	70.4	87.1	84.3
SR	892.7	1100.1	963.9	1082.1	1037.3	1176.8	1113.6	1022.7	957.5
RB	47.4	41.7	47.8	27.7	40.9	54.5	13.6	48.9	27.4
ZR	230.3	146.4	223.4	238.5	175.4	153.2	160.4	220.8	229.3
NB	15.4	2.9	14.7	18.7	10.9	10.4	5.4	15.0	15.1
BA	757.2	1359.0	985.6	626.5	1150.5	1242.5	694.8	942.1	824.0
TH	8.0	2.9	8.9	6.6	4.2	5.6	*	6.1	6.6
LA	39.4	34.5	40.9	36.9	37.8	39.5	21.1	41.8	39.7
CE	88.6	73.2	91.1	80.1	73.1	71.2	56.3	91.5	86.4
NO	38.8	33.1	43.7	35.9	35.3	32.1	33.2	43.0	38.7
SM	7.6	7.1	7.4	13.3	11.0	2.4	10.8	10.1	8.8
Y	23.6	14.6	21.7	22.0	15.5	14.3	26.5	22.1	22.5
TiO2CR	1.338	0.825	1.326	1.662	1.041	0.744	1.651	1.399	1.385
TiO2W	1.359	0.810	1.349	1.714	1.041	0.739	1.589	1.367	1.385

TABLE B17

	L2607	L29013	L30013	L34045	L35021	L38020	L41020	L42019	L43022
SI02	54.57	62.45	62.67	53.14	74.77	62.73	57.75	71.76	58.84
AL203	15.57	15.37	16.32	17.26	14.60	17.71	17.16	14.43	16.21
FE203	7.73	5.31	5.09	9.51	1.14	3.84	5.45	2.28	3.45
MGO	6.61	2.79	3.10	5.36	0.85	3.43	5.45	0.41	6.88
CAO	7.42	3.90	3.25	5.35	0.97	2.20	5.15	4.21	1.99
NA20	3.46	4.06	4.75	5.35	2.66	4.25	4.14	4.02	4.15
K20	2.272	3.197	2.930	1.986	5.355	2.224	1.900	2.776	3.540
TIO2	1.336	0.840	0.831	1.227	0.216	0.805	0.984	0.271	0.601
MNO	0.085	0.090	0.077	0.100	0.060	0.033	0.121	0.045	0.062
P205	0.466	0.269	0.267	0.407	0.654	0.310	0.344	0.090	0.210
TOTAL	99.56	99.25	99.25	99.53	100.06	99.53	99.45	100.29	99.98
LOI	3.29	2.76	1.86	5.35	2.40	4.34	2.22	4.45	3.77
NI	172.7	40.3	40.4	173.5	8.1	73.6	92.7	13.1	19.1
CR	295.3	65.3	66.2	354.6	5.4	121.6	140.4	13.9	38.9
V	138.7	99.0	100.4	162.7	8.0	109.2	133.1	21.7	60.9
SC	16.2	13.1	12.5	26.3	3.4	14.6	18.5	4.6	8.2
CU	27.5	23.0	22.7	34.7	2.3	10.2	21.8	4.0	8.1
ZN	75.9	63.3	64.8	104.3	41.9	32.3	106.3	17.2	29.4
SR	1200.0	1059.9	1179.5	997.9	264.1	515.4	1024.2	328.8	465.1
RE	45.3	70.5	69.3	44.9	124.0	37.8	32.0	68.6	80.0
ZR	199.4	194.5	196.5	181.2	181.8	153.4	169.3	122.8	188.3
NB	14.4	9.2	9.0	8.9	14.5	8.3	9.5	12.1	12.4
BA	1051.1	1562.0	1302.9	1049.5	1056.6	345.6	932.2	1143.6	1059.9
TH	8.9	9.7	8.1	4.9	12.4	7.2	4.5	10.1	12.0
LA	44.0	35.2	35.1	34.6	35.4	31.6	29.2	28.5	38.0
CE	97.1	73.8	71.4	73.0	73.2	51.2	55.2	54.7	73.7
ND	45.2	33.3	33.0	36.7	36.5	28.9	29.8	24.0	30.2
SM	5.4	4.2	*	6.2	5.7	4.3	2.9	4.0	2.0
Y	22.4	18.9	18.0	20.6	18.8	15.5	18.3	17.6	15.4
TIO2CR	1.282	0.838	0.842	1.248	0.230	0.816	0.979	0.300	0.604
TIO2W	1.317	0.837	0.842	1.279	0.242	0.830	0.993	0.303	0.628
	L4401	L4508	L50345	L5139	L5209	L54022	L55022	L5601	L5801
SI02	55.33	61.27	59.51	60.30	50.83	56.25	57.26	52.53	53.01
AL203	16.21	16.92	15.65	15.48	15.50	15.28	19.05	16.19	16.70
FE203	9.71	5.39	6.09	5.92	6.40	5.81	8.37	7.91	8.47
MGO	5.63	3.50	4.34	3.51	4.58	5.00	2.21	7.50	6.74
CAO	5.74	4.37	5.79	5.75	2.82	5.75	1.34	7.44	6.44
NA20	3.43	4.53	3.58	3.98	4.70	4.37	5.11	3.54	3.79
K20	1.709	2.634	2.442	2.529	2.239	4.338	4.412	2.689	2.119
TIO2	1.427	0.806	1.031	0.919	0.933	0.885	0.817	1.166	1.608
MNO	0.075	0.068	0.082	0.075	0.062	0.098	0.043	0.130	0.150
P205	0.369	0.356	0.390	0.353	0.343	0.593	0.625	0.553	0.466
TOTAL	99.62	99.84	99.51	99.82	99.41	99.38	99.24	99.75	99.50
LOI	1.95	1.35	2.42	2.10	2.49	5.11	2.33	2.71	2.18
NI	181.3	44.7	132.7	81.1	82.9	195.5	14.0	215.6	158.2
CR	338.5	88.8	233.1	166.1	174.3	376.8	6.9	412.9	279.0
V	175.8	95.0	116.0	109.7	118.4	113.9	137.0	160.2	156.1
SC	24.1	12.3	14.3	14.5	15.3	16.6	10.6	18.0	17.7
CU	114.4	25.9	24.6	27.4	23.8	26.6	29.5	38.0	41.1
ZN	77.1	70.3	72.9	72.3	80.4	79.2	151.1	81.6	75.7
SR	726.8	1141.9	927.9	1065.5	1155.8	2236.3	1728.2	1435.0	1040.4
RB	32.7	43.1	40.9	47.6	31.1	57.0	81.0	45.1	22.5
ZR	205.1	149.8	188.5	159.3	172.7	157.3	225.9	192.3	197.4
NB	13.7	9.4	11.3	11.0	11.5	7.4	9.8	10.0	17.4
BA	773.3	1318.0	1105.2	1073.3	1042.4	2998.0	1772.0	1258.9	849.8
TH	4.2	3.4	3.6	6.5	6.8	7.5	15.0	3.1	6.3
LA	28.1	32.8	34.6	36.7	34.3	75.7	80.7	38.6	29.2
CE	62.7	67.8	76.6	76.4	72.2	155.8	193.5	88.2	73.2
ND	28.5	32.2	33.4	33.2	32.2	91.0	87.4	43.7	34.6
SM	10.3	8.0	6.4	6.7	6.5	11.7	11.5	6.8	5.9
Y	20.2	14.1	15.7	15.6	16.7	16.6	17.2	16.7	18.7
TIO2CR	1.277	0.818	1.035	0.942	0.940	0.939	0.845	1.244	1.707
TIO2W	1.371	0.832	1.050	0.944	0.952	0.917	0.839	1.239	1.668

TABLE B17

	L61247	L63247	L6497	L6527	L6721	L6321	L7121	L73212	L75219
SI02	59.38	54.92	58.10	53.54	53.72	55.56	56.87	50.92	55.97
AL203	16.72	17.25	15.90	15.75	17.34	15.86	16.12	17.55	17.38
FE203	6.24	8.05	7.39	7.40	7.80	7.11	7.27	9.60	3.80
MGO	3.14	3.55	4.25	7.75	6.21	5.12	5.03	4.77	0.78
CAO	7.11	7.42	5.88	6.19	6.65	7.79	6.25	10.35	1.58
NA20	4.12	4.26	3.33	3.91	4.54	3.74	3.86	3.56	5.49
K20	2.148	1.979	2.554	3.065	1.997	2.406	2.433	1.236	3.736
TI02	0.975	1.451	1.020	1.185	1.197	1.087	1.321	1.590	0.838
MNO	0.072	0.073	0.080	0.136	0.100	0.098	0.074	0.108	0.037
P205	0.339	0.508	0.425	0.512	0.429	0.455	0.484	0.387	0.263
TOTAL	100.25	99.47	99.41	99.55	99.97	99.22	99.71	100.08	99.86
LOI	4.15	4.55	2.81	2.71	1.48	2.79	3.32	5.18	1.32
NI	96.1	113.9	182.4	210.4	146.4	155.3	162.5	152.8	12.2
CR	169.4	225.7	270.5	320.1	366.0	255.1	273.5	330.0	19.9
V	130.6	223.5	135.7	139.0	145.6	128.1	137.4	200.5	71.5
SC	17.4	18.7	18.3	14.0	21.8	16.6	20.8	34.8	7.8
CU	23.7	12.6	23.5	35.4	15.4	27.7	23.0	58.2	3.9
ZN	70.6	84.6	76.0	76.8	67.0	74.8	76.1	81.6	54.6
SR	1047.0	1184.2	1311.9	1538.1	1201.5	1424.1	1150.6	887.7	1063.9
RB	21.9	23.7	42.5	58.1	28.2	39.5	41.2	18.3	79.0
ZR	165.3	195.6	170.5	181.6	148.9	181.0	214.7	203.3	769.2
NB	10.6	17.6	12.1	11.0	9.7	12.3	17.3	11.4	10.1
BA	1436.8	872.0	1162.3	1770.7	1040.0	1050.0	868.0	581.5	3227.2
TH	3.3	1.3	6.8	*	1.2	6.0	4.7	4.3	1.9
LA	31.5	29.5	43.9	33.4	31.5	43.2	43.9	28.6	38.6
CE	63.6	68.9	86.9	77.6	69.8	93.2	88.8	61.5	79.2
ND	31.4	32.7	39.2	38.2	33.8	41.6	41.1	30.7	38.7
SM	6.4	6.9	7.3	7.8	6.9	7.1	4.8	3.2	7.5
Y	17.2	18.3	16.2	15.7	16.7	19.8	19.0	25.8	21.7
TI02CR	1.030	1.502	1.034	1.253	1.080	1.059	1.356	1.622	0.892
TI02W	1.025	1.515	1.045	1.252	1.139	1.102	1.373	1.642	0.871

	L77219	L79213	L82225	L85213	L8723	L9123	L92219	L95213	L9727
SI02	67.00	63.34	63.90	62.69	61.08	60.33	77.61	62.91	58.33
AL203	16.07	16.95	16.09	16.52	17.21	14.38	12.05	16.44	16.44
FE203	3.46	4.88	5.75	4.96	8.66	7.35	1.33	5.21	6.40
MGO	2.51	2.10	3.43	3.49	2.83	5.77	0.28	3.04	6.38
CAO	1.46	2.62	3.59	3.65	2.93	2.57	0.95	4.09	5.80
NA20	5.17	5.87	3.52	4.15	1.07	3.65	2.36	3.75	3.34
K20	3.468	3.259	2.535	2.997	3.994	2.580	5.278	3.423	2.090
TI02	0.520	0.952	0.787	0.850	1.362	1.137	0.205	0.826	0.790
MNO	0.036	0.070	0.061	0.064	0.065	0.086	0.035	0.056	0.104
P205	0.226	0.310	0.240	0.275	0.415	0.346	0.017	0.262	0.281
TOTAL	99.91	100.34	99.91	99.55	99.61	99.20	100.11	100.00	99.96
LOI	2.04	1.60	1.14	2.97	5.83	4.29	1.61	2.93	2.38
NI	45.7	17.0	69.5	39.9	150.2	180.3	4.6	38.5	126.9
CR	86.1	21.0	153.1	66.0	464.9	394.1	4.0	62.7	305.1
V	72.7	118.0	110.1	114.9	133.1	129.2	8.8	110.9	146.3
SC	9.2	11.2	15.4	14.4	24.5	22.5	2.8	14.7	21.6
CU	15.0	20.5	4.7	22.6	26.3	25.9	3.1	19.4	24.8
ZN	59.3	64.3	44.8	67.0	61.5	94.3	22.8	63.0	67.4
SR	1612.1	1130.1	821.1	979.8	309.8	900.7	325.4	906.9	882.2
RB	54.8	71.0	70.0	74.2	117.2	53.1	105.5	74.0	35.6
ZR	114.8	226.8	183.8	202.1	242.6	197.1	203.5	206.4	138.6
NB	6.8	11.1	9.2	9.7	17.2	14.0	12.4	9.9	7.7
BA	1223.4	1274.9	1092.8	1238.5	626.9	951.1	2125.9	1359.0	996.3
TH	3.3	7.9	6.9	7.6	8.7	7.2	7.7	6.5	3.4
LA	23.7	34.9	31.2	36.9	37.5	28.0	43.0	37.0	26.8
CE	50.6	77.3	63.8	75.9	71.1	53.1	85.3	76.8	59.7
ND	24.8	35.7	27.1	34.2	32.9	28.8	35.9	34.3	27.2
SM	5.4	7.0	6.3	6.7	7.6	6.0	6.1	6.4	5.4
Y	9.0	20.4	16.7	18.6	19.3	17.7	16.0	17.7	17.5
TI02CR	0.562	0.971	0.858	0.855	1.350	1.162	0.228	0.873	0.807
TI02W	0.557	0.974	0.834	0.866	1.394	1.192	0.240	0.865	0.816

TABLE B17

	L98a6	L99a19	L100a6	L101a9	L102a13	L113a15	L120a19	L111a13	L122a26
SI02	60.67	73.58	63.00	58.44	63.08	57.11	58.45	60.22	52.69
AL203	17.11	13.29	17.22	17.05	15.45	15.22	14.51	16.92	15.91
FE203	5.65	3.32	4.83	6.90	5.12	5.45	4.36	5.92	8.33
MGO	2.16	0.64	1.64	4.25	3.37	4.58	2.17	3.57	6.56
CAJ	4.03	1.95	2.21	5.13	3.56	5.09	0.47	4.73	8.72
NA20	5.83	3.32	6.01	3.55	4.32	4.11	4.50	3.94	3.65
K20	3.158	3.069	3.287	2.022	3.083	5.006	4.620	3.189	2.046
TIO2	0.934	0.607	0.929	0.914	0.783	0.918	0.552	1.057	1.064
MNO	0.069	0.040	0.057	0.069	0.073	0.074	0.068	0.083	0.084
P205	0.288	0.231	0.268	0.204	0.240	0.615	0.211	0.315	0.465
TOTAL	99.87	100.04	99.47	99.51	100.07	99.17	99.91	99.95	99.52
LOI	4.07	1.85	2.20	2.11	2.36	2.06	1.35	2.95	3.61
NI	24.1	7.1	12.4	52.5	45.7	96.8	27.1	66.4	184.6
CR	37.0	33.1	14.7	84.8	82.9	114.2	43.3	115.4	320.1
V	98.3	30.9	98.5	138.2	104.5	104.8	60.0	127.8	169.8
SC	12.3	4.2	9.3	19.3	13.7	11.1	10.2	17.7	25.1
CU	14.9	1.9	10.9	20.1	23.9	26.8	7.7	22.8	22.4
ZN	65.6	31.7	63.4	65.6	63.9	78.4	63.4	66.4	72.7
SR	821.3	506.1	1120.6	936.5	792.4	1898.4	520.7	748.0	1766.6
RB	73.4	51.7	71.0	33.2	67.8	148.0	104.2	75.5	20.2
ZR	501.3	617.1	654.7	115.8	186.6	351.3	172.3	219.2	112.5
NB	8.9	8.4	10.8	6.1	8.8	9.2	33.6	10.6	7.2
BA	1912.8	1973.0	2223.9	969.9	1184.7	2107.0	1265.6	870.9	1372.5
TH	3.2	1.0	3.2	2.6	6.1	1.1	13.0	6.2	0.3
LA	36.7	30.8	35.4	16.3	33.7	40.7	28.2	37.3	34.7
CE	76.9	63.5	75.9	40.8	57.2	36.6	56.4	76.8	85.8
ND	35.3	30.6	36.9	21.2	30.1	48.2	26.4	33.1	45.1
SM	5.6	4.2	5.0	4.6	2.6	4.2	3.9	5.5	6.6
Y	21.5	16.5	22.7	17.5	17.8	13.6	26.1	20.9	17.9
TIO2CR	1.004	0.644	0.994	0.963	0.769	0.987	0.623	1.105	1.121
TIO2W	1.002	0.651	0.979	0.951	0.784	0.971	0.611	1.120	1.128
L125a15	L126a7	L128a13	L129a1	L130a19	L131a5	L132a5	L133a1	L137a26	
SI02	62.95	55.97	61.32	55.79	66.68	64.48	59.32	57.29	53.10
AL203	15.49	16.60	16.71	17.25	17.19	15.96	18.32	17.30	16.31
FE203	4.09	7.43	5.59	6.50	3.61	4.55	4.99	7.04	7.91
MGO	3.23	4.71	3.00	5.14	2.20	2.55	3.40	3.73	6.04
CAC	3.95	6.24	5.02	6.97	0.63	1.75	5.15	3.83	7.28
NA20	4.69	4.26	3.96	4.05	5.58	4.20	4.51	6.46	4.34
K20	4.432	2.990	2.583	2.079	2.742	5.477	2.927	2.382	2.920
TIO2	0.513	1.076	0.896	1.382	0.631	0.700	1.270	1.143	1.065
MNO	0.064	0.077	0.071	0.096	0.052	0.083	0.055	0.102	0.106
P205	0.338	0.533	0.277	0.482	0.165	0.223	0.351	0.464	0.472
TOTAL	99.74	99.88	99.52	99.84	99.47	99.98	100.30	99.74	99.55
LOI	1.08	2.06	1.63	2.86	2.17	1.94	2.66	3.39	5.41
NI	66.0	81.0	73.9	133.1	18.1	29.1	57.4	85.0	142.0
CR	66.5	192.8	128.1	207.9	36.3	51.7	108.8	164.0	187.6
V	69.7	124.5	110.8	152.9	51.2	88.8	149.7	135.6	170.2
SC	8.7	15.0	15.6	22.6	6.3	10.5	21.4	15.5	23.1
CU	20.9	20.3	27.7	35.9	4.9	12.1	57.6	24.3	18.3
ZN	55.9	77.0	58.4	86.9	64.6	54.5	58.8	93.4	84.1
SR	1978.2	1559.4	1003.9	1016.3	1197.9	847.1	918.5	2008.7	971.0
RB	68.7	43.1	57.3	27.2	71.7	112.1	64.6	37.1	28.9
ZR	170.2	187.3	187.3	229.0	526.7	213.4	242.9	194.3	126.1
NB	8.1	13.3	9.4	16.4	10.2	12.6	10.5	16.1	6.9
BA	2239.0	1688.3	1058.2	900.9	1929.5	2315.9	1074.8	970.1	1877.1
TH	12.7	2.1	5.6	3.0	3.7	7.9	5.9	1.5	0.2
LA	66.4	39.3	33.5	39.8	38.2	27.2	39.4	37.9	37.4
CE	140.6	87.4	71.4	89.2	81.0	52.8	78.0	76.1	84.5
ND	62.7	42.3	32.1	40.1	42.5	29.2	34.5	37.6	44.9
SM	7.6	5.6	3.6	5.5	6.0	3.9	4.2	4.5	5.9
Y	13.5	16.2	17.8	22.8	22.8	15.8	18.2	17.1	18.4
TIO2CR	0.539	1.102	0.926	1.368	0.638	0.730	1.308	1.128	1.123
TIO2W	0.536	1.095	0.922	1.391	0.645	0.739	1.333	1.166	1.131

TABLE B17

	L14021	L14121	L14627	L14831	L15021	L15121	L15221	L15321	L15527
SI02	55.34	52.67	54.76	53.50	73.11	53.26	54.99	52.64	53.99
AL203	17.43	16.87	17.04	16.58	14.94	17.26	16.56	16.25	16.59
FE203	6.35	8.70	7.50	7.90	1.39	9.43	8.20	9.38	8.37
MGO	5.83	5.52	5.79	6.92	0.36	4.72	5.55	6.11	4.59
CAO	5.74	6.48	6.66	5.87	0.77	1.96	7.24	8.33	7.86
NA20	4.41	4.90	3.95	3.85	4.30	3.99	3.72	3.46	4.29
K20	2.559	1.963	2.257	2.062	4.923	2.622	1.851	1.713	2.160
TI02	1.295	1.575	1.209	1.464	0.313	1.605	1.435	1.636	1.524
MNO	0.079	0.230	0.067	0.158	0.045	0.069	0.090	0.105	0.122
P205	0.466	0.547	0.385	0.512	0.048	0.484	0.393	0.416	0.520
TOTAL	99.49	99.46	99.61	99.82	100.21	99.39	100.03	100.02	100.05
LOI	1.72	2.09	1.69	2.17	1.19	2.14	1.76	1.88	2.12
NI	124.1	99.3	142.2	151.0	6.6	147.8	179.8	184.2	158.2
CR	266.0	222.6	302.1	283.5	6.3	319.6	316.8	322.8	295.5
V	159.0	167.4	151.6	156.5	18.9	97.5	207.0	158.0	175.3
SC	19.5	16.6	19.9	20.1	4.0	23.8	22.9	22.2	20.1
CJ	49.1	23.5	32.1	16.6	6.7	32.9	41.5	42.8	30.8
ZN	89.9	91.5	66.0	80.0	34.4	92.9	89.2	81.1	77.7
SR	1326.9	1629.9	984.1	942.8	279.8	1177.8	856.1	924.8	1077.9
RB	37.0	10.3	36.8	37.0	106.4	38.2	40.3	33.5	41.9
ZR	167.3	170.7	186.5	236.6	251.9	215.4	229.0	230.6	248.3
NB	11.8	12.9	13.6	18.6	13.5	19.0	15.9	15.1	18.4
BA	1163.1	1338.4	849.5	796.7	1709.0	1690.8	546.3	651.2	873.6
TH	*	*	2.1	3.6	11.0	3.0	3.7	3.1	1.6
LA	33.1	31.1	34.0	35.4	69.4	45.4	36.5	33.2	35.5
CE	69.4	71.6	74.1	78.9	115.2	90.0	72.0	72.3	82.8
ND	32.2	36.2	33.6	35.2	51.7	41.6	34.1	33.0	38.6
SM	0.6	3.4	7.1	4.1	5.7	6.3	4.3	5.0	8.1
Y	16.4	16.5	20.0	22.0	20.4	23.6	22.3	26.2	20.9
TI02CR	1.316	1.658	1.149	1.370	0.356	1.667	1.369	1.373	1.377
TI02W	1.346	1.635	1.172	1.443	0.357	1.651	1.403	1.491	1.458
	L156219	L157213	L158213	GC127	GC3244	GC4244	GC5221	GC6217	GC8219
SI02	65.06	60.02	61.58	55.85	61.36	62.91	67.51	65.21	75.16
AL203	16.91	17.52	16.50	16.77	16.23	15.00	16.02	16.27	14.10
FE203	3.97	5.98	5.42	7.77	5.78	5.30	3.37	4.32	0.96
MGO	1.77	3.12	3.21	4.10	3.23	2.83	1.42	2.20	0.29
CAO	1.81	5.30	5.22	5.92	4.78	4.67	2.40	3.19	0.58
NA20	4.96	3.87	3.73	4.92	3.90	3.21	4.23	4.16	4.46
K20	3.998	3.011	3.328	2.190	2.687	3.499	3.687	3.250	4.079
TI02	0.761	0.878	0.858	1.349	0.885	0.840	0.555	0.641	0.169
MNO	0.032	0.055	0.071	0.122	0.080	0.084	0.062	0.059	0.052
P205	0.247	0.353	0.270	0.405	0.324	0.294	0.158	0.223	0.047
TOTAL	99.50	100.11	100.19	99.39	99.25	99.64	99.41	99.53	99.90
LOI	1.26	3.95	4.70	1.58	1.68	2.17	2.07	1.75	0.44
NI	14.4	53.1	77.3	74.2	49.3	40.7	15.9	32.2	3.8
CR	35.2	89.0	137.7	136.1	98.3	87.4	29.2	51.5	4.7
V	59.6	117.7	117.3	116.1	105.0	94.4	47.2	72.6	4.5
SC	6.8	15.6	15.7	15.5	13.3	13.2	6.9	7.8	2.1
CJ	1.9	19.7	26.9	19.9	22.0	20.6	9.9	15.1	2.7
ZN	58.2	80.9	66.5	84.1	73.8	58.7	56.1	61.7	30.5
SR	939.5	1269.3	857.3	1236.2	1205.8	1253.6	817.2	988.9	182.3
RB	78.2	51.7	70.2	36.9	78.1	35.2	85.6	75.2	110.6
ZR	740.6	190.5	188.4	189.0	248.0	261.0	261.1	177.5	110.3
NB	10.2	8.6	9.9	12.0	11.8	11.4	10.9	10.7	11.4
BA	3260.5	1334.6	944.7	920.9	1272.1	1399.8	1635.3	1309.0	1215.2
TH	0.0	7.4	5.7	1.5	5.0	6.6	6.5	5.7	10.6
LA	34.8	40.2	29.0	30.6	39.0	40.2	37.8	31.3	28.2
CE	77.5	87.3	61.2	59.5	81.5	99.0	76.4	67.3	56.9
ND	37.0	42.4	29.5	31.5	38.3	39.9	33.5	28.6	23.5
SM	3.8	4.3	2.7	6.1	4.8	5.8	4.1	4.5	2.5
Y	20.2	16.7	16.6	21.1	23.1	23.0	19.1	16.3	15.0
TI02CR	0.802	0.950	0.919	1.210	0.903	0.874	0.571	0.632	0.179
TI02W	0.808	0.933	0.918	1.259	0.909	0.886	0.571	0.631	0.194

TABLE B17

	GC10214	GC11211	GC12210	GC13219	GC16219	GC17221	GC18213	GC19225	GC20225
SI02	63.09	53.87	57.91	78.42	70.74	75.59	62.24	59.88	62.58
AL203	16.25	16.66	16.77	12.47	15.49	14.07	18.03	15.49	16.76
FE203	5.30	8.71	6.78	0.77	2.09	1.34	4.35	6.36	5.06
MGO	2.86	4.37	4.12	0.29	0.44	0.42	2.35	4.53	2.39
CAO	4.57	7.06	5.91	0.57	1.64	0.68	3.45	4.94	3.83
NA20	3.97	3.80	4.42	5.25	4.58	2.82	5.10	3.90	4.32
K20	2.723	2.824	2.490	2.445	4.245	4.430	3.058	2.353	3.369
TI02	0.719	1.512	1.158	0.161	0.318	0.230	0.614	1.246	0.862
MNO	0.065	0.111	0.097	0.027	0.033	0.038	0.056	0.091	0.068
P205	0.244	0.462	0.397	0.036	0.115	0.039	0.228	0.413	0.284
TOTAL	99.79	99.37	100.05	100.44	99.69	99.65	99.48	99.49	99.52
LOI	0.87	1.54	0.71	0.84	1.19	1.56	2.13	1.05	1.32
NI	59.7	103.1	61.3	4.4	6.7	5.3	43.5	75.2	25.9
CR	126.9	249.0	114.5	4.7	8.1	7.1	82.3	189.1	41.0
V	85.9	619.9	127.3	4.8	25.3	10.7	71.7	112.0	93.4
SC	11.5	19.7	14.9	2.1	2.4	2.3	9.1	15.9	12.7
CU	23.8	7.6	24.2	4.4	4.7	2.6	11.7	25.2	17.4
ZN	66.6	81.2	84.3	13.6	41.6	26.7	70.6	104.0	66.0
SR	908.5	1069.5	987.9	204.2	598.8	292.3	1118.2	802.0	763.8
RB	56.7	37.1	46.4	52.8	59.9	142.7	65.5	73.1	74.1
ZR	174.3	216.3	192.6	109.5	171.0	173.6	141.6	289.8	199.7
NB	8.8	14.5	11.6	11.0	11.0	10.6	7.7	18.1	11.5
BA	1190.3	1009.7	981.9	926.8	1415.7	1383.2	1489.1	1104.3	1254.4
TH	4.1	2.3	4.7	9.8	8.2	7.8	2.4	10.6	3.3
LA	35.9	29.3	33.5	23.7	29.9	32.7	28.0	50.9	34.3
CE	69.4	69.7	73.9	53.1	64.1	57.7	54.9	100.0	71.9
ND	32.4	34.3	32.4	22.5	26.9	27.4	25.0	41.6	29.4
SM	5.7	6.9	6.6	3.9	4.8	5.9	3.6	6.5	4.3
Y	17.1	21.3	19.7	14.0	15.6	15.6	12.1	21.5	16.5
TI02CR	0.751	1.594	1.146	0.174	0.324	0.221	0.596	1.096	0.892
TI02W	0.738	1.556	1.138	0.185	0.339	0.232	0.616	1.058	0.877
GC2326	GC24221	GC25219	GC26216	GC28213	GC29216	GC30222	GC31219	BN1224	
SI02	64.56	56.89	77.84	59.86	62.69	61.33	66.07	76.24	65.04
AL203	16.91	16.63	12.96	16.81	16.25	16.31	15.71	13.55	16.96
FE203	4.19	3.34	0.68	6.62	5.27	5.79	3.92	0.84	4.28
MGO	1.83	1.29	0.19	3.55	2.88	3.27	2.09	0.30	1.88
CAO	3.41	2.69	0.40	4.71	4.30	4.99	3.07	0.76	3.24
NA20	4.46	4.41	4.62	4.23	4.77	3.31	4.32	2.40	4.30
K20	3.376	3.703	3.611	2.694	2.476	3.551	3.642	6.135	3.525
TI02	0.729	0.618	0.134	0.951	0.742	0.871	0.604	0.154	0.616
MNO	0.067	0.053	0.041	0.098	0.072	0.081	0.073	0.057	0.076
P205	0.277	0.173	0.034	0.366	0.267	0.311	0.185	0.035	0.219
TOTAL	99.80	99.80	100.52	99.88	99.72	99.80	99.59	100.48	100.13
LOI	0.95	0.85	0.51	1.19	1.80	1.34	1.75	1.33	0.80
NI	22.1	14.7	3.8	63.1	59.9	51.8	22.4	5.4	17.0
CR	42.6	24.5	4.3	116.4	118.8	110.4	44.7	4.4	22.8
V	66.2	46.1	3.2	110.2	93.4	104.6	74.0	3.2	74.7
SC	7.5	6.7	1.5	13.3	12.2	13.1	9.7	2.3	8.8
CU	11.1	13.4	4.2	17.9	17.9	22.8	24.5	3.7	34.2
ZN	69.1	56.6	16.7	80.7	71.5	70.3	50.5	27.3	63.4
SR	1090.6	937.8	163.0	1017.8	966.1	1183.3	632.7	252.8	1022.4
RB	75.9	85.4	94.8	59.0	48.0	80.9	91.2	126.3	70.1
ZR	362.8	346.7	101.6	174.8	156.1	243.0	177.1	111.9	165.0
NB	11.8	11.4	8.8	10.9	8.6	11.0	10.6	12.8	11.1
BA	1536.7	1909.1	1211.1	1138.0	1096.6	1544.1	1130.2	1436.5	1370.5
TH	5.5	7.0	6.7	3.2	5.0	6.1	9.1	7.2	5.0
LA	40.0	40.9	18.1	33.6	29.3	37.5	33.6	23.5	33.1
CE	85.7	83.9	40.2	71.9	62.7	94.7	57.0	53.8	67.2
ND	35.8	36.9	19.0	29.6	26.1	38.6	24.9	24.0	30.7
SM	4.7	6.6	3.0	5.3	4.7	8.1	2.9	10.6	2.0
Y	17.2	19.5	11.9	16.9	14.4	21.5	15.3	16.8	16.3
TI02CR	0.761	0.661	0.139	0.974	0.728	0.888	0.659	0.182	0.646
TI02W	0.749	0.656	0.154	0.970	0.735	0.891	0.663	0.194	0.651

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	BN2021	BN3024	BN4016	BN5024	BN6016	BN7016	BN8016	BN9016	BN10016
SI02	62.55	63.78	64.94	65.56	66.58	64.71	64.71	65.21	63.76
AL203	16.84	17.01	16.53	16.31	15.58	15.43	15.41	16.58	16.68
FE203	5.36	4.48	4.28	4.07	3.82	4.37	4.04	4.59	4.81
MGO	2.73	2.51	2.19	2.20	2.44	2.59	1.97	2.31	2.49
CAO	4.06	4.10	3.54	3.53	3.57	4.17	3.56	3.50	4.07
NA2O	4.50	4.63	4.73	4.54	3.65	4.13	4.79	4.08	4.21
K2O	3.225	2.733	2.965	3.000	3.515	3.074	2.985	2.555	2.884
TiO2	0.774	0.582	0.559	0.551	0.563	0.593	0.576	0.585	0.654
MNO	0.074	0.067	0.076	0.065	0.074	0.058	0.046	0.073	0.080
P2O5	0.291	0.239	0.212	0.195	0.203	0.214	0.204	0.203	0.230
TOTAL	100.10	100.13	100.03	100.03	99.99	100.35	99.29	99.78	99.86
LOI	0.25	0.43	0.65	0.60	0.65	0.48	0.53	1.35	0.50
NI	38.9	34.2	36.4	30.5	39.2	41.7	27.6	31.1	39.8
CR	76.6	56.2	65.3	56.1	68.8	71.2	45.6	51.5	61.1
V	92.8	81.5	77.3	72.9	69.6	95.1	74.2	76.0	84.7
SC	11.4	10.0	9.7	9.3	10.1	10.3	9.0	8.3	10.8
CU	15.8	5.9	6.7	4.3	4.4	74.8	6.9	5.6	31.4
ZN	71.1	66.0	58.4	47.4	60.2	65.2	60.7	66.6	60.3
SR	965.2	1091.2	1008.3	1101.6	1049.0	1101.1	1032.6	1064.1	1091.6
RB	80.5	49.5	54.5	61.0	56.5	53.6	52.0	60.2	58.0
ZR	163.0	130.4	125.2	121.6	131.7	137.9	141.7	142.8	134.3
NB	9.5	6.9	7.6	6.5	7.0	7.2	7.5	7.3	7.9
BA	1179.4	1533.0	1396.6	1350.5	1540.1	1347.1	1340.2	1313.0	1363.1
TH	4.4	2.4	4.0	3.4	0.8	3.2	3.5	4.7	3.5
LA	34.7	27.8	26.2	26.8	26.0	26.2	29.5	26.4	26.8
CE	67.6	59.2	57.6	49.9	54.6	55.8	58.8	52.3	55.8
ND	30.9	26.0	25.8	23.1	24.4	25.4	26.2	24.0	26.0
SM	2.6	3.9	3.0	3.5	2.9	4.8	4.9	4.1	5.1
Y	14.8	13.0	12.0	12.0	11.5	13.0	12.3	12.6	13.2
TiO2CR	0.829	0.642	0.584	0.589	0.599	0.627	0.604	0.565	0.683
TiO2W	0.807	0.623	0.579	0.579	0.586	0.620	0.591	0.570	0.680
	BN11024	SC106	SC206	SC3019	SC4016	SC5019	SC6019	SC7025	SC8016
SI02	63.00	59.86	60.00	71.13	64.91	68.57	76.59	74.79	64.21
AL203	16.53	17.80	19.31	15.27	16.15	15.90	12.31	13.11	16.08
FE203	4.78	6.40	4.71	3.22	4.35	3.63	1.48	2.25	5.29
MGO	2.77	1.75	1.82	0.80	2.05	1.62	0.65	0.34	1.33
CAO	4.26	0.64	1.47	2.41	4.25	2.81	0.39	0.69	5.29
NA2O	4.55	5.09	6.48	4.46	4.14	4.22	3.53	3.15	4.14
K2O	2.678	6.553	4.431	2.254	2.730	2.275	4.924	5.441	2.551
TiO2	0.610	0.813	1.085	0.429	0.782	0.473	0.190	0.232	0.501
MNO	0.071	0.100	0.049	0.031	0.092	0.040	0.062	0.028	0.085
P2O5	0.216	0.227	0.232	0.117	0.176	0.118	0.018	0.022	0.139
TOTAL	99.47	99.24	99.58	100.13	99.64	99.66	100.14	100.05	99.62
LOI	0.65	1.31	1.51	0.79	1.15	1.25	0.80	0.38	3.62
NI	48.6	19.5	43.6	14.3	32.5	21.7	4.4	4.9	33.5
CR	88.5	7.7	174.6	24.0	86.6	34.3	3.7	4.3	72.3
V	84.8	81.3	98.8	56.2	122.1	82.9	16.9	5.8	76.6
SC	11.6	10.7	18.3	8.2	15.8	9.6	3.7	11.1	10.3
CU	4.6	15.9	17.9	7.2	8.4	11.9	18.5	4.2	7.5
ZN	60.9	47.5	46.9	27.2	56.1	45.2	21.8	58.9	146.9
SR	997.0	324.7	492.6	455.8	485.5	453.9	61.8	91.9	379.4
RB	43.7	191.4	130.0	58.7	78.8	53.3	133.8	146.9	72.6
ZR	130.4	445.2	229.6	108.1	184.5	106.5	166.1	415.7	145.9
NB	7.5	25.2	15.4	5.8	15.0	4.9	20.8	27.3	7.5
BA	1414.2	1497.4	1017.3	492.1	559.4	475.2	721.4	837.9	504.6
TH	3.8	9.6	11.2	6.9	10.3	4.7	16.2	20.1	11.0
LA	22.6	47.7	60.0	30.4	31.6	19.0	31.2	69.0	22.5
CE	52.0	325.7	78.7	45.2	62.9	35.5	156.7	151.4	49.0
ND	23.7	48.3	40.8	21.1	28.1	17.3	35.1	64.7	17.2
SM	3.1	9.3	5.4	3.3	4.0	2.3	7.0	11.9	1.5
Y	11.3	43.3	18.8	9.6	19.5	10.7	27.2	49.1	13.1
TiO2CR	0.625	0.784	1.073	0.429	0.793	0.472	0.174	0.243	0.510
TiO2W	0.626	0.802	1.082	0.439	0.804	0.483	0.185	0.257	0.516

TABLE B17

	SC9824	SC10814	SC1181	SC1237	SC13812	SC1481	SC15819	SC16821	MT1811
SI02	59.77	61.12	50.94	52.28	52.23	52.08	78.82	76.43	53.31
AL203	17.30	15.98	16.61	15.51	16.74	15.88	11.68	12.96	18.11
FE203	6.20	6.35	9.71	7.68	10.82	9.39	1.28	2.21	8.66
MGO	3.03	4.73	7.04	7.53	2.74	3.56	0.18	0.66	4.30
CAO	3.51	3.50	8.11	8.79	6.46	7.09	0.59	0.46	6.90
NA20	5.36	3.65	3.64	3.36	4.42	3.67	2.38	2.55	4.12
K20	3.290	2.925	1.426	1.924	2.721	1.673	5.243	4.959	1.884
TIO2	0.712	1.015	1.829	1.516	2.097	1.664	0.096	0.198	1.711
MNO	0.038	0.141	0.134	0.235	0.128	0.265	0.029	0.031	0.145
P205	0.282	0.254	0.332	0.511	0.807	0.438	0.014	0.039	0.420
TOTAL	99.51	99.67	99.77	99.44	99.15	99.71	100.31	100.49	99.56
LOI	0.97	3.52	1.92	2.03	1.00	2.44	0.62	1.22	1.32
NI	56.8	31.1	98.7	170.3	46.1	223.7	5.0	7.4	26.2
CR	113.2	51.9	197.6	423.0	57.4	433.9	3.9	8.3	9.3
V	109.2	124.2	182.2	187.7	206.6	177.6	6.7	13.2	174.6
SC	15.9	17.5	24.5	30.6	17.5	21.5	3.2	2.9	19.5
CU	15.7	15.2	27.1	36.1	31.6	6.7	20.6	3.1	34.5
ZN	45.9	94.8	75.6	83.7	79.8	31.4	73.4	22.2	72.3
SR	656.8	365.5	577.3	825.0	745.2	758.3	29.3	113.9	634.7
RB	77.6	66.7	24.2	38.7	58.6	18.4	237.8	120.0	43.1
ZR	165.9	208.5	204.3	224.1	377.2	224.2	158.0	112.9	248.1
NB	9.5	14.2	14.6	17.0	29.3	16.8	27.0	19.1	12.8
BA	840.6	816.7	289.0	526.6	596.2	506.2	163.6	444.8	513.5
TH	14.7	11.6	6.3	6.4	12.2	5.5	26.0	23.9	9.5
LA	58.1	40.4	23.6	50.4	80.7	41.9	42.0	37.1	30.3
CE	108.9	82.2	53.5	111.6	172.6	93.2	100.3	74.2	75.1
NO	44.1	35.7	25.3	51.5	72.7	42.6	49.0	27.4	38.6
SM	7.4	9.6	4.6	7.3	12.0	4.6	13.1	3.3	5.3
Y	16.5	21.9	27.0	24.2	35.7	23.3	68.0	15.0	29.3
TIO2CR	0.767	0.940	1.727	1.546	2.169	1.708	0.097	0.217	1.540
TIO2W	0.759	0.958	1.827	1.570	2.187	1.740	0.110	0.224	1.647
MT2811	MT381	MT4811	MT5818	MT681	MT781	MT881	MT9818	MT10810	
SI02	52.60	55.34	54.93	61.57	52.56	52.81	53.89	62.16	56.93
AL203	16.28	17.85	17.82	17.74	18.36	19.37	18.37	17.91	16.25
FE203	8.23	9.42	8.85	6.69	9.79	9.00	8.10	5.20	6.89
MGO	7.79	2.84	3.54	0.99	5.36	5.57	4.03	1.52	6.49
CAO	8.39	5.86	5.90	2.42	3.99	3.53	7.06	2.40	6.54
NA20	3.25	4.04	4.30	5.08	3.46	4.99	4.26	4.76	3.48
K20	1.135	1.879	2.280	4.054	3.646	2.599	1.972	4.371	1.474
TIO2	1.500	1.700	1.611	0.700	1.757	1.756	1.728	0.714	1.130
MNO	0.165	0.063	0.076	0.052	0.079	0.120	0.067	0.050	0.131
P205	0.271	0.427	0.581	0.403	0.433	0.439	0.440	0.405	0.270
TOTAL	99.61	99.41	99.90	99.70	99.44	99.18	99.92	99.49	99.59
LOI	1.84	0.99	1.10	0.99	2.58	2.74	1.05	1.32	1.60
NI	171.0	24.1	13.8	5.6	22.6	26.7	25.6	5.2	154.4
CR	353.0	7.5	7.0	4.8	7.1	8.5	6.1	5.6	277.9
V	176.5	156.3	124.1	15.2	185.9	198.2	163.7	11.1	142.7
SC	23.7	21.0	15.9	4.7	23.0	21.8	19.8	4.6	19.8
CU	29.9	24.3	25.2	6.8	30.3	11.4	34.9	8.5	26.3
ZN	73.4	58.9	79.5	69.4	88.6	147.4	51.2	80.4	77.0
SR	537.1	653.8	577.3	354.0	459.4	431.3	672.8	337.8	545.4
RB	20.3	43.9	62.4	131.7	52.5	43.0	44.4	134.4	18.1
ZR	176.1	241.6	322.7	642.0	252.9	256.4	253.0	651.2	215.9
NB	10.8	12.4	16.6	29.4	13.8	13.3	12.4	29.7	12.9
BA	311.2	535.9	529.3	836.1	478.6	554.9	544.2	989.0	495.7
TH	2.7	5.5	10.3	23.7	9.0	6.7	6.4	21.4	7.3
LA	17.8	31.7	39.4	69.4	32.9	33.0	33.8	66.2	34.6
CE	43.2	79.6	96.6	146.7	70.8	73.5	77.4	141.6	67.7
NO	20.7	39.4	48.0	60.0	34.4	37.4	35.8	58.5	29.9
SM	2.9	5.3	9.6	10.7	6.7	6.9	11.5	9.6	3.6
Y	24.5	28.4	37.9	39.5	31.2	30.4	30.7	36.0	23.5
TIO2CR	1.539	1.359	1.368	0.597	1.602	1.697	1.450	0.597	1.232
TIO2W	1.596	1.482	1.469	0.708	1.677	1.723	1.559	0.700	1.227

TABLE B17

	MT11213	MT12211	MT13210	MT14212	MT15213	MT16213	MT1721	MT18210	MT19210
SI02	57.28	56.98	57.72	55.47	58.39	59.93	49.73	56.06	56.20
AL203	15.96	16.49	15.95	16.04	16.19	15.78	17.06	16.09	16.36
FE203	6.80	6.58	7.29	7.95	6.98	5.61	11.58	7.79	7.17
MGO	6.26	5.54	5.08	5.71	5.08	5.06	5.54	5.09	5.85
CAO	6.07	6.65	6.59	7.20	7.03	5.69	8.72	6.95	6.55
NA20	3.59	3.83	3.61	3.79	3.61	4.06	3.25	3.46	3.73
K20	2.070	1.924	1.980	1.523	1.105	0.929	1.359	1.966	1.926
TI02	1.125	1.292	1.174	1.402	1.126	1.112	1.899	1.380	1.282
MNO	0.114	0.127	0.089	0.140	0.186	0.123	0.159	0.173	0.087
P205	0.277	0.300	0.292	0.279	0.248	0.244	0.443	0.319	0.326
TOTAL	99.55	99.72	99.77	99.59	99.94	99.54	99.73	99.26	99.47
LOI	1.13	1.38	1.67	1.38	1.93	1.68	1.76	1.46	1.58
NI	166.6	120.6	163.9	110.4	98.6	92.2	94.2	130.0	167.8
CR	265.5	193.1	287.1	217.3	175.1	157.8	154.2	253.4	239.2
V	129.5	162.1	147.0	159.2	152.1	148.9	184.9	165.1	148.9
SC	18.5	21.7	20.5	22.0	20.0	19.7	24.9	23.0	21.5
CU	31.7	17.4	17.2	24.9	30.8	35.2	21.7	34.8	25.9
ZN	68.4	73.4	67.6	74.2	67.7	72.6	71.8	61.9	81.3
SR	507.6	522.1	512.9	457.2	549.7	669.6	556.2	463.8	585.8
RB	58.2	51.5	55.0	39.0	18.1	33.9	19.2	55.1	46.8
ZR	213.6	227.3	217.1	208.2	222.3	217.2	236.5	264.5	206.2
NB	12.4	14.7	12.7	14.3	12.7	13.4	19.3	15.0	13.5
BA	494.9	406.0	422.4	311.5	437.4	428.7	291.3	380.1	526.1
TH	8.4	10.8	9.6	7.3	13.0	11.5	6.2	10.2	9.9
LA	30.7	33.7	25.9	26.9	33.8	35.2	26.8	30.5	33.6
CE	61.6	70.6	58.7	61.6	72.4	71.4	59.1	65.9	66.2
ND	27.5	30.0	26.0	25.7	29.0	27.1	26.2	29.6	29.9
SM	5.2	3.8	3.9	5.2	6.5	3.1	8.8	9.2	5.3
Y	24.8	23.7	23.9	24.8	23.8	22.6	29.6	27.7	22.5
TI02CR	1.091	1.388	1.173	1.372	1.240	1.214	1.629	1.446	1.292
TI02W	1.139	1.397	1.201	1.413	1.202	1.187	1.792	1.452	1.336

	MT2021	MT21210	MT22211	MT2321	MT24211	MT25211	MT26211	MT27218	MT29218
SI02	52.31	54.97	52.72	53.02	54.30	53.70	52.20	62.06	60.26
AL203	16.52	15.85	16.30	17.62	18.70	18.88	17.83	17.88	17.89
FE203	9.22	7.01	9.00	8.20	7.87	7.97	8.69	4.94	6.16
MGO	10.81	6.58	6.74	6.56	3.63	3.92	4.79	1.55	2.19
CAO	2.09	7.03	7.51	5.89	6.57	6.52	7.79	3.08	3.21
NA20	1.80	3.64	3.48	4.34	4.43	4.27	3.74	4.83	4.88
K20	4.007	2.145	1.782	1.919	2.035	1.973	2.000	4.057	3.731
TI02	1.933	1.518	1.361	1.707	1.539	1.564	1.647	0.735	0.825
MNO	0.056	0.109	0.100	0.102	0.078	0.113	0.101	0.035	0.085
P205	0.440	0.455	0.358	0.386	0.359	0.369	0.435	0.416	0.437
TOTAL	99.19	99.33	99.36	99.85	99.50	99.28	99.21	99.58	99.69
LOI	5.93	1.50	1.64	1.57	1.13	1.38	1.38	1.18	1.09
NI	197.8	208.0	162.0	127.9	29.2	29.7	74.2	7.3	8.7
CR	400.2	343.1	307.3	217.7	8.2	7.4	112.7	7.7	12.2
V	196.8	148.7	174.7	171.4	153.4	145.0	178.2	11.9	27.3
SC	32.0	17.0	22.9	29.8	16.3	16.3	20.7	5.4	7.2
CU	6.1	48.0	14.2	24.4	30.5	16.5	33.5	6.8	9.2
ZN	170.0	80.7	74.1	90.0	75.8	93.3	80.0	58.7	98.2
SR	237.0	816.8	693.7	576.4	739.6	719.4	590.2	396.5	385.8
RB	34.8	43.4	36.1	35.6	46.8	44.1	59.5	133.8	124.3
ZR	242.6	273.4	205.2	232.2	230.1	230.1	302.8	637.2	916.0
NB	18.4	17.1	13.0	14.7	13.0	12.7	15.0	29.0	28.0
BA	333.7	674.4	596.4	367.9	528.3	535.1	440.5	772.0	678.7
TH	5.0	10.6	8.0	3.8	7.7	7.9	14.4	27.1	27.1
LA	26.4	41.5	28.9	24.0	30.8	28.4	34.6	65.9	61.8
CE	54.6	93.4	65.0	59.0	67.1	70.2	78.7	142.0	141.1
ND	24.4	42.0	30.8	28.0	32.9	33.7	39.3	56.0	57.6
SM	4.3	10.0	6.7	5.8	5.9	6.9	8.9	8.0	9.4
Y	23.2	26.7	24.1	27.0	27.9	29.2	32.3	36.4	36.3
TI02CR	1.576	1.453	1.359	1.586	1.393	1.449	1.445	0.712	0.846
TI02W	1.737	1.518	1.375	1.682	1.483	1.533	1.538	0.739	0.859

TABLE B17

	MT30a12	MT31a12	MT32a10	MT33a20	MT34a13	MT35a20	MT36a28	MT37a28	MT38a1
SI02	57.71	56.42	55.45	57.75	59.72	54.51	57.71	57.62	55.81
AL203	17.19	17.40	16.15	17.36	15.76	13.45	16.06	15.77	17.02
FE2O3	6.54	7.61	8.07	6.52	6.53	3.08	5.86	7.27	7.07
MGO	3.07	3.81	5.29	3.27	3.81	3.82	5.68	5.71	5.12
CAO	5.87	6.00	6.89	5.67	4.98	5.54	4.87	5.59	7.47
NA2O	4.24	3.96	3.69	3.95	3.42	4.41	4.21	3.30	3.92
K2O	2.642	2.613	2.050	2.630	2.972	1.998	2.310	2.260	1.465
TiO2	1.332	1.341	1.375	1.350	1.136	1.533	1.323	1.298	1.481
MNO	0.144	0.130	0.061	0.089	0.128	0.076	0.080	0.036	0.137
P2O5	0.376	0.381	0.374	0.375	0.294	0.365	0.360	0.347	0.373
TOTAL	99.12	99.65	99.40	99.55	99.75	99.79	99.46	99.80	99.87
LOI	1.06	1.45	1.21	1.32	1.27	1.59	1.31	1.33	1.14
NI	17.9	18.9	175.1	8.6	48.4	27.7	109.5	101.4	88.5
CR	13.2	13.6	308.8	3.7	106.8	7.3	321.0	298.4	121.8
V	164.0	169.0	172.5	137.2	135.8	147.8	140.3	129.8	150.6
SC	19.4	19.6	23.0	16.6	22.2	14.8	21.8	18.7	19.8
CU	9.7	10.7	29.2	11.6	21.2	24.5	17.4	18.5	27.5
ZN	89.4	97.2	82.6	84.7	151.1	98.4	70.6	74.8	69.6
SR	779.4	746.3	721.6	831.6	527.6	636.9	562.6	566.3	736.9
RB	78.5	80.1	52.0	74.5	92.3	44.0	54.8	55.4	15.4
ZR	274.7	276.1	213.7	284.2	266.8	221.6	254.1	248.9	239.7
NB	15.9	16.6	14.4	17.4	15.4	12.0	18.2	16.6	15.4
BA	620.5	631.3	564.0	675.4	692.1	530.5	562.2	573.4	585.7
TH	12.0	13.4	9.1	13.6	16.2	9.9	7.1	8.6	7.3
LA	46.5	48.3	30.3	52.1	39.0	30.7	35.0	37.0	32.1
CE	98.8	102.8	73.1	109.9	85.7	57.7	70.4	73.4	74.7
ND	43.7	44.2	31.9	48.8	40.2	32.0	31.9	33.7	34.2
SM	4.9	6.4	6.2	7.1	7.1	6.3	5.4	5.9	7.4
Y	25.6	25.0	22.8	26.3	28.8	27.5	25.1	24.7	25.8
TiO2CR	1.367	1.398	1.296	1.389	1.066	1.363	1.290	1.216	1.505
TiO2W	1.362	1.406	1.339	1.399	1.090	1.473	1.323	1.269	1.524

	MT39a1	MT40a11	MT41a5	MT42a7	MT43a12	MT44a12	MT45a12	MT46a5	MT47a13
SI02	55.24	54.56	59.88	53.80	54.99	54.27	54.85	58.34	59.97
AL203	16.95	17.29	16.53	15.72	16.18	15.99	15.70	16.96	17.28
FE2O3	7.87	7.08	5.65	7.67	7.61	7.68	8.25	8.22	6.30
MGO	4.96	5.67	4.36	8.54	6.47	6.86	6.80	3.75	3.02
CAO	6.73	7.47	5.23	7.83	7.59	3.36	8.03	3.19	3.47
NA2O	4.15	4.23	3.92	3.37	3.48	3.32	3.34	4.45	4.42
K2O	1.924	1.403	2.548	1.584	2.031	1.342	1.358	3.040	3.376
TiO2	1.529	1.535	0.999	1.303	1.341	1.312	1.285	1.116	1.232
MNO	0.082	0.187	0.063	0.097	0.074	0.146	0.128	0.055	0.077
P2O5	0.370	0.381	0.263	0.363	0.371	0.353	0.349	0.255	0.345
TOTAL	99.81	99.81	99.43	100.38	100.13	99.64	100.10	99.39	99.48
LOI	1.06	0.90	1.14	1.98	1.23	1.29	1.60	2.84	2.23
NI	77.5	84.8	115.2	267.0	141.9	146.2	138.3	72.1	47.8
CR	114.4	126.7	232.0	540.3	318.1	236.1	293.1	165.0	98.2
V	136.3	160.7	123.9	165.9	175.0	175.6	169.2	115.0	140.8
SC	21.0	20.3	19.6	25.5	28.4	24.8	24.8	23.2	24.2
CU	14.8	27.0	19.8	29.9	34.5	20.8	49.8	17.2	17.8
ZN	105.9	71.9	57.7	73.0	73.4	57.7	68.3	43.7	54.4
SR	666.3	699.4	688.1	559.8	562.6	628.7	603.5	401.3	557.3
RB	41.6	14.7	66.3	37.2	54.2	15.3	17.4	103.6	100.6
ZR	234.8	239.2	180.9	228.1	264.6	253.6	248.9	249.4	310.6
NB	15.9	16.0	11.1	11.4	11.9	12.6	12.4	13.9	15.0
BA	537.5	552.7	836.8	435.2	524.4	539.2	541.7	1197.7	898.4
TH	4.2	6.0	7.6	5.4	10.2	7.4	11.5	12.9	17.8
LA	28.1	37.3	29.8	28.8	32.5	32.9	33.4	47.1	45.6
CE	70.0	74.7	57.6	61.9	76.4	76.1	75.2	74.1	88.5
ND	31.7	33.9	26.5	30.9	36.4	34.5	35.2	41.5	41.6
SM	3.5	6.2	5.2	5.3	7.0	5.8	5.3	8.5	9.1
Y	23.9	25.0	17.6	24.6	26.2	25.8	26.0	25.5	22.6
TiO2CR	1.267	1.653	0.969	1.235	1.289	1.335	1.353	1.013	1.125
TiO2W	1.381	1.653	0.980	1.290	1.357	1.373	1.327	1.055	1.173

TABLE B17

	MT48210	MT4921	MT50220	MT51215	MT52222	MT53216	MT54213	MT5521	MT5621
SI02	59.35	57.87	55.95	64.18	68.10	55.89	60.67	50.34	58.44
AL203	17.00	16.87	16.74	16.10	15.33	15.52	18.51	17.13	17.99
FE203	7.05	6.01	7.56	5.26	3.18	7.16	6.35	9.59	5.24
MGO	2.48	1.20	5.01	1.21	2.40	5.40	1.95	9.00	4.01
CAO	4.00	10.75	6.95	4.00	2.22	7.43	4.88	8.26	4.88
NA20	4.66	3.75	3.55	4.26	4.85	3.29	3.17	2.88	5.26
K20	3.020	2.278	1.928	3.379	3.114	2.037	2.060	1.044	0.827
TI02	1.284	1.054	1.291	0.977	0.369	1.224	1.420	1.571	2.005
MNO	0.083	0.107	0.117	0.041	0.048	0.079	0.053	0.082	0.078
P205	0.290	0.261	0.287	0.279	0.110	0.289	0.294	0.415	0.508
TOTAL	99.21	100.14	99.38	99.74	99.73	99.33	99.36	100.32	99.23
LOI	2.01	5.62	0.74	1.54	1.82	1.53	3.71	8.80	3.55
NI	71.5	71.3	41.3	24.0	30.7	114.2	23.8	205.3	160.3
CR	223.7	194.9	113.6	27.8	43.9	258.0	27.9	487.6	480.7
V	189.6	137.6	145.2	84.9	63.5	165.9	158.1	189.0	203.5
SC	26.8	21.8	23.4	13.4	8.5	25.8	15.7	32.5	35.7
CU	17.7	13.5	28.7	12.2	9.2	26.3	32.0	21.1	35.4
ZN	45.8	53.9	78.1	18.7	40.3	73.2	105.2	76.6	87.5
SR	602.2	641.1	680.1	516.1	383.6	622.5	356.2	443.3	810.3
RB	96.0	59.8	46.6	98.8	72.7	53.8	45.3	22.1	16.8
ZR	314.5	199.6	199.4	273.5	106.5	218.8	292.2	224.7	233.0
NB	15.9	11.6	12.9	16.6	4.8	14.5	15.3	16.0	15.8
BA	1017.3	614.5	550.2	898.1	725.6	583.5	428.1	405.3	381.5
TH	17.5	12.2	11.5	14.8	5.5	7.6	13.3	12.5	4.4
LA	42.2	30.3	29.3	54.7	11.7	34.4	25.5	35.2	26.0
CE	85.4	67.3	61.9	105.4	26.4	71.1	64.1	77.2	69.9
ND	37.3	29.5	29.4	37.8	13.4	31.7	32.3	38.7	36.4
SM	6.8	5.3	7.2	4.5	1.8	6.3	6.0	7.3	5.6
Y	21.5	21.0	25.8	16.3	10.2	24.3	28.8	24.3	27.6
TI02CR	1.247	1.043	1.148	0.968	0.400	1.274	1.440	1.476	1.977
TI02W	1.292	1.109	1.238	0.989	0.403	1.272	1.482	1.596	2.105
	MT58219	MT59219	MT60219	S1212	S2212	S4220	S5211	S6211	S8211
SI02	65.20	65.37	64.60	52.69	52.98	52.11	52.34	54.16	51.76
AL203	17.13	17.16	17.47	19.31	18.83	19.21	16.49	17.11	17.03
FE203	4.42	4.50	4.86	7.19	8.24	8.63	9.14	8.21	10.92
MGO	1.42	1.17	1.50	5.20	4.71	5.03	6.90	5.12	4.50
CAO	3.06	2.48	0.55	7.90	7.91	7.79	8.63	7.85	7.83
NA20	3.98	4.15	3.85	4.14	4.22	4.06	3.03	3.57	3.94
K20	3.525	3.634	5.825	1.191	1.204	1.350	1.038	1.471	1.408
TI02	0.659	0.676	0.675	1.582	1.507	1.612	1.399	1.625	2.027
MNO	0.047	0.033	0.070	0.153	0.147	0.146	0.139	0.089	0.196
P205	0.296	0.299	0.277	0.318	0.307	0.321	0.211	0.286	0.332
TOTAL	99.73	99.48	99.68	99.67	100.06	99.25	99.31	99.49	99.94
LOI	2.01	1.43	1.66	1.55	1.05	1.21	1.56	1.18	0.55
NI	5.8	6.7	7.4	46.6	47.4	45.3	129.9	51.2	20.4
CR	6.1	7.5	7.3	113.9	112.1	29.3	351.3	111.0	33.6
V	45.5	38.5	31.8	174.3	170.7	154.5	156.8	187.8	247.6
SC	9.7	9.6	8.8	27.6	26.6	24.2	24.2	25.0	26.1
CU	10.1	5.2	3.3	21.3	16.8	28.4	24.6	45.0	22.8
ZN	67.5	60.5	51.8	106.2	80.1	64.6	75.5	64.9	84.4
SR	365.9	379.9	119.7	516.2	502.9	626.0	429.2	563.3	525.2
RB	102.4	105.4	105.1	25.3	26.8	32.1	24.5	28.5	31.5
ZR	322.9	320.1	322.4	227.6	225.8	210.6	160.0	212.5	215.9
NB	20.1	19.8	20.2	9.8	5.6	7.7	8.1	14.8	10.9
BA	827.3	815.8	743.8	299.2	316.9	339.2	247.2	367.8	358.7
TH	17.9	15.7	15.1	*	0.0	*	*	3.6	2.6
LA	48.4	46.2	52.4	20.2	23.6	22.8	16.6	23.7	22.0
CE	106.7	105.7	116.5	50.3	53.9	53.4	34.0	48.6	52.6
ND	44.8	44.6	48.1	27.3	28.5	30.2	17.7	25.8	27.0
SM	7.5	7.8	7.8	6.5	7.8	6.0	5.8	7.4	5.5
Y	28.9	29.0	28.0	31.5	32.1	32.2	25.6	31.3	33.3
TI02CR	0.698	0.669	0.698	1.670	1.646	1.312	1.317	1.574	1.922
TI02W	0.709	0.697	0.717	1.559	1.602	1.423	1.370	1.608	1.983

TABLE B17

	S9912	S10920	S12912	S13910	S15912	S16911	S17920	S18911	S19911
S102	54.40	53.48	56.49	56.59	56.68	53.94	52.88	54.37	52.08
AL203	17.42	17.93	16.37	17.10	17.89	17.97	19.45	16.37	18.99
FE203	10.98	8.40	7.31	7.33	7.08	3.04	8.37	8.43	7.43
MGO	4.25	4.39	5.39	4.10	3.36	4.65	4.85	6.52	5.77
CAO	5.41	7.69	7.46	5.17	5.32	7.63	7.20	7.41	8.68
NA20	3.79	3.95	3.60	4.17	4.40	4.07	4.15	3.51	3.56
K20	1.898	1.945	1.664	2.865	1.791	1.484	1.451	1.387	1.312
TIO2	1.105	1.538	1.217	1.734	1.475	1.579	1.650	1.104	1.400
MNO	0.047	0.082	0.391	0.133	0.094	0.111	0.065	0.107	0.099
P205	0.285	0.363	0.291	0.547	0.361	0.305	0.311	0.291	0.295
TOTAL	99.60	99.77	99.89	99.85	99.65	99.76	99.37	99.90	99.61
LOI	1.50	1.39	1.23	1.19	0.81	0.86	1.37	1.11	1.55
NI	78.1	10.4	80.8	59.0	22.1	28.7	27.8	159.2	46.5
CR	54.6	5.2	113.0	51.3	31.2	24.8	16.9	285.7	76.4
V	141.6	149.7	150.5	129.5	134.9	134.2	150.7	122.3	180.6
SC	21.2	20.9	23.1	19.1	19.2	18.1	22.7	19.9	29.5
CU	27.4	18.5	25.7	62.4	17.3	21.4	16.7	21.4	21.4
ZN	54.6	61.4	69.2	112.9	61.1	93.5	93.2	75.3	68.5
SR	682.6	1197.9	613.4	410.5	559.6	555.9	583.6	647.7	521.9
RB	33.4	32.1	43.0	117.8	42.8	37.0	36.7	28.4	21.1
ZR	215.6	242.1	205.0	540.5	260.1	213.4	204.8	187.3	183.7
NB	11.7	8.3	11.7	24.5	13.6	13.0	12.0	10.6	7.2
BA	516.5	880.3	434.7	459.9	418.2	390.3	368.1	368.4	326.3
TH	4.5	3.2	5.4	22.9	3.8	2.5	4.4	5.2	4.9
LA	31.7	32.3	33.2	58.0	27.9	29.4	23.3	22.3	21.3
CE	58.7	76.7	67.0	130.8	63.6	56.7	56.0	44.3	47.4
ND	26.4	42.6	32.6	57.8	30.0	28.1	25.1	21.8	24.0
SM	4.6	7.3	8.6	8.9	6.0	8.6	5.3	3.4	4.7
Y	20.6	31.0	25.5	47.3	28.0	27.0	25.3	23.8	23.1
TIO2CR	1.156	1.334	1.213	1.756	1.438	1.126	1.195	0.992	1.249
TIO2W	1.154	1.407	1.233	1.781	1.503	1.254	1.380	1.038	1.357
	S20918	S21912	S22920	S23911	S24911	S25912	S26911	S27911	S28912
S102	55.48	53.74	54.54	54.48	53.80	53.78	54.19	58.29	54.04
AL203	17.62	16.80	17.87	18.55	17.75	17.60	18.09	17.36	16.53
FE203	8.67	8.54	7.89	7.24	8.44	9.57	8.27	8.08	8.53
MGO	4.38	5.70	4.62	4.11	4.42	4.65	4.49	2.22	6.69
CAO	1.35	7.95	7.33	7.54	7.37	7.70	7.47	4.57	7.98
NA20	4.71	3.62	3.89	4.13	3.97	3.86	3.94	5.18	3.42
K20	5.331	1.542	1.541	1.476	1.457	1.581	1.508	2.206	1.000
TIO2	1.382	1.486	1.522	1.624	1.558	1.675	1.579	1.236	1.176
MNO	0.080	0.118	0.154	0.117	0.156	0.151	0.093	0.100	0.176
P205	0.604	0.346	0.306	0.319	0.304	0.371	0.362	0.647	0.288
TOTAL	99.62	99.85	99.76	99.69	99.24	99.94	99.94	99.38	99.83
LOI	2.17	1.31	1.00	1.12	0.42	0.82	1.15	1.03	1.58
NI	14.3	94.8	31.9	25.9	26.5	46.5	27.0	N.O.	94.4
CR	6.7	127.5	29.2	17.9	20.9	59.5	17.7	N.O.	80.8
V	150.3	175.8	155.5	186.8	161.7	153.5	157.1	30.3	137.7
SC	12.4	22.7	19.8	20.6	20.1	20.3	18.9	11.6	16.6
CU	14.8	51.5	35.0	19.2	18.4	17.3	21.0	9.0	18.7
ZN	112.7	64.0	79.8	85.0	74.0	70.0	83.6	91.3	59.7
SR	326.8	800.6	527.2	558.1	531.9	595.3	545.5	386.6	695.9
RB	68.7	33.9	39.3	35.4	34.2	33.7	38.9	57.7	17.6
ZR	351.0	212.5	210.4	220.3	215.4	255.1	220.1	417.9	200.0
NB	17.7	11.1	13.7	13.9	13.3	16.5	13.4	19.8	11.8
BA	787.0	523.4	392.8	374.6	362.9	414.2	378.7	473.5	431.0
TH	11.0	9.4	8.7	2.7	5.9	6.9	3.8	8.4	8.0
LA	45.5	29.1	28.5	25.9	24.7	31.9	27.4	38.4	32.4
CE	99.8	65.8	62.7	58.0	54.3	59.8	56.2	96.4	63.9
ND	46.0	33.6	28.5	29.3	27.1	33.0	27.6	49.8	33.2
SM	9.3	5.2	4.7	4.8	5.1	6.4	5.8	10.4	6.6
Y	30.7	28.6	28.6	27.7	28.4	30.1	27.9	48.0	23.8
TIO2CR	1.431	1.450	1.410	1.454	1.518	1.473	1.245	1.152	1.190
TIO2W	1.449	1.523	1.482	1.540	1.542	1.562	1.357	1.175	1.204

TABLE B17

	S29a12	S30a11	S31a11	S32a11	S33a11	S34a11	S35a11	S36a11	S37a6
SI02	53.85	55.53	53.15	53.24	53.89	54.13	55.56	56.01	64.79
AL203	17.45	18.05	16.95	17.76	16.91	19.53	16.59	16.57	17.11
FE203	8.63	8.94	8.12	8.67	8.02	3.10	8.01	6.80	4.21
MGO	4.20	3.12	6.54	4.32	6.54	4.29	4.97	5.62	1.04
CAO	7.72	6.40	9.28	7.74	8.63	7.63	7.13	6.83	2.81
NA20	3.99	4.29	3.35	3.92	3.34	4.00	3.64	3.67	5.29
K20	1.606	1.654	0.625	1.512	1.026	1.436	1.904	1.942	2.925
TIO2	1.680	1.710	1.379	1.723	1.384	1.613	1.391	1.418	0.688
MNO	0.133	0.094	0.140	0.075	0.095	0.092	0.100	0.072	0.045
P205	0.374	0.284	0.218	0.388	0.225	0.320	0.334	0.335	0.331
TOTAL	99.63	100.08	99.77	99.46	100.06	100.14	99.64	99.26	99.24
LOI	0.86	0.67	1.61	0.96	1.66	1.25	1.54	1.34	1.28
NI	46.0	15.1	N.D.	43.2	68.5	28.0	120.1	119.7	N.D.
CR	64.8	21.3	N.D.	53.8	231.1	19.7	161.9	164.5	N.D.
V	157.5	107.6	178.7	134.2	166.7	159.2	138.8	141.6	34.4
SC	20.4	18.1	26.8	21.2	24.0	20.9	18.1	17.8	5.5
CU	23.5	13.7	32.9	22.4	26.7	22.5	24.3	26.2	19.0
ZN	77.2	67.0	72.5	53.7	66.8	55.7	83.1	82.0	137.8
SR	597.5	539.1	441.9	622.1	413.3	574.0	717.4	704.9	448.0
RB	34.9	45.8	5.5	35.1	17.1	26.4	45.3	44.2	65.3
ZR	255.1	208.3	165.3	259.0	168.4	228.3	207.1	207.2	434.5
NB	15.3	11.0	8.0	15.1	8.5	12.6	12.5	12.6	17.6
BA	410.4	398.8	247.4	412.6	246.7	373.0	630.6	647.6	719.4
TH	11.8	11.5	7.5	6.2	4.8	3.9	8.1	6.8	10.9
LA	31.6	23.6	15.8	33.2	18.9	27.2	30.0	31.3	41.8
CE	65.6	56.3	34.9	69.5	34.0	56.1	68.2	66.5	86.5
ND	31.3	27.3	18.7	33.4	17.6	27.0	28.5	29.6	37.3
SM	7.2	4.1	4.2	7.6	4.1	4.7	4.3	4.4	4.9
Y	29.7	33.5	25.8	30.4	26.1	29.0	24.8	24.1	30.6
TIO2CR	1.487	1.218	1.457	1.218	1.348	1.595	1.379	1.308	0.739
TIO2W	1.566	1.354	1.475	1.339	1.440	1.634	1.405	1.358	0.737
	S38a16	S39a11	S40a22	S41a22	S42a12	S43a12	S44a25	S45a1	S46a1
SI02	61.67	54.48	53.92	66.14	54.11	53.65	56.99	52.18	54.98
AL203	15.24	15.89	17.35	14.35	17.68	17.80	15.34	17.96	16.52
FE203	6.60	7.90	8.27	4.26	7.87	3.58	7.00	8.39	8.26
MGO	3.80	7.19	5.39	1.94	4.09	4.41	7.25	6.16	5.04
CAO	2.20	7.27	6.46	2.06	7.51	7.62	6.24	7.07	7.32
NA20	4.55	3.52	4.56	4.00	4.24	4.06	3.73	3.99	3.94
K20	3.658	1.624	1.730	5.956	1.697	1.571	1.846	1.506	1.696
TIO2	1.405	1.299	1.471	0.829	1.679	1.685	1.150	1.625	1.599
MNO	0.048	0.145	0.089	0.071	0.193	0.116	0.128	0.139	0.151
P205	0.322	0.283	0.302	0.207	0.377	0.374	0.240	0.341	0.382
TOTAL	99.49	99.60	99.55	99.71	99.45	99.86	99.90	99.36	99.89
LOI	2.43	1.56	1.98	1.47	0.95	0.90	0.75	2.10	1.53
NI	N.D.	N.D.	34.9	5.3	N.D.	38.2	176.3	N.D.	N.D.
CR	N.D.	N.D.	85.7	5.2	N.D.	52.0	366.5	N.D.	N.D.
V	192.0	145.6	172.0	57.2	167.1	154.7	118.7	189.7	151.7
SC	17.1	18.9	23.9	13.7	22.2	19.8	18.2	26.1	20.5
CU	35.0	45.9	36.2	43.2	17.9	20.0	32.4	30.9	37.8
ZN	195.8	72.1	129.2	42.2	75.0	78.3	67.5	154.7	73.6
SR	307.1	494.7	618.3	212.6	587.6	614.0	558.7	560.1	713.1
RB	88.6	39.5	41.1	104.8	36.0	34.3	55.7	33.4	34.6
ZR	261.7	193.8	203.0	532.8	268.8	259.8	200.5	247.1	240.2
NB	13.7	10.1	12.7	22.9	17.3	14.8	10.6	11.1	15.9
BA	996.6	421.0	400.8	695.4	446.1	416.9	468.4	436.8	515.1
TH	10.8	9.3	7.5	16.4	8.4	7.0	10.9	7.0	6.6
LA	37.5	26.2	25.8	45.1	33.3	30.8	26.8	29.0	30.9
CE	76.5	51.3	52.7	96.9	69.6	59.1	55.4	59.7	62.3
ND	35.7	23.8	24.3	40.4	33.5	31.4	25.8	31.5	31.4
SM	6.5	6.7	5.8	8.8	7.9	7.6	3.8	7.0	8.1
Y	29.3	22.6	27.1	38.4	29.2	29.1	21.4	38.1	26.8
TIO2CR	1.426	1.355	1.324	0.809	1.615	1.360	1.069	1.658	1.629
TIO2W	1.427	1.339	1.384	0.834	1.620	1.441	1.112	1.666	1.632

TABLE B17

	S47211	S48211	S4921	S50211	S51211	S52210	OC1211	OC2210	OC3210
SI02	51.98	52.81	51.58	56.47	52.30	52.23	56.85	55.19	57.04
AL203	18.26	19.91	16.19	17.10	18.43	15.41	17.75	17.58	17.51
FE203	10.07	8.17	9.41	9.32	9.93	9.59	7.58	7.74	7.46
MGO	4.64	3.43	7.80	2.38	3.95	5.12	3.88	3.66	5.25
CAO	6.96	6.80	8.78	6.45	7.32	3.14	6.13	7.89	3.99
NA20	4.17	4.68	3.19	4.15	4.27	3.68	3.87	3.79	2.93
K2O	1.478	1.613	1.037	1.745	1.485	1.492	2.329	2.128	3.968
TI02	1.699	1.799	1.629	1.912	1.731	1.601	1.293	1.535	1.283
MNO	0.105	0.290	0.165	0.076	0.137	0.162	0.087	0.086	0.058
P2O5	0.341	0.395	0.306	0.425	0.346	0.345	0.234	0.333	0.297
TOTAL	99.70	99.89	100.08	100.22	99.90	99.78	100.00	99.93	99.80
LOI	1.39	1.25	1.95	0.91	1.45	1.20	3.19	3.70	3.30
NI	11.9	10.6	169.2	27.2	12.7	63.5	50.5	42.4	58.9
CR	7.3	5.4	374.0	39.7	9.5	152.0	85.0	95.9	109.1
V	146.9	190.8	170.7	166.7	174.0	159.6	179.3	196.1	180.1
SC	16.4	22.1	23.8	21.9	18.5	24.6	27.1	28.8	25.7
CU	20.2	14.6	19.1	29.1	14.9	21.4	11.3	15.5	11.5
ZN	82.1	86.2	77.6	60.0	75.2	79.3	77.0	78.8	298.8
SR	703.8	762.9	625.5	470.4	688.2	507.1	554.7	516.5	417.5
RB	33.5	31.7	20.9	49.4	31.1	39.7	43.9	57.4	63.0
ZR	210.3	247.1	191.0	280.3	214.7	247.1	191.5	302.1	261.8
NB	10.9	11.8	11.8	16.3	10.7	9.9	9.8	14.1	12.3
BA	445.9	450.8	352.0	481.8	435.5	359.8	594.3	542.2	514.0
TH	6.6	5.4	6.4	8.9	8.1	8.1	3.5	9.8	9.3
LA	25.2	32.1	19.8	28.4	28.0	23.7	21.8	32.6	26.5
CE	64.1	76.9	49.5	67.0	60.8	51.4	49.3	74.7	59.7
ND	34.7	40.4	25.8	35.4	33.2	32.4	26.7	37.0	29.4
SM	7.4	7.4	6.4	7.6	7.1	6.6	6.2	8.8	7.8
Y	32.9	36.4	28.9	39.0	32.6	33.7	27.4	36.9	27.9
TI02CR	1.328	1.858	1.402	1.306	1.641	1.366	1.397	1.635	1.367
TI02W	1.446	1.860	1.514	1.873	1.681	1.433	1.390	1.629	1.367
	OC4213	OC5210	OC7213	OC8213	OC9210	OC10219	OC1125	OC12210	OC13212
SI02	59.93	57.96	60.16	61.08	60.78	57.71	57.91	60.05	57.35
AL203	17.35	17.30	16.20	16.12	16.45	18.40	17.60	16.42	16.77
FE203	6.39	7.31	7.07	6.07	6.04	3.05	7.62	6.98	7.57
MGO	3.28	3.66	3.01	3.25	4.29	1.93	3.95	3.90	2.90
CAO	4.78	4.72	4.99	2.92	2.29	0.92	2.47	4.55	6.38
NA20	4.42	3.40	4.10	4.49	4.36	5.70	4.13	3.98	4.10
K2O	2.496	4.374	3.122	3.736	4.448	5.199	4.562	3.100	2.475
TI02	1.175	1.316	1.239	1.198	1.259	1.625	1.545	1.085	1.303
MNO	0.062	0.073	0.114	0.114	0.123	0.073	0.094	0.081	0.094
P2O5	0.289	0.318	0.339	0.337	0.339	0.430	0.415	0.297	0.300
TOTAL	100.18	100.43	100.34	99.32	100.38	100.64	100.28	100.33	99.25
LOI	1.24	3.63	1.08	1.55	2.02	1.51	2.06	2.22	3.81
NI	30.2	64.2	29.6	24.0	27.8	13.2	14.0	24.3	25.4
CR	34.6	136.0	70.2	43.8	66.9	6.3	6.6	32.2	20.2
V	135.1	159.9	123.8	123.2	126.1	127.0	166.8	126.8	141.4
SC	17.4	23.1	17.5	15.2	19.3	16.4	15.9	19.1	18.6
CU	16.0	20.7	22.5	26.5	37.5	25.3	17.3	24.4	24.5
ZN	75.9	119.2	66.4	68.7	116.4	71.0	126.3	69.1	76.5
SR	629.0	381.9	430.8	431.7	300.2	552.5	451.2	765.3	705.5
RB	69.8	85.6	101.8	117.8	126.4	104.4	97.9	72.3	72.0
ZR	272.5	302.2	392.4	403.7	410.2	409.1	387.7	289.7	296.3
NB	14.2	14.4	17.3	16.8	17.3	17.7	16.5	12.1	13.6
BA	829.0	774.8	787.2	775.2	1178.7	1759.3	1261.0	938.9	715.9
TH	12.2	11.2	16.2	16.3	16.4	11.7	13.7	13.3	13.1
LA	31.8	34.3	36.0	40.1	39.4	41.8	36.8	34.6	30.9
CE	70.7	68.8	87.0	90.2	90.7	90.5	86.9	82.5	69.8
ND	34.6	32.5	43.2	42.3	44.4	45.1	43.4	41.2	33.8
SM	6.8	5.3	6.7	7.3	9.0	9.9	9.0	7.2	6.3
Y	29.0	29.5	39.2	40.0	41.5	38.9	36.8	29.6	33.6
TI02CR	1.241	1.422	1.206	1.189	1.254	1.684	1.645	1.023	1.254
TI02W	1.233	1.399	1.244	1.179	1.260	1.680	1.608	1.033	1.261

TABLE B17

	OC15a10	OC17a12	OC18a12	OC19a13	OC20a16	OC21a20	OC22a10	OC23a16	OC24a18
SI02	56.76	53.46	55.08	61.87	61.67	54.08	53.72	58.02	58.21
AL203	16.03	17.42	17.58	17.07	17.24	17.36	16.28	17.86	17.53
FE203	7.60	8.03	7.91	5.89	6.06	7.98	8.26	6.51	6.76
MGO	5.92	5.23	4.25	0.88	2.75	4.67	5.49	4.28	1.21
CAO	6.92	7.85	8.20	5.80	3.91	8.65	8.76	5.71	8.36
NA20	3.62	3.95	3.85	4.36	5.15	3.75	3.38	4.51	4.05
K20	1.709	1.742	1.730	2.676	2.401	1.919	2.363	1.877	2.016
TI02	1.135	1.301	1.278	0.823	0.753	1.123	1.159	0.980	1.392
MNO	0.134	0.089	0.116	0.098	0.102	0.086	0.119	0.055	0.075
P205	0.286	0.346	0.316	0.377	0.177	0.250	0.349	0.286	0.453
TOTAL	100.11	99.45	100.30	99.86	100.20	100.06	99.88	100.09	100.06
LOI	0.86	1.68	1.22	2.99	1.68	2.75	0.96	1.57	3.80
NI	129.5	67.8	59.3	13.1	31.2	113.6	33.5	42.2	40.3
CR	248.9	63.4	51.2	19.1	45.8	174.0	45.8	64.2	15.7
V	166.0	178.0	182.5	54.8	116.4	170.4	160.2	108.8	150.1
SC	21.4	21.8	20.3	9.6	16.5	23.1	21.5	14.5	18.6
CU	29.2	40.5	41.0	11.0	18.3	23.7	39.8	18.0	13.2
ZN	84.7	74.3	66.9	57.4	67.9	56.8	82.1	71.4	90.5
SR	579.8	784.3	814.0	516.5	547.9	677.4	1785.0	641.0	652.9
RB	38.1	35.0	33.2	66.8	55.7	47.0	41.1	40.9	28.5
ZR	183.5	195.0	184.0	315.7	159.8	156.1	186.0	218.2	272.6
NB	11.9	10.4	9.2	15.7	8.8	8.5	5.2	11.8	18.6
BA	456.9	614.2	632.0	703.9	698.6	563.0	1167.9	488.0	564.2
TH	6.9	4.8	1.4	8.7	4.7	6.9	6.3	4.7	5.7
LA	29.1	25.6	25.3	34.0	20.9	24.9	42.8	20.5	39.3
CE	57.2	62.9	58.2	77.4	42.2	50.0	100.9	51.6	87.9
ND	26.6	32.9	32.7	35.9	20.7	23.4	55.2	25.5	38.8
SM	5.6	7.0	5.2	7.7	6.8	7.8	10.4	5.7	6.2
Y	20.6	25.6	26.0	27.3	18.9	21.4	27.8	22.9	27.4
TI02CR	1.171	1.314	1.240	0.826	0.745	1.033	1.000	0.965	1.484
TI02W	1.183	1.351	1.261	0.820	0.748	1.081	1.050	0.982	1.484
	OC25a16	OC26a16	OC27a18	OC28a10	OC30a22	OC31a10	OC32a5	OC33a5	OC35a18
SI02	61.72	62.24	57.32	58.33	69.11	55.40	69.60	56.51	63.67
AL203	17.43	17.41	17.52	17.74	15.55	17.62	16.36	20.26	16.27
FE203	5.62	5.55	7.26	5.83	3.71	7.06	1.68	4.78	4.74
MGO	2.21	2.26	3.11	4.30	1.26	4.16	0.68	5.77	2.89
CAO	4.72	4.62	5.58	6.70	0.22	3.86	0.52	1.56	3.97
NA20	4.79	4.53	4.37	3.50	3.33	3.53	4.38	5.48	4.27
K20	2.494	2.527	2.812	1.596	5.519	1.850	5.534	3.157	2.677
TI02	0.770	0.773	1.462	1.255	0.462	1.498	0.513	1.243	0.772
MNO	0.103	0.131	0.174	0.144	0.025	0.147	0.019	0.105	0.053
P205	0.241	0.250	0.505	0.270	0.096	0.333	0.209	0.290	0.192
TOTAL	100.09	100.29	100.10	99.67	99.29	100.45	99.49	99.15	99.51
LOI	0.88	0.98	0.84	1.16	1.63	3.75	1.21	4.32	1.53
NI	11.9	12.6	7.2	55.4	5.1	45.3	5.4	78.6	57.3
CR	9.3	10.1	4.7	59.4	3.6	101.5	10.9	87.9	138.7
V	85.3	86.0	142.2	147.5	10.0	183.3	30.2	158.6	95.1
SC	9.9	10.0	16.8	20.4	8.8	27.6	4.7	21.9	16.6
CU	15.6	13.3	16.5	15.4	3.0	14.8	1.7	2.1	10.3
ZN	60.5	63.7	89.5	68.1	39.0	118.8	17.3	58.7	67.4
SR	588.1	567.0	818.2	750.7	162.7	542.5	282.7	596.8	413.1
RB	61.4	64.1	78.1	19.9	135.3	53.6	115.7	50.3	57.8
ZR	226.0	226.4	371.1	204.7	716.7	294.8	333.4	194.6	164.7
NB	11.9	11.5	14.8	11.6	27.0	13.4	15.5	11.6	17.5
BA	712.3	734.8	947.6	701.2	1145.7	525.8	1710.0	884.2	702.3
TH	8.7	9.3	10.9	5.5	29.8	11.7	6.9	5.2	9.2
LA	28.2	28.7	45.3	20.8	59.3	26.4	28.2	31.0	37.7
CE	61.4	65.0	106.4	53.6	134.2	53.6	65.6	63.2	77.4
ND	29.4	30.3	56.2	27.3	59.6	33.2	30.3	34.6	32.4
SM	6.4	7.2	10.8	3.8	11.5	9.4	4.5	4.5	4.1
Y	24.1	24.7	35.1	28.4	48.7	33.5	21.1	27.8	22.7
TI02CR	0.713	0.730	1.525	1.306	0.472	1.559	0.570	1.220	0.821
TI02W	0.725	0.749	1.505	1.308	0.479	1.557	0.573	1.261	0.800

TABLE B17

	OC36213	OC38220	OC39220	OC4126	OC42210	OC43213	OC44211	OC47222	OC48222
SI02	63.89	55.70	63.10	63.67	53.81	62.06	54.59	54.22	56.35
AL203	17.56	18.60	16.70	17.42	17.46	17.52	18.53	17.86	15.83
FE203	4.22	8.44	5.08	4.35	9.34	5.18	8.10	8.19	4.29
MGO	1.97	4.01	4.56	1.46	4.33	2.13	2.99	7.41	1.12
CAO	1.25	4.26	1.61	3.72	7.87	3.86	7.65	5.86	1.68
NA20	6.23	4.18	3.92	4.56	3.59	3.08	4.06	3.82	4.96
K20	3.145	2.252	3.549	2.386	1.531	2.473	1.677	1.691	4.019
TIO2	0.719	1.217	0.830	0.724	1.213	0.798	1.296	0.884	0.897
MNO	0.062	0.077	0.072	0.100	0.118	0.098	0.113	0.087	0.037
P205	0.249	0.335	0.198	0.334	0.219	0.275	0.328	0.205	0.189
TOTAL	99.30	99.07	99.61	99.33	99.49	99.48	99.53	100.23	99.37
LOI	1.88	2.08	2.66	1.01	1.05	1.04	1.98	2.37	1.63
NI	9.7	5.0	38.2	4.6	23.7	17.4	19.1	79.2	8.4
CR	13.2	3.6	120.3	3.1	17.8	24.8	3.9	184.4	6.6
V	62.3	133.1	106.0	32.7	206.7	79.2	163.0	145.1	57.3
SC	8.4	15.8	19.3	6.4	25.4	9.9	14.9	26.7	10.3
CU	6.1	12.1	19.2	12.9	52.8	17.5	23.5	32.6	7.9
ZN	35.7	168.8	63.8	109.0	74.6	53.7	73.1	78.5	44.9
SR	581.1	473.1	301.2	504.9	719.2	573.8	775.0	541.2	246.5
RB	53.7	37.2	55.9	56.2	29.6	53.4	35.6	43.8	81.7
ZR	280.7	201.7	172.6	257.2	173.1	259.6	207.7	159.5	574.8
NB	12.8	10.0	16.0	15.4	7.9	12.5	11.3	7.6	13.4
BA	1011.2	491.6	847.4	688.3	654.7	704.6	519.2	380.6	761.3
TH	8.4	6.6	8.1	5.4	5.0	10.3	7.1	5.0	19.3
LA	34.8	21.9	34.6	29.6	20.0	32.4	24.4	16.1	40.4
CE	79.6	52.4	69.5	64.8	43.2	72.3	60.9	34.8	91.9
ND	35.9	27.5	27.9	28.4	24.2	36.2	31.0	18.9	41.7
SM	4.5	6.9	6.7	6.9	6.2	6.4	5.2	4.0	7.7
Y	25.4	26.5	23.3	23.1	27.9	29.5	25.0	23.7	40.0
TIO2CR	0.719	1.277	0.832	0.730	1.221	0.804	1.280	0.823	0.950
TIO2W	0.726	1.262	0.835	0.735	1.263	0.806	1.282	0.846	0.929

	OC50210	OC51213	OC52210	OC53216	OC54214	OC55222	OC56216	OC57218	OC58219
SI02	55.89	60.84	55.76	62.19	64.43	63.73	61.56	62.60	70.70
AL203	17.90	18.44	18.15	17.36	16.85	17.41	17.14	16.44	16.03
FE203	7.63	4.67	7.07	4.39	4.32	4.32	5.57	5.71	2.82
MGO	3.57	2.30	2.46	2.71	2.39	2.29	2.45	1.86	0.85
CAO	7.20	5.37	7.22	3.99	4.27	2.50	4.56	2.73	0.39
NA20	4.25	4.47	5.09	4.81	4.31	5.31	4.58	4.62	2.65
K20	1.474	2.031	2.318	2.143	2.185	2.975	2.394	3.674	5.888
TIO2	1.148	0.904	1.281	0.768	0.568	0.547	0.775	1.151	0.245
MNO	0.085	0.071	0.105	0.063	0.062	0.053	0.091	0.112	0.052
P205	0.312	0.316	0.284	0.215	0.180	0.213	0.244	0.409	0.123
TOTAL	99.44	99.41	99.75	99.24	99.56	99.34	99.35	99.30	99.74
LOI	1.15	1.48	2.95	1.33	1.18	1.56	1.17	1.22	1.82
NI	46.1	24.2	28.8	24.7	26.2	13.4	12.1	5.8	16.4
CR	64.2	23.7	26.4	29.2	38.8	22.2	9.8	3.2	25.8
V	136.4	104.5	171.0	91.0	66.0	57.9	74.2	88.8	7.9
SC	18.5	11.2	20.9	12.0	9.9	6.6	10.5	13.5	2.6
CU	33.9	19.9	14.6	10.7	21.3	32.9	15.7	22.5	45.3
ZN	63.2	100.3	47.5	55.7	111.2	59.3	72.4	95.2	45.1
SR	734.8	575.4	607.1	615.7	577.9	494.9	561.6	391.5	169.2
RB	28.8	48.2	61.8	44.1	60.4	46.6	57.2	115.7	128.6
ZR	199.9	230.4	189.2	187.8	169.5	216.3	224.5	409.3	191.8
NB	10.5	9.7	11.0	10.4	7.9	11.3	11.2	17.8	18.4
BA	418.8	540.2	506.4	648.2	677.2	904.1	740.8	827.6	937.3
TH	3.9	7.4	5.4	6.3	7.4	5.6	7.5	15.5	11.1
LA	19.4	24.1	21.3	22.4	22.6	22.9	31.7	42.5	45.1
CE	48.0	53.5	42.5	47.9	43.5	50.9	65.1	96.0	85.0
ND	23.8	24.5	20.3	23.2	20.6	22.6	31.0	46.3	33.1
SM	6.1	3.9	3.8	4.5	4.0	3.5	6.0	8.7	3.8
Y	25.7	19.7	23.3	20.2	14.0	15.4	24.7	38.2	20.3
TIO2CR	1.128	0.973	1.271	0.809	0.553	0.579	0.743	1.195	0.256
TIO2W	1.154	0.958	1.284	0.804	0.565	0.570	0.759	1.174	0.266

TABLE B17

	OC59819	OC61816	OC63818	OC64820	OC65816	OC57816	OC69885	OC71822	OC72822
SIO2	73.27	60.27	61.55	64.97	62.95	65.01	62.64	59.66	53.24
AL203	14.53	17.83	18.08	17.22	17.02	15.69	17.55	17.21	17.72
FE203	1.58	5.67	5.21	4.40	4.88	4.22	4.61	5.87	8.11
MGO	0.45	2.88	2.45	0.33	2.30	1.35	3.38	3.84	5.33
CAO	0.36	5.24	3.78	3.34	4.14	4.38	2.88	3.80	7.71
NA2O	4.14	4.60	4.23	4.77	4.17	3.89	3.56	4.33	4.03
K2O	4.892	2.277	3.020	3.085	3.153	2.973	4.099	3.201	1.670
TIO2	0.224	0.704	0.685	0.575	0.646	0.638	0.762	1.061	1.224
MNO	0.041	0.085	0.118	0.059	0.055	0.048	0.034	0.093	0.116
P2O5	0.110	0.239	0.442	0.325	0.300	0.290	0.199	0.343	0.347
TOTAL	99.59	99.78	99.65	99.67	99.61	99.49	99.70	99.41	99.50
LOI	0.83	0.94	1.51	1.81	0.95	0.57	2.31	1.62	1.01
NI	10.6	29.2	4.4	5.3	18.9	18.8	24.5	49.9	81.9
CR	21.5	40.1	3.6	6.1	26.6	28.1	20.7	75.8	124.9
V	4.8	114.4	26.2	30.5	75.9	71.0	97.5	102.5	141.7
SC	2.0	13.4	7.5	6.3	10.1	9.3	11.6	15.1	16.9
CU	4.1	25.5	4.3	3.8	17.5	17.1	17.1	35.2	50.1
ZN	37.6	57.5	118.8	55.3	70.7	55.6	56.8	64.7	63.6
SR	254.2	876.9	592.0	354.8	514.4	548.1	330.1	509.5	647.0
RB	100.0	55.6	55.8	73.0	101.4	94.7	73.8	73.1	38.6
ZR	170.8	175.4	325.8	274.9	343.7	334.0	183.4	270.9	211.4
NB	17.2	9.2	13.6	14.0	11.2	10.3	9.3	13.3	9.2
BA	1144.4	989.9	596.9	687.9	751.2	751.1	637.6	648.1	458.3
TH	8.2	10.1	6.2	6.2	13.2	14.2	8.9	12.0	5.3
LA	36.4	28.3	37.6	34.5	32.6	32.8	27.2	34.7	25.1
CE	74.0	58.7	87.8	67.8	68.3	67.4	55.1	70.4	58.4
ND	27.5	27.6	41.3	37.0	28.8	27.2	23.8	28.5	29.0
SM	4.7	5.7	6.6	5.1	3.7	4.4	4.2	6.8	7.3
Y	16.1	18.7	28.8	32.4	16.9	16.0	18.9	23.1	24.4
TIO2CR	0.244	0.728	0.738	0.655	0.697	0.694	0.797	0.937	1.152
TIO2W	0.252	0.730	0.733	0.679	0.689	0.673	0.794	1.008	1.192
	OC73811	OC74812	OC75812	OC7681	OC77810	OC78812	OC79812	OC80820	OC81812
SIO2	55.03	53.23	52.70	53.60	58.14	54.55	52.79	57.84	52.13
AL203	17.30	16.73	16.54	16.70	16.26	18.09	17.23	18.24	17.91
FE203	7.46	8.71	8.84	7.65	6.20	7.46	8.56	6.81	7.81
MGO	5.01	5.84	5.31	6.49	4.83	4.94	5.47	2.29	6.59
CAO	6.47	8.21	8.76	8.29	6.62	7.72	8.96	6.13	6.32
NA2O	3.90	3.43	3.43	3.54	3.81	3.65	3.49	4.40	4.77
K2O	2.470	1.670	1.127	1.489	2.301	1.505	1.334	2.036	1.436
TIO2	1.208	1.480	1.581	1.362	1.016	1.019	1.646	1.190	1.512
MNO	0.057	0.089	0.093	0.092	0.071	0.139	0.140	0.130	0.231
P2O5	0.390	0.367	0.248	0.322	0.285	0.247	0.303	0.442	0.357
TOTAL	99.30	99.76	99.33	99.53	99.53	99.32	99.92	99.51	99.06
LOI	3.42	2.10	1.52	2.38	1.10	0.85	1.05	1.24	2.77
NI	76.9	116.9	62.4	146.4	111.2	74.0	55.0	6.9	99.0
CR	83.8	155.5	141.6	239.6	178.1	104.0	131.3	4.3	134.6
V	163.6	201.1	186.6	157.9	149.9	147.0	215.7	121.2	221.8
SC	21.6	25.7	24.5	24.1	18.3	18.7	26.3	14.1	25.3
CU	42.0	42.6	19.9	18.8	52.2	39.2	30.8	12.2	18.4
ZN	109.1	82.5	61.3	72.4	53.7	59.6	78.5	56.0	123.8
SR	638.1	536.1	609.8	661.7	823.2	631.0	685.9	595.0	926.6
RB	50.3	44.4	20.9	24.9	55.2	30.4	25.7	48.0	26.1
ZR	249.5	232.3	160.4	205.5	211.4	169.5	193.9	262.6	229.8
NB	9.4	11.3	6.5	10.1	9.9	7.3	7.7	14.0	11.2
BA	582.1	432.4	433.0	544.9	735.3	407.5	496.7	532.0	472.0
TH	5.7	7.0	3.3	0.5	5.4	*	3.2	6.4	5.7
LA	33.4	27.4	17.0	22.7	29.3	21.2	23.9	32.9	28.0
CE	78.1	61.4	38.9	50.8	64.5	47.7	57.6	72.7	64.9
ND	39.2	32.0	24.9	26.4	32.3	24.4	31.5	35.0	33.8
SM	6.4	8.0	7.2	7.2	10.5	5.4	9.3	5.0	5.2
Y	27.4	28.5	29.2	24.9	20.4	21.6	30.7	30.5	29.2
TIO2CR	1.333	1.598	1.370	1.280	1.040	1.047	1.748	1.252	1.622
TIO2W	1.319	1.581	1.472	1.336	1.025	1.040	1.746	1.236	1.604

TABLE B17

	0C82a12	0C83a10	0C84a10	0C85a10	0C86a38	0C87a38	0C88a38	0C88a34	0C88a34
SI02	54.73	55.75	55.50	52.22	55.20	61.34	61.39	53.94	52.78
AL203	18.15	17.18	17.34	17.76	16.27	17.78	17.61	16.77	15.90
FE203	7.85	7.63	7.51	8.63	8.08	5.24	5.69	13.41	10.58
MGO	4.32	4.54	4.80	5.23	3.71	2.16	2.42	6.78	7.67
CAO	8.32	7.25	7.17	8.87	5.61	2.53	2.46	3.46	3.29
NA20	3.68	3.89	3.63	3.76	4.38	4.87	4.43	2.75	1.32
K2O	1.343	1.700	1.567	1.350	1.624	4.128	4.339	3.784	6.048
TIO2	1.353	1.336	1.325	1.201	1.428	0.775	0.779	1.438	1.589
MNO	0.154	0.131	0.127	0.161	0.094	0.058	0.073	0.122	0.159
P2O5	0.283	0.288	0.291	0.292	0.359	0.399	0.403	0.619	0.338
TOTAL	106.17	99.72	99.36	99.49	99.75	99.28	99.60	100.07	99.68
LOI	0.74	0.78	0.76	1.06	0.76	1.17	1.37	3.62	5.76
NI	52.0	63.2	61.9	103.0	19.2	6.7	5.9	9.1	15.9
CR	28.4	91.5	84.6	221.7	26.2	6.4	6.4	3.7	16.4
V	186.7	150.2	137.9	190.7	117.1	46.9	43.4	109.4	153.2
SC	26.5	20.5	19.1	25.9	16.0	6.7	6.5	19.0	28.0
CU	90.2	29.6	27.3	29.7	17.4	8.7	6.6	13.9	23.8
ZN	75.0	65.0	68.1	67.0	63.8	91.2	66.4	122.2	103.7
SR	626.8	521.1	540.8	565.6	627.8	392.2	425.6	371.5	99.1
RB	31.3	42.1	43.1	29.9	34.0	51.6	58.9	25.7	68.5
ZR	186.9	199.2	199.9	188.4	249.3	307.3	298.5	70.0	154.4
NB	9.7	12.3	11.6	7.0	12.7	15.3	15.1	10.4	8.9
BA	389.7	400.4	412.4	421.5	425.1	638.5	1041.6	384.8	432.2
TH	4.4	5.8	6.5	4.0	4.7	6.6	6.4	2.8	5.1
LA	23.3	24.8	26.4	22.1	26.0	35.7	37.0	28.2	39.7
CE	55.2	55.2	55.2	48.6	65.2	77.0	78.5	61.0	77.9
ND	26.1	28.1	25.5	25.3	30.4	34.1	37.0	29.5	35.3
SM	4.7	6.4	5.6	7.2	7.4	6.6	5.9	3.8	3.6
Y	24.8	27.8	26.2	25.1	31.2	28.4	27.8	15.8	15.3
TIO2CR	1.404	1.301	1.186	1.204	1.184	0.814	0.771	1.389	1.594
TIO2W	1.422	1.324	1.261	1.210	1.266	0.815	0.777	1.409	1.601
	0C88a34	0C89a13	0C90a1	0C91a12	0C92a12	0C93a13	0C94a13	0C95a20	0C96a1
SI02	53.67	64.75	52.84	52.30	52.40	53.79	59.26	56.63	52.36
AL203	18.42	17.88	16.23	16.09	18.75	15.72	15.55	18.22	15.77
FE203	8.66	2.54	8.46	7.25	7.23	6.49	6.83	7.79	8.36
MGO	6.90	1.02	6.92	6.84	3.23	4.83	3.74	2.81	8.19
CAO	0.83	3.97	9.90	10.66	9.88	5.08	7.03	5.91	7.73
NA20	3.69	4.68	3.35	3.16	4.47	3.37	3.13	4.54	3.14
K2O	4.964	3.604	1.135	1.680	1.618	2.691	2.737	1.936	1.829
TIO2	1.929	0.901	1.249	1.242	1.572	1.075	1.068	1.240	1.405
MNO	0.102	0.026	0.086	0.100	0.096	0.072	0.081	0.118	0.149
P2O5	0.217	0.283	0.234	0.294	0.300	0.291	0.291	0.439	0.370
TOTAL	99.38	99.67	100.41	99.61	99.53	99.41	99.65	99.64	99.31
LOI	3.92	1.73	2.75	3.53	3.10	1.39	2.76	1.13	2.53
NI	15.1	9.4	210.3	296.3	40.6	90.1	88.5	5.9	207.2
CR	15.5	9.8	408.7	506.9	33.3	134.4	152.9	3.2	432.6
V	179.9	102.9	166.5	183.5	199.6	112.4	110.4	111.6	166.3
SC	30.4	11.0	25.9	26.2	21.9	17.1	18.6	14.5	24.0
CU	13.1	7.9	32.3	37.2	28.2	36.5	25.6	10.6	25.7
ZN	144.8	17.8	73.4	93.4	126.7	65.9	51.3	62.4	73.5
SR	193.7	480.9	597.4	674.1	705.3	734.7	561.3	614.9	544.0
RB	64.9	90.7	16.8	33.6	39.5	79.6	83.2	45.2	46.4
ZR	186.0	221.3	169.1	227.6	208.6	243.5	250.5	257.8	266.4
NB	11.5	12.8	7.7	7.6	7.6	13.3	14.0	13.4	9.3
BA	926.1	789.1	330.4	518.5	446.0	796.0	724.9	511.0	516.9
TH	0.5	8.0	4.3	5.9	3.7	11.2	9.6	4.8	6.0
LA	71.5	30.8	18.6	22.4	20.2	41.7	39.6	27.6	27.1
CE	124.4	65.0	37.6	49.8	47.8	38.5	82.3	67.7	57.6
ND	44.9	27.5	18.2	28.3	26.9	38.8	36.6	33.0	30.6
SM	5.1	4.8	4.2	3.7	6.7	11.0	8.6	7.8	6.6
Y	11.5	17.3	22.7	24.3	29.6	23.4	25.3	29.8	27.8
TIO2CR	1.811	1.004	1.298	1.288	1.514	0.855	0.893	1.160	1.345
TIO2W	1.859	0.981	1.330	1.294	1.567	0.931	0.936	1.190	1.435

TABLE B17

	OC97a20	OC98a13	OC99a20	OC100a11	OC101a1	OC102a11	OC103a13	OC104a11	OC105a1
SI02	57.30	60.55	57.25	56.35	54.73	50.84	55.55	53.57	55.80
AL203	18.08	15.87	17.93	15.78	16.70	17.51	15.73	16.47	18.41
FE203	7.54	5.79	7.41	7.29	7.64	10.45	5.72	8.10	7.04
MGO	2.46	4.52	2.50	5.13	5.73	5.24	7.10	6.83	4.71
CAO	5.53	5.21	5.37	7.17	8.14	3.09	7.25	7.54	4.01
NA20	4.76	3.90	4.39	4.09	3.70	3.69	3.66	3.91	4.31
K20	1.786	1.973	1.905	1.186	0.911	1.032	1.916	1.183	3.005
TI02	1.127	1.045	1.113	1.238	1.304	1.510	1.158	1.384	1.560
MNO	0.154	0.158	0.140	0.099	0.109	0.080	0.085	0.112	0.052
P205	0.609	0.358	0.597	0.251	0.281	0.241	0.306	0.309	0.365
TOTAL	99.34	99.37	99.20	99.59	99.25	99.68	99.48	99.51	99.27
LOI	0.95	1.49	0.59	0.59	1.07	1.60	0.97	1.41	1.90
NI	5.1	79.2	4.0	56.1	99.2	193.4	192.5	171.5	23.4
CR	4.2	144.7	4.0	130.2	134.9	330.3	397.8	245.0	7.9
V	57.1	108.4	61.7	136.0	154.7	198.9	154.4	137.2	164.0
SC	10.7	12.9	10.1	20.0	22.7	29.9	22.6	19.1	20.5
CU	7.1	22.9	7.5	25.7	35.1	49.3	27.7	18.2	15.2
ZN	83.5	70.7	79.3	66.2	69.7	57.9	71.1	77.4	119.6
SR	632.5	849.9	607.4	558.1	610.4	440.9	550.3	551.6	536.9
RB	36.4	19.0	41.3	25.3	7.7	20.7	52.8	17.1	48.8
ZR	285.7	245.4	279.4	161.7	183.4	150.5	236.1	192.8	239.5
NB	14.6	15.1	13.9	8.7	11.3	6.7	9.0	11.5	13.1
BA	500.8	959.2	485.3	334.6	371.3	295.7	512.1	409.8	461.4
TH	1.0	8.3	5.7	1.1	3.8	2.6	4.8	0.0	7.0
LA	32.6	45.5	33.1	17.6	22.3	18.2	24.5	23.9	30.9
CE	76.5	87.8	78.4	40.1	47.8	36.7	54.8	50.6	64.0
ND	38.8	37.0	39.5	20.4	23.1	20.1	27.9	23.9	30.4
SM	6.6	5.8	8.6	4.7	6.4	5.0	6.5	4.5	4.8
Y	34.5	20.2	33.0	21.3	24.1	27.4	23.2	25.4	27.5
TI02CR	1.066	1.123	1.139	1.125	1.340	1.574	1.184	1.399	1.539
TI02W	1.075	1.099	1.133	1.157	1.341	1.595	1.224	1.400	1.564

	OC106a13	OC107a22	OC108a13	OC109a13	OC110a12	OC111a22	OC112a12	OC113a11	OC115a11
SI02	61.47	55.73	58.03	61.56	53.33	74.81	55.90	52.84	53.80
AL203	17.28	18.52	17.61	17.27	18.58	14.56	18.71	18.54	15.81
FE203	5.10	7.02	6.62	5.48	7.69	1.22	7.43	9.41	6.79
MGO	2.94	4.62	2.93	2.32	5.18	0.38	2.76	3.51	7.20
CAO	4.53	4.38	6.19	4.71	8.85	0.91	6.90	7.49	8.26
NA20	4.29	3.18	4.36	4.13	3.62	2.40	4.55	3.99	3.71
K20	2.351	4.454	2.035	2.516	1.611	5.077	1.644	1.598	1.415
TI02	0.996	1.266	1.358	1.013	1.163	0.128	1.542	1.669	1.277
MNO	0.115	0.075	0.101	0.099	0.132	0.042	0.110	0.074	0.125
P205	0.267	0.253	0.251	0.232	0.161	0.047	0.338	0.344	0.273
TOTAL	99.34	99.48	99.47	99.43	99.72	100.57	99.88	99.57	99.66
LOI	1.15	3.71	0.98	0.84	0.64	2.01	0.59	1.19	1.17
NI	22.2	14.8	12.1	7.7	23.3	4.2	14.3	17.0	219.3
CR	22.9	11.5	7.9	6.6	43.8	3.7	14.0	7.9	513.2
V	107.4	182.8	162.3	115.4	196.6	2.7	162.0	165.9	179.4
SC	13.5	21.7	17.0	12.6	26.3	1.2	16.9	19.5	29.5
CU	19.2	16.0	20.4	9.8	18.3	3.4	24.6	16.0	20.3
ZN	65.2	83.5	69.3	67.8	67.6	23.5	67.1	81.7	62.6
SR	623.2	500.2	656.3	579.9	657.9	101.5	541.6	665.4	542.6
RB	59.2	52.6	53.2	74.5	18.6	126.8	41.2	32.6	29.3
ZR	222.4	172.9	194.2	231.7	117.1	114.7	244.2	226.4	186.3
NB	12.5	9.4	13.4	13.6	6.7	20.3	11.4	16.0	8.4
BA	644.9	619.3	594.7	640.2	269.2	1009.5	399.8	408.0	399.3
TH	10.4	8.3	7.3	13.1	2.1	12.0	5.4	5.9	3.8
LA	34.6	31.1	25.7	36.5	12.3	23.4	26.0	28.0	21.3
CE	79.3	60.8	61.9	73.7	31.1	54.7	61.3	57.1	44.6
ND	34.9	30.2	28.4	30.2	17.4	24.4	30.7	30.0	22.8
SM	5.7	5.4	6.0	4.8	4.0	5.2	8.0	7.6	6.9
Y	24.9	23.0	25.8	24.3	22.8	26.5	32.2	30.4	23.6
TI02CR	1.011	1.294	1.335	1.014	1.210	0.146	1.483	1.594	1.273
TI02W	1.000	1.350	1.374	1.025	1.208	0.159	1.535	1.678	1.294

TABLE B17

	OC11624	OC117319	OC118311	OC119311	OC120312	OC121312	OC12239	OC12339	OC12439
SI02	54.00	79.13	51.97	51.10	57.15	55.13	60.27	59.86	60.15
AL203	16.86	13.89	17.19	17.03	17.53	17.41	15.55	16.44	16.52
FE203	7.57	0.82	7.76	9.32	6.58	5.59	6.16	6.18	6.12
MGO	6.25	0.20	7.67	6.50	4.71	4.99	3.33	3.88	3.55
CAO	7.80	0.85	7.86	7.64	6.50	5.81	5.68	6.16	5.89
NA20	3.95	0.17	3.83	4.02	4.33	4.02	3.94	4.32	4.11
K20	1.398	4.725	1.019	1.124	1.798	1.741	2.269	1.468	2.114
TI02	1.413	0.130	1.657	1.601	1.096	1.113	1.047	1.061	1.058
MNO	0.142	0.059	0.132	0.103	0.120	0.120	0.072	0.145	0.113
P205	0.334	0.054	0.300	0.296	0.284	0.283	0.257	0.250	0.257
TOTAL	99.71	100.10	99.39	99.32	100.11	99.21	99.57	99.76	99.89
LOI	1.04	3.56	1.92	1.46	1.18	1.01	1.10	1.06	0.88
NI	153.5	8.6	126.7	138.8	81.4	93.2	33.5	30.3	30.9
CR	249.7	3.7	333.0	342.4	154.4	170.7	92.8	66.6	68.9
V	146.7	10.6	188.1	193.2	143.5	149.7	125.2	124.7	123.3
SC	19.9	0.9	31.2	32.1	21.4	21.7	19.9	16.9	17.8
CU	39.3	48.3	16.0	26.5	32.3	31.5	19.4	17.2	17.5
ZV	61.2	5.4	89.7	75.6	72.5	72.0	65.9	66.6	63.7
SR	584.3	258.2	547.4	572.9	709.8	719.2	586.5	657.1	667.2
RB	23.5	92.5	17.2	18.9	41.8	37.0	54.9	29.7	60.2
ZR	208.0	109.6	189.7	184.0	191.3	186.2	226.2	224.7	224.2
NB	11.7	18.2	9.4	10.6	11.5	11.1	13.9	14.6	14.0
BA	455.8	656.3	250.4	285.3	559.5	542.3	564.6	586.9	552.4
TH	1.6	13.0	0.9	1.7	4.1	6.1	11.0	10.0	12.8
LA	29.1	37.0	17.4	19.2	26.6	24.7	35.1	37.4	35.9
CE	58.3	72.8	42.2	41.5	54.6	50.3	73.2	72.1	75.2
ND	26.7	26.2	23.7	22.7	26.6	25.4	30.7	29.6	33.1
SM	5.8	4.5	6.9	5.7	5.1	6.0	0.9	6.4	5.0
Y	25.6	17.0	26.5	30.5	24.2	23.0	21.9	23.1	23.4
TI02CR	1.457	0.148	1.463	1.603	1.132	1.120	1.078	1.152	1.083
TI02W	1.463	0.158	1.574	1.560	1.136	1.130	1.076	1.116	1.092
OC126219	OC127222	OC128319	OC12931	OC130218	OC131210	OC13221	OC13321	OC13429	
SI02	75.59	61.93	78.86	55.32	59.03	59.99	55.10	57.12	60.26
AL203	13.43	17.61	12.02	17.43	17.97	15.18	16.36	15.91	16.92
FE203	1.75	4.50	0.76	6.78	6.55	5.82	7.72	7.18	5.83
MGO	0.30	0.91	0.16	5.30	2.57	2.83	6.35	5.84	3.91
CAO	0.29	6.35	0.45	7.15	4.46	5.16	7.10	6.71	5.25
NA20	5.61	4.73	4.57	4.24	4.58	4.13	3.92	3.65	3.97
K20	3.067	2.431	3.128	1.570	2.431	2.440	1.467	1.674	2.189
TI02	0.120	1.045	0.109	1.389	1.275	1.225	1.303	1.078	1.076
MNO	0.028	0.056	0.038	0.089	0.110	0.061	0.089	0.115	0.063
P205	0.047	0.252	0.044	0.258	0.297	0.391	0.244	0.245	0.261
TOTAL	100.24	99.82	100.14	99.52	99.26	99.22	99.66	99.53	99.73
LOI	0.63	2.95	0.51	1.99	1.41	0.79	1.04	0.82	1.22
NI	4.9	53.7	3.6	102.5	7.3	83.4	115.1	126.8	31.2
CR	4.2	94.2	3.9	265.5	2.9	113.4	254.9	248.6	89.9
V	2.3	114.8	7.5	147.4	138.0	144.3	137.0	125.3	131.3
SC	0.8	20.9	0.6	23.0	15.6	18.3	22.6	19.1	20.8
CU	31.8	33.1	4.7	22.0	8.6	18.5	25.5	21.8	18.8
ZV	26.3	31.9	13.4	64.1	68.1	73.3	57.5	66.6	72.1
SR	141.2	474.0	128.2	510.3	644.5	744.8	493.0	482.8	505.1
RB	39.3	78.1	65.6	39.6	62.3	55.5	36.5	45.2	63.1
ZR	105.1	199.1	93.8	197.4	230.6	231.1	185.7	209.1	228.0
NB	19.7	10.6	16.7	11.9	14.3	14.8	11.3	14.7	14.2
BA	852.8	520.8	791.0	355.8	618.2	844.4	337.4	389.2	579.4
TH	13.2	10.2	10.4	8.2	9.8	8.6	7.0	10.6	9.2
LA	22.8	25.4	19.0	25.4	30.5	45.0	25.5	31.3	37.5
CE	53.0	56.5	43.1	57.2	69.0	97.7	53.0	65.7	74.0
ND	23.6	25.1	20.9	25.1	31.7	37.1	23.0	26.7	31.2
SM	4.9	7.8	4.4	7.5	8.2	6.9	6.0	6.0	4.3
Y	21.9	20.3	21.3	25.2	25.6	20.3	24.3	24.2	21.6
TI02CR	0.133	0.945	0.117	1.154	1.339	1.274	1.119	1.014	1.095
TI02W	0.144	1.016	0.135	1.253	1.368	1.259	1.205	1.059	1.109

TABLE B17

	OC13539	OC13639	OC137322	OC13839	OC139322	OC140312	OC141322	OC143322	OC145313
SI02	59.38	59.03	54.95	59.35	54.97	52.80	58.45	56.94	59.44
AL203	16.94	16.60	17.31	16.68	17.31	17.94	15.50	17.23	16.19
FE203	6.20	6.38	7.41	6.78	7.80	9.97	5.53	7.06	6.11
MGO	3.41	3.62	4.65	3.66	4.37	4.95	4.22	4.16	4.75
CAO	5.96	6.05	8.06	5.41	7.94	7.66	5.81	6.04	6.02
NA20	4.06	4.26	3.97	3.79	3.94	4.16	4.17	4.49	3.94
K20	2.178	2.189	1.431	2.229	1.373	1.233	2.204	1.962	1.595
TIO2	1.155	1.153	1.491	1.149	1.410	1.593	1.142	1.309	1.119
MNO	0.104	0.080	0.142	0.053	0.130	0.149	0.091	0.121	0.157
P205	0.278	0.272	0.302	0.274	0.267	0.281	0.258	0.297	0.231
TOTAL	99.67	99.64	99.70	99.37	99.50	99.72	99.38	99.61	99.54
LOI	1.04	0.98	0.56	1.14	0.56	0.61	0.96	1.07	1.19
NI	32.9	43.3	41.7	34.9	29.6	29.4	46.4	40.7	60.3
CR	51.6	83.4	109.9	53.3	59.2	28.0	96.4	36.2	78.2
V	132.0	116.3	158.1	99.5	139.3	178.1	112.9	125.0	121.4
SC	18.3	18.3	23.4	18.4	19.4	21.7	17.5	17.9	16.2
CU	21.5	19.7	29.5	18.5	26.8	20.9	23.3	25.5	32.6
ZN	59.2	65.3	60.7	72.5	61.1	39.0	64.7	65.2	90.2
SR	611.8	590.0	611.1	617.1	567.1	617.7	610.0	584.6	640.2
RB	60.7	60.4	32.0	63.5	33.5	25.0	60.5	50.2	23.2
ZR	236.2	229.4	206.5	232.7	193.6	208.5	220.0	219.9	208.9
NB	14.3	15.0	11.2	14.2	10.2	11.1	13.4	13.0	14.2
BA	575.8	558.8	398.8	575.3	409.5	356.6	619.7	517.8	584.4
TH	9.5	11.3	4.2	12.2	5.8	1.5	10.3	6.2	14.0
LA	35.2	32.5	23.4	32.4	22.0	22.5	32.3	29.1	36.5
CE	76.3	72.5	51.4	67.9	51.0	51.5	70.6	62.0	78.8
ND	31.4	30.4	25.7	28.5	24.8	26.9	29.3	28.9	32.3
SM	6.0	6.5	5.7	6.8	5.9	6.8	6.2	8.5	4.3
Y	23.8	25.7	26.8	25.5	27.8	30.2	24.5	25.2	22.1
TIO2CR	1.139	1.028	1.516	0.921	1.296	1.389	1.065	1.173	1.149
TIO2W	1.162	1.078	1.551	0.968	1.355	1.470	1.119	1.221	1.149

	OC146319	OC147318	OC148311	OC149311	OC150322	OC152312	OC153310	PE131	PE3311
SI02	70.74	59.11	54.76	55.04	54.54	50.59	56.74	50.13	53.83
AL203	14.61	17.88	17.38	16.90	18.11	14.62	15.56	16.95	19.07
FE203	2.82	6.20	7.79	7.47	8.40	9.16	7.25	10.84	3.90
MGO	1.07	2.90	4.41	5.29	3.36	10.82	6.65	2.79	0.48
CAO	2.16	4.72	8.13	7.91	6.09	9.20	6.61	11.95	13.93
NA20	4.22	4.78	3.86	3.65	4.17	2.60	3.63	4.10	5.20
K20	3.134	2.356	1.344	1.655	2.387	1.093	1.808	1.105	1.799
TIO2	0.346	1.278	1.428	1.503	1.664	1.145	1.100	1.847	1.583
MNO	0.029	0.160	0.095	0.109	0.067	0.135	0.105	0.159	0.172
P205	0.135	0.300	0.264	0.332	0.578	0.298	0.276	0.387	0.345
TOTAL	99.27	99.69	99.45	99.76	99.36	99.66	99.73	100.25	100.31
LOI	0.78	1.00	0.89	1.15	1.01	1.08	0.86	6.75	7.95
NI	8.0	7.1	31.3	110.8	14.1	241.8	164.0	176.1	6.0
CR	8.3	3.7	80.8	215.1	7.9	659.8	333.5	320.5	5.5
V	17.1	132.6	156.9	168.7	125.1	188.0	124.7	255.7	138.3
SC	2.6	15.3	20.3	22.2	15.2	30.8	18.9	28.5	16.6
CU	6.6	9.1	24.4	31.8	31.9	44.6	35.5	20.8	32.6
ZN	32.9	88.3	60.8	69.0	71.8	57.4	66.0	83.4	87.3
SR	387.6	657.5	598.9	641.2	591.5	552.3	573.4	626.3	517.5
RB	79.4	59.8	29.6	30.4	65.3	23.1	42.0	20.6	36.1
ZR	214.2	228.6	189.1	211.6	325.5	152.5	187.9	245.8	245.1
NB	9.9	14.2	10.0	14.4	17.9	7.6	11.7	7.9	11.6
BA	581.2	615.6	399.4	460.8	551.5	398.1	583.6	274.2	335.1
TH	11.8	10.6	3.1	5.8	9.9	5.7	7.7	8.9	9.4
LA	24.5	31.5	21.3	27.7	43.0	21.7	27.2	16.6	22.6
CE	53.2	69.4	49.4	59.8	92.2	47.1	60.8	46.0	61.0
ND	21.9	32.7	24.9	28.2	46.2	26.1	25.7	27.2	33.2
SM	2.2	6.1	7.4	7.5	10.1	2.2	3.0	6.9	5.8
Y	14.3	25.7	26.6	25.7	37.8	23.4	20.7	30.3	35.5
TIO2CR	0.298	1.304	1.251	1.502	1.355	1.164	1.014	1.857	1.692
TIO2W	0.368	1.298	1.340	1.509	1.466	1.184	1.034	1.922	1.706

TABLE B17

	PE3A011	PE4019	PE5020	PE601	PE8011	PE9011	PE10020	PE11012	PE12029
SI02	55.17	73.01	49.74	53.02	56.04	54.93	56.28	50.53	67.36
AL203	18.15	15.28	18.62	16.92	16.85	17.75	18.54	19.13	17.08
FE203	9.28	1.74	10.81	8.76	8.65	7.68	8.71	8.52	3.50
MGO	3.29	0.33	5.31	6.36	4.25	5.01	2.24	3.53	0.64
CA0	6.43	1.86	7.99	7.97	7.76	7.66	4.53	9.88	2.78
NA20	4.53	3.55	3.91	3.48	3.44	3.43	5.33	4.12	4.02
K20	1.371	4.051	0.936	0.910	0.965	1.125	2.155	1.552	4.120
TIO2	1.637	0.190	2.081	1.520	1.263	1.187	1.185	1.348	0.484
MNO	0.109	0.072	0.138	0.094	0.060	0.159	0.076	0.210	0.063
P205	0.340	0.090	0.334	0.257	0.206	0.184	0.466	0.471	0.221
TOTAL	100.30	100.16	100.45	99.79	99.47	100.12	99.51	100.08	100.27
LOI	1.76	2.89	2.62	1.57	1.85	3.78	2.86	6.92	2.29
NI	7.5	7.5	20.0	81.9	117.7	124.7	5.0	42.1	4.4
CR	4.6	4.2	11.4	281.5	265.3	312.0	3.9	57.8	3.7
V	121.4	0.9	184.0	180.9	194.4	179.5	100.5	207.9	10.7
SC	15.0	1.1	24.8	30.6	33.1	36.4	12.5	26.5	5.3
CU	12.4	9.2	13.7	9.9	23.7	28.0	16.5	13.7	3.7
ZN	100.2	20.0	107.2	80.7	177.0	195.9	89.3	364.1	60.1
SR	535.6	218.8	733.1	489.2	472.5	467.4	468.8	340.2	251.2
RB	31.9	99.7	15.2	9.3	20.1	21.1	42.5	52.4	121.8
ZR	231.1	269.9	208.4	192.2	150.3	143.9	269.3	431.2	427.6
NB	11.3	17.4	8.1	9.3	7.2	6.6	12.8	17.4	27.8
BA	359.7	731.7	327.0	262.8	254.5	336.2	536.5	256.7	855.0
TH	7.7	14.1	5.1	7.1	3.7	6.4	9.9	17.7	16.8
LA	22.3	46.5	19.9	16.6	13.3	17.4	34.0	37.6	52.8
CE	53.7	93.6	46.0	38.7	31.9	32.6	70.8	94.3	107.8
NO	29.0	35.9	28.1	22.2	16.3	17.8	37.7	47.8	45.5
SM	5.5	5.2	6.6	6.2	4.0	3.6	7.3	9.5	5.9
Y	33.6	25.9	35.8	28.8	23.6	25.2	32.6	50.0	37.2
TIO2CR	1.513	0.214	1.803	1.535	1.314	1.244	1.187	2.084	0.462
TIO2W	1.591	0.217	1.884	1.597	1.335	1.243	1.197	2.075	0.462

	PE13011	PE1405	PE1505	PE1605	PE17012	PE18013	PE19029	PE20029	PE2106
SI02	57.55	55.16	56.98	59.69	53.21	60.68	69.27	62.17	56.73
AL203	16.86	17.26	15.91	15.47	16.07	18.07	16.58	18.22	18.88
FE203	8.92	4.17	7.05	5.39	10.30	5.81	2.80	5.52	8.70
MGO	4.94	3.15	7.45	5.18	4.19	1.81	0.68	0.53	4.38
CA0	6.85	13.84	6.62	8.74	5.64	1.67	1.49	6.40	2.30
NA20	3.32	3.50	3.37	3.21	6.05	9.43	5.00	4.00	5.89
K20	0.378	1.599	1.587	1.632	1.836	1.653	3.858	2.177	1.690
TIO2	1.164	1.041	0.997	0.770	1.639	1.162	0.344	0.800	1.085
MNO	0.058	0.158	0.092	0.085	0.124	0.073	0.038	0.061	0.050
P205	0.188	0.208	0.181	0.201	0.522	0.378	0.154	0.339	0.252
TOTAL	100.23	100.08	100.25	100.37	99.79	99.74	100.21	100.22	99.96
LOI	3.92	8.21	2.61	3.91	4.25	1.45	0.88	4.38	4.31
NI	102.5	159.9	166.2	245.5	139.8	11.2	5.1	5.1	31.0
CR	290.6	449.4	380.6	424.8	330.7	12.2	4.4	4.7	19.1
V	156.4	158.3	131.2	120.0	176.6	108.3	11.6	83.3	133.4
SC	33.6	25.8	20.2	18.8	29.9	13.5	2.5	8.7	17.0
CU	53.8	19.2	20.4	30.3	26.3	14.5	1.7	7.9	37.4
ZN	79.8	105.9	68.5	101.4	94.5	106.0	65.5	45.2	83.4
SR	419.7	464.7	445.3	534.2	847.4	313.9	396.4	731.1	269.1
RB	5.0	42.9	43.7	25.9	34.5	21.4	86.0	51.0	44.8
ZR	137.6	165.3	152.2	156.1	353.0	313.7	351.7	302.5	254.7
NB	6.1	9.6	9.5	12.9	15.1	23.3	11.7	10.4	15.5
BA	236.1	371.3	422.6	574.2	794.4	235.0	1505.6	899.3	521.5
TH	5.5	6.9	7.9	6.4	12.4	16.8	11.8	8.7	11.4
LA	12.9	21.6	21.1	24.0	44.0	38.0	45.9	36.0	38.1
CE	24.7	44.9	40.7	48.6	103.3	81.6	94.6	80.4	74.6
NO	14.7	21.7	17.6	21.3	55.2	37.8	42.5	38.1	30.3
SM	3.9	2.2	3.9	6.3	14.5	8.5	5.5	5.4	5.8
Y	19.7	21.7	20.8	15.7	43.9	32.7	25.3	23.6	24.3
TIO2CR	1.142	1.061	0.942	0.833	1.880	1.225	0.372	0.858	1.072
TIO2W	1.183	1.102	0.991	0.825	1.858	1.203	0.367	0.853	1.102

TABLE B17

	PE22020	PE23020	PE2407	PE25022	PE26013	PE27022	PE28022	PE29022	PE31022
SI02	55.95	55.12	56.34	75.64	56.92	74.53	74.59	59.88	75.84
AL203	16.98	17.23	18.26	14.61	16.27	14.69	15.06	17.87	14.22
FE203	10.38	9.55	7.66	0.56	7.75	1.03	1.76	7.13	0.98
MGO	5.08	3.47	6.04	0.27	6.42	0.27	0.20	2.74	0.15
CAO	3.31	5.78	3.99	0.46	6.33	0.69	0.12	3.75	0.10
NA20	3.85	4.67	4.81	4.37	3.40	4.64	4.72	5.01	4.02
K20	2.343	2.102	1.051	4.230	1.633	4.187	3.612	1.945	4.515
TI02	1.733	1.743	1.205	0.103	1.283	0.111	0.048	0.857	0.089
MNO	0.095	0.123	0.113	0.030	0.097	0.086	0.045	0.119	0.019
P205	0.296	0.311	0.157	0.045	0.222	0.048	0.055	0.478	0.039
TOTAL	100.02	100.20	99.63	100.32	100.32	100.28	100.21	99.79	99.95
LOI	2.54	1.18	3.06	0.99	1.06	0.30	0.89	1.79	0.35
NI	24.9	22.6	32.8	4.1	119.1	3.9	3.9	4.4	3.8
CR	36.3	30.8	121.8	3.3	281.1	3.7	3.0	3.9	3.0
V	172.6	188.2	191.5	1.8	139.2	2.3	2.3	26.6	4.1
SC	29.4	25.1	33.4	1.7	22.8	1.9	*	7.6	1.1
CU	13.8	16.9	28.4	2.8	19.9	3.2	3.1	6.0	3.1
ZN	149.0	95.7	78.0	30.0	67.6	59.4	61.1	119.1	15.3
SR	277.0	449.4	714.4	93.4	412.6	154.7	103.6	440.7	180.8
RB	59.4	62.0	18.5	95.1	49.2	94.9	90.6	45.8	98.8
ZR	218.0	233.6	145.9	91.6	210.9	100.4	96.5	267.5	66.0
NB	12.0	13.6	8.2	16.5	9.6	15.6	15.6	11.0	18.0
BA	478.6	403.4	638.9	1359.1	371.7	1647.2	927.0	574.6	959.2
TH	8.1	9.4	5.5	10.3	7.0	9.1	10.1	6.7	7.9
LA	23.1	28.2	16.1	19.7	21.9	27.2	26.5	29.2	14.5
CE	49.1	61.5	26.8	48.8	45.6	56.0	57.7	60.8	32.8
NO	24.7	32.2	15.7	22.3	23.5	24.9	24.5	33.1	17.7
SM	7.0	7.6	4.3	4.9	6.2	5.0	5.3	5.8	4.7
Y	34.9	37.3	26.3	23.2	27.1	23.2	7.0	33.1	25.7
TI02CR	1.513	1.556	1.197	0.106	1.171	0.120	0.049	0.896	0.093
TI02W	1.590	1.611	1.194	0.120	1.223	0.129	0.064	0.898	0.115

	PE32028	PE33020	PE34019	PE36019	PE37045	PE38029	PE39029	PE40049	PE41010
SI02	47.94	55.12	80.24	79.81	49.56	63.53	64.88	50.94	57.87
AL203	18.09	18.53	14.64	15.83	17.32	17.39	17.32	17.09	16.29
FE203	10.55	6.96	1.00	0.31	10.08	5.39	4.60	9.37	6.66
MGO	2.71	4.85	0.25	0.19	6.07	1.09	1.23	5.81	6.38
CAO	13.91	7.61	1.87	0.06	9.90	3.46	2.15	8.39	7.43
NA20	3.57	3.81	0.08	*	3.63	4.46	5.62	4.22	3.37
K20	1.197	1.398	2.562	3.855	1.648	2.694	3.022	1.664	0.940
TI02	1.768	1.610	0.029	0.029	1.623	0.659	0.510	1.516	0.871
MNO	0.147	0.067	0.040	0.059	0.148	0.061	0.033	0.135	0.133
P205	0.487	0.353	0.045	0.065	0.523	0.348	0.271	0.330	0.184
TOTAL	100.37	100.30	100.75	100.65	100.50	100.09	99.64	99.47	100.13
LOI	8.67	5.03	4.76	3.45	3.47	4.40	1.02	7.21	1.83
NI	122.5	31.0	5.3	5.1	195.4	5.7	4.9	110.8	106.6
CR	271.9	94.3	3.1	3.0	340.8	6.5	4.6	339.3	190.5
V	212.2	204.4	1.6	2.4	178.7	27.7	17.0	202.4	150.9
SC	31.4	32.3	0.6	0.1	22.6	8.1	4.5	30.6	22.0
CU	14.1	33.5	2.3	3.0	32.8	4.9	3.9	11.8	18.0
ZN	202.4	191.9	65.3	64.5	85.7	90.9	64.1	100.1	66.1
SR	678.6	624.6	323.2	372.1	817.7	309.8	790.1	684.4	718.7
RB	23.2	24.7	90.7	121.8	33.7	90.1	64.6	27.3	24.8
ZR	234.9	241.2	40.8	44.3	239.9	273.9	355.0	228.0	163.1
NB	14.9	13.5	24.2	26.2	9.5	14.5	11.7	7.4	11.0
BA	432.5	397.9	69.7	168.0	531.0	511.0	1264.2	705.5	552.3
TH	8.5	5.8	7.8	9.8	9.1	8.0	7.6	3.0	6.7
LA	26.7	29.6	11.3	12.1	34.2	33.5	42.2	32.9	24.0
CE	63.9	64.9	27.0	30.1	80.8	59.8	89.9	74.5	51.2
NO	32.3	33.2	12.7	14.8	45.8	33.8	43.9	37.1	21.8
SM	8.1	5.7	2.5	3.7	12.4	6.2	4.2	8.2	3.8
Y	29.5	27.8	5.3	4.9	31.4	36.6	28.0	26.7	20.8
TI02CR	1.775	1.641	0.031	0.030	1.667	0.658	0.487	1.528	0.977
TI02W	1.867	1.685	0.050	0.045	1.669	0.671	0.489	1.548	0.947

TABLE B17

	PE4286	PE44811	PE46820	PE4881	PE51819	AY186	AY2813	AY3811	AY485
SIO2	62.89	51.73	70.01	53.51	71.43	63.80	60.81	50.33	57.18
AL2O3	18.09	17.44	15.21	17.76	15.01	19.15	18.15	17.75	15.57
FE2O3	5.19	9.46	3.42	8.19	2.76	3.64	5.64	7.25	6.81
MGO	1.13	5.14	0.65	5.40	0.64	1.62	2.28	5.57	6.75
CAO	4.51	9.90	2.81	8.94	1.97	3.52	3.61	12.31	7.31
NA2O	3.96	2.83	3.30	3.16	4.42	4.49	3.84	3.69	3.25
K2O	3.096	1.486	3.491	0.788	3.115	3.368	3.587	1.238	1.704
TiO2	0.715	1.389	0.510	1.106	0.310	1.002	0.992	1.279	0.996
MNO	0.052	0.055	0.120	0.071	0.018	0.035	0.036	0.085	0.092
P2O5	0.285	0.233	0.140	0.168	0.127	0.191	0.190	0.238	0.210
TOTAL	99.91	99.65	99.66	99.09	99.80	99.81	99.12	99.74	99.87
LOI	2.82	9.55	2.14	3.91	0.75	1.38	1.75	8.63	1.33
NI	7.4	117.5	34.0	93.3	7.2	15.1	14.6	197.0	164.9
CR	7.3	320.9	98.2	280.6	8.3	11.5	10.0	394.0	326.7
V	38.3	179.1	61.7	201.6	19.1	133.1	124.0	191.3	130.1
SC	6.2	27.8	10.5	36.3	2.6	15.1	15.5	30.2	20.2
CU	7.8	33.4	14.5	16.8	6.9	14.9	13.9	155.4	40.6
ZN	86.0	56.2	34.4	66.2	31.0	142.6	90.8	143.6	65.9
SR	645.1	457.8	264.5	404.2	602.2	330.1	314.5	485.6	517.0
RB	96.3	52.9	93.0	13.4	66.8	70.4	78.4	13.8	41.6
ZR	258.0	193.6	175.3	135.5	173.2	138.2	187.2	170.7	173.6
NB	13.3	7.6	11.8	7.2	11.3	9.9	8.9	6.4	9.9
BA	897.5	357.7	1037.8	318.4	1249.9	532.7	676.3	492.9	453.7
TH	7.6	5.0	13.4	6.1	13.3	12.3	13.5	10.0	0.5
LA	31.8	16.2	30.8	13.1	26.9	20.9	22.8	19.5	23.3
CE	69.6	37.1	59.2	31.3	55.2	50.9	49.5	41.8	43.2
ND	33.0	20.4	24.4	16.2	22.3	23.1	22.9	22.5	20.5
SM	7.1	5.5	2.6	4.3	4.4	5.1	3.2	3.3	4.1
Y	24.7	24.1	16.1	23.0	13.1	18.9	21.2	21.1	18.8
TiO2CR	0.777	1.433	0.550	1.234	0.339	1.078	1.018	1.375	1.041
TiO2W	0.768	1.438	0.534	1.210	0.333	1.045	1.014	1.380	1.049
	AY5810	AY6811	AY7820	AY8811	AY986	AY10828	AY1185	AY12813	AY1385
SIO2	56.50	53.11	56.57	56.37	62.98	57.47	57.08	65.03	56.78
AL2O3	17.08	17.75	17.20	16.56	18.93	15.79	17.16	16.29	16.53
FE2O3	7.61	9.02	8.39	7.80	2.82	7.09	8.43	4.02	7.71
MGO	3.78	7.78	3.31	4.82	0.25	4.39	5.20	1.35	4.78
CAO	8.30	2.87	6.07	6.09	2.34	7.01	5.74	5.58	6.50
NA2O	3.62	5.13	4.10	4.14	9.80	3.61	3.56	3.76	3.91
K2O	1.738	1.648	2.000	1.945	2.098	1.756	0.982	2.388	1.711
TiO2	1.103	1.503	1.576	1.302	0.829	1.189	1.189	0.796	1.163
MNO	0.051	0.064	0.088	0.042	0.020	0.109	0.077	0.097	0.095
P2O5	0.179	0.277	0.292	0.296	0.196	0.245	0.243	0.169	0.235
TOTAL	99.96	99.15	99.60	99.27	99.27	99.66	99.65	99.49	99.42
LOI	4.88	4.20	0.97	1.36	1.27	1.73	4.37	0.64	0.98
NI	78.3	185.2	11.1	96.3	10.9	107.2	105.4	55.2	103.2
CR	189.2	269.0	19.8	154.8	30.4	205.6	207.1	161.3	190.5
V	172.9	193.9	166.7	139.7	34.5	146.1	160.8	108.1	129.5
SC	29.8	29.1	26.4	20.6	11.5	22.9	24.3	18.1	20.5
CU	20.5	92.2	27.9	24.2	6.4	13.6	26.5	12.2	34.5
ZN	200.7	383.9	80.3	40.2	10.0	70.2	508.7	40.7	62.7
SR	382.8	201.9	447.1	443.7	247.8	454.8	348.7	499.8	446.7
RB	47.2	43.4	58.2	49.7	25.1	51.0	21.3	73.7	52.3
ZR	157.1	214.1	254.9	231.7	163.9	211.8	207.8	160.5	205.5
NB	8.2	11.9	11.4	13.1	10.0	9.5	9.2	7.6	8.5
BA	332.1	319.6	485.0	428.7	521.6	431.4	255.7	667.5	433.8
TH	3.0	0.3	10.8	10.9	9.2	8.3	9.8	9.6	9.2
LA	18.4	21.2	23.6	24.7	12.0	19.5	20.2	21.2	22.1
CE	34.4	45.7	52.9	53.8	32.6	43.0	45.3	41.5	44.2
ND	18.1	22.4	27.8	26.0	19.9	21.5	22.0	20.0	22.3
SM	1.7	3.1	5.7	4.9	3.5	4.2	2.8	3.1	4.2
Y	20.9	25.4	33.5	28.1	16.1	26.7	27.9	18.3	26.1
TiO2CR	1.141	1.414	1.461	1.231	0.884	1.181	1.298	0.844	1.086
TiO2W	1.164	1.452	1.535	1.256	0.855	1.194	1.262	0.827	1.144

TABLE B17

	AY14B13	AY15B5	AY16B10	AY17B12	AY18B5	AY19B13	AY19AB10	AY20B10	AY21B22
SIO2	60.32	60.53	55.42	56.19	56.30	59.91	55.31	55.54	55.70
AL203	16.99	17.28	16.85	16.95	18.14	15.47	17.31	17.15	16.92
FE203	5.45	5.09	7.83	7.63	6.08	5.82	7.15	7.48	7.98
MGO	3.96	5.24	5.05	4.73	6.59	4.75	5.26	5.08	6.96
CAO	5.39	3.66	7.18	7.08	4.12	5.70	6.91	7.11	5.03
NA2O	4.11	4.58	3.91	3.88	4.71	3.60	4.11	4.14	3.68
K2O	2.251	1.956	1.517	1.676	1.723	2.160	1.660	1.580	1.453
TIO2	0.829	0.858	1.269	1.262	0.903	0.811	1.264	1.291	1.116
MNO	0.115	0.128	0.106	0.145	0.165	0.111	0.049	0.086	0.056
P2O5	0.169	0.175	0.263	0.266	0.182	0.169	0.267	0.260	0.199
TOTAL	99.57	99.50	99.39	99.80	98.92	99.49	99.30	99.73	99.09
LOI	1.10	3.77	1.05	1.12	3.13	0.99	1.27	0.91	4.81
NI	96.9	99.0	82.1	79.1	95.9	92.7	72.5	75.8	66.6
CR	182.5	191.9	175.3	180.2	190.6	156.4	172.4	176.9	168.5
V	115.8	138.3	180.6	159.5	150.9	110.0	153.6	151.3	195.0
SC	19.4	23.3	24.6	24.6	23.4	18.0	25.0	24.6	33.3
CU	19.1	30.5	26.7	44.1	22.6	22.0	34.8	34.9	35.3
ZN	55.1	163.2	134.8	58.0	1000.1	51.9	56.1	60.9	549.7
SR	483.8	368.0	521.1	507.8	400.3	495.0	496.7	488.4	316.3
RB	61.0	52.4	24.1	40.0	18.6	59.9	42.8	42.0	29.0
ZR	168.0	174.2	206.1	204.8	180.1	153.0	203.3	211.5	163.0
NB	7.1	7.2	8.7	9.1	6.7	6.5	9.7	9.4	8.2
BA	669.6	416.1	462.4	440.0	571.3	682.8	458.2	437.8	403.6
TH	9.0	10.2	3.9	4.6	7.2	4.4	0.0	3.3	8.1
LA	22.0	20.3	21.4	24.1	26.3	17.3	20.0	21.8	17.8
CE	39.0	43.6	49.2	50.2	53.8	42.3	47.7	49.5	38.0
ND	18.3	19.2	24.6	25.1	25.4	18.9	23.6	24.1	18.7
SM	3.5	2.9	3.6	6.6	5.0	2.1	5.2	2.9	2.9
Y	19.2	18.9	27.8	26.3	20.9	19.0	26.3	28.4	26.7
TIO2CR	0.850	0.854	1.223	1.235	1.011	0.838	1.140	1.164	1.222
TIO2W	0.864	0.884	1.264	1.295	0.970	0.833	1.189	1.249	1.215
	AY22B13	AY23B5	AY24B10	AY25B10	AY26B11	AY27B10	AY28B5	AY30B1	AY31B11
SIO2	59.73	58.26	55.20	53.31	56.58	55.48	61.37	52.10	52.82
AL203	16.55	17.61	17.02	17.94	17.43	17.62	16.57	17.13	17.83
FE203	6.38	5.96	7.60	8.45	10.03	6.93	6.75	8.66	8.58
MGO	3.59	4.04	5.55	5.46	5.36	5.48	3.39	3.31	5.64
CAO	5.41	5.66	6.99	6.64	2.05	7.14	2.65	11.76	7.18
NA2O	4.06	4.16	3.95	4.01	3.89	4.10	4.53	3.17	4.37
K2O	2.055	2.082	1.640	1.549	2.560	1.539	2.634	1.567	1.499
TIO2	1.094	1.172	1.257	1.621	1.199	1.264	1.427	1.183	1.622
MNO	0.063	0.066	0.068	0.058	0.025	0.067	0.054	0.041	0.120
P2O5	0.248	0.269	0.261	0.283	0.199	0.264	0.279	0.260	0.250
TOTAL	99.18	99.27	99.53	99.33	99.32	99.89	99.64	99.20	99.92
LOI	1.12	1.94	1.21	1.33	3.35	1.12	2.06	8.93	4.68
NI	100.5	96.9	78.5	65.4	59.7	90.7	7.3	187.9	93.9
CR	213.7	221.6	175.9	187.7	169.1	182.3	6.2	325.0	182.0
V	131.2	142.1	147.8	201.5	174.1	177.5	180.6	327.4	203.1
SC	23.4	24.5	24.3	31.4	33.4	27.0	24.8	26.1	34.1
CU	21.4	14.3	29.9	37.7	9.0	23.3	7.5	11.7	18.1
ZN	135.1	430.7	55.8	115.6	262.8	133.1	125.6	76.8	65.5
SR	428.4	443.5	491.1	503.8	209.7	516.8	229.9	390.4	373.3
RB	64.7	54.8	39.5	35.0	31.5	27.4	58.5	26.4	28.1
ZR	210.8	225.8	200.9	214.3	163.5	211.1	245.2	165.3	184.1
NB	10.1	12.2	11.7	9.9	9.5	11.1	14.7	8.6	9.2
BA	432.5	437.5	457.5	407.6	347.0	454.6	457.1	471.4	304.1
TH	8.8	8.3	4.2	4.1	5.1	8.0	8.8	7.7	7.0
LA	22.7	22.8	22.2	20.3	15.5	22.8	28.2	14.3	15.6
CE	47.3	48.9	47.6	44.3	31.6	48.1	51.3	36.4	38.1
ND	22.8	24.5	23.3	23.9	16.6	24.3	30.2	18.2	21.4
SM	4.3	4.9	4.5	5.1	4.2	4.7	6.1	6.8	5.8
Y	22.0	26.8	25.3	28.8	22.7	25.4	29.9	24.2	30.4
TIO2CR	1.055	1.151	1.103	1.522	1.186	1.329	1.489	1.284	1.541
TIO2W	1.090	1.171	1.173	1.575	1.201	1.337	1.481	1.291	1.613

TABLE B17

	AY32210	AY33222	AY34222	AY35210	AY37210	AY38212	AY40226	AY41221	C12231
SI02	57.04	57.41	68.21	57.05	55.16	52.16	59.59	54.24	54.81
AL203	17.74	17.93	16.19	16.81	18.43	19.01	17.47	18.43	15.64
FE203	6.47	7.46	3.37	6.89	8.60	3.17	5.07	8.45	5.08
MGO	5.78	5.51	1.26	4.58	4.92	3.54	2.83	4.86	3.36
CAO	4.84	3.72	1.59	7.51	3.65	10.41	2.88	3.80	1.89
NA20	4.31	4.09	4.50	3.41	4.53	3.71	3.59	5.01	2.65
K20	1.740	1.517	3.924	1.846	1.905	1.387	5.921	3.293	5.084
TI02	1.209	1.296	0.484	1.102	1.684	1.460	0.695	1.340	0.813
MNO	0.093	0.012	0.026	0.071	0.078	0.125	0.045	0.139	0.024
P205	0.196	0.259	0.191	0.186	0.270	0.241	0.269	0.202	0.272
TOTAL	99.42	99.20	99.64	99.56	99.22	99.20	99.35	99.77	99.63
LOI	2.81	3.42	1.22	1.48	2.95	5.14	3.57	2.92	2.26
NI	88.9	30.5	5.3	81.0	15.2	17.8	18.1	47.9	53.5
CR	245.1	42.6	5.6	215.9	51.2	59.3	20.6	10.8	69.2
V	171.7	174.1	13.1	147.1	218.9	192.3	73.8	144.8	77.4
SC	31.5	25.8	4.7	23.3	37.6	29.8	8.3	23.6	12.3
CU	19.6	27.8	0.9	28.3	17.8	23.9	8.3	14.8	24.5
ZN	62.6	419.8	116.2	59.9	77.7	52.3	80.2	81.4	80.3
SR	319.5	304.8	236.8	404.9	338.1	494.3	188.9	1428.5	217.9
RB	58.5	42.7	73.4	58.9	45.6	35.1	157.5	78.5	162.6
ZR	244.3	247.6	298.0	212.3	277.2	225.5	232.7	153.6	278.3
NB	9.3	10.3	14.9	8.9	10.4	7.5	10.1	6.0	16.0
BA	288.2	422.0	915.0	425.2	680.5	329.6	1460.7	804.8	700.7
TH	12.7	13.8	12.3	11.6	9.4	10.1	10.1	6.6	29.0
LA	20.7	22.1	34.9	19.6	21.6	18.6	22.4	16.5	49.3
CE	47.1	48.3	73.7	42.7	49.8	45.7	46.6	35.3	103.1
ND	24.8	24.2	34.1	21.2	25.7	23.6	22.5	21.0	39.8
SM	5.4	5.5	6.0	5.4	7.5	4.6	4.1	3.6	5.9
Y	30.0	28.6	28.7	27.1	32.0	32.2	21.7	24.1	19.6
TI02CR	1.204	1.294	0.527	1.079	1.656	1.292	0.767	1.130	0.777
TI02W	1.248	1.380	0.527	1.106	1.723	1.385	0.754	1.175	0.786
	C2233	C5231	C7230	C8230	C9233	C10231	C11231	C12230	C13230
SI02	63.14	61.74	62.20	62.39	62.85	61.85	61.54	60.88	61.74
AL203	16.34	16.18	15.97	15.93	15.94	16.23	16.21	16.07	15.83
FE203	5.25	5.30	4.88	5.10	5.05	5.41	5.27	5.43	5.55
MGO	3.76	3.11	2.99	2.34	3.25	3.21	3.36	3.42	2.81
CAO	2.75	4.64	5.47	5.43	5.01	4.06	5.12	5.36	4.77
NA20	3.68	3.67	3.62	3.50	4.20	3.52	3.71	3.71	3.75
K20	3.847	3.466	3.369	3.631	2.356	3.581	3.507	3.413	3.621
TI02	0.931	1.052	1.046	0.917	0.929	1.091	1.081	1.068	1.025
MNO	0.061	0.056	0.070	0.081	0.100	0.055	0.109	0.116	0.069
P205	0.317	0.353	0.348	0.338	0.341	0.388	0.391	0.374	0.368
TOTAL	100.08	99.57	99.97	99.66	100.02	99.39	100.30	99.84	99.54
LOI	2.10	3.42	1.70	3.52	2.14	2.31	1.60	1.26	3.51
NI	75.7	57.3	51.4	57.0	49.7	50.1	49.4	45.5	49.1
CR	135.9	93.6	75.8	94.9	81.7	90.2	80.5	67.2	77.2
V	103.5	109.9	94.5	89.1	85.9	104.7	98.3	101.3	96.7
SC	14.9	16.1	12.7	13.7	11.3	16.1	14.2	13.7	13.4
CU	38.5	23.9	21.8	22.0	27.0	16.1	21.5	21.3	20.0
ZN	88.7	116.1	65.4	68.5	62.4	91.3	75.5	66.3	71.5
SR	397.7	354.7	494.9	556.0	1025.3	459.8	535.1	573.7	543.6
RB	140.5	146.1	146.8	140.2	55.4	140.5	142.2	137.4	147.1
ZR	290.8	302.3	297.3	281.2	284.8	315.1	318.2	319.5	306.3
NB	16.3	17.2	14.2	13.5	13.3	18.0	17.6	16.7	15.8
BA	766.8	638.2	695.9	731.3	1097.4	736.0	764.5	745.3	798.9
TH	23.6	28.4	23.3	24.9	23.6	23.0	23.1	25.0	22.3
LA	55.8	55.7	56.0	59.1	55.2	59.0	51.5	63.6	60.2
CE	118.6	117.2	112.6	121.5	127.7	122.1	126.3	131.9	119.5
ND	42.9	44.9	43.1	46.3	47.3	47.9	47.6	48.9	46.5
SM	6.1	7.3	7.1	6.0	3.9	8.2	7.3	6.1	8.3
Y	20.2	22.0	22.1	20.0	19.7	23.0	24.1	24.0	22.1
TI02CR	0.951	1.088	1.010	0.899	0.950	1.049	1.052	1.040	0.977
TI02W	0.952	1.072	1.033	0.909	0.929	1.076	1.039	1.038	0.997

TABLE B17

	C15a33	C16a14	C17a31	C18a32	C19a30	C21a31	C22a33	C23a22	C27a30
SI02	63.27	63.45	62.23	62.08	62.28	63.61	61.22	70.43	62.01
AL203	15.93	15.94	16.11	16.15	16.51	15.88	15.73	15.37	15.88
FE203	4.91	4.92	5.17	5.50	3.34	4.89	4.74	2.23	5.65
MGO	3.31	3.04	2.37	3.10	2.19	2.42	3.52	0.60	3.21
CAO	4.61	4.73	5.25	4.89	7.00	4.83	1.70	0.45	3.39
NA20	4.07	3.38	3.59	3.34	3.78	3.34	3.13	4.08	3.82
K20	2.541	3.257	3.661	3.266	3.492	3.896	7.527	6.152	3.900
TIO2	0.907	0.863	1.006	1.031	1.021	0.874	0.886	0.369	0.926
MNO	0.065	0.067	0.063	0.086	0.098	0.073	0.031	0.025	0.075
P205	0.323	0.290	0.346	0.339	0.338	0.294	0.317	0.072	0.333
TOTAL	99.94	99.93	99.78	99.97	100.06	100.10	99.81	99.77	99.20
LOI	1.78	2.59	3.46	1.67	3.52	4.48	2.94	0.96	2.46
NI	46.3	49.4	56.1	48.1	58.3	58.1	47.9	5.7	53.3
CR	80.0	96.6	95.9	83.1	104.7	105.9	84.0	3.2	105.9
V	86.5	92.0	108.8	101.5	102.9	96.0	91.7	17.8	93.5
SC	10.8	11.8	14.6	13.2	15.8	14.3	14.1	4.5	14.9
CU	21.4	18.2	17.3	23.9	31.1	23.8	11.0	4.9	6.2
ZN	59.9	65.5	71.5	64.4	114.2	57.9	84.5	49.9	142.7
SR	810.3	632.5	645.5	614.1	529.6	579.3	134.4	155.2	385.5
RB	74.5	88.8	145.2	75.1	151.5	158.5	171.2	185.9	145.6
ZR	282.8	280.5	307.1	308.3	298.9	277.2	280.3	419.0	276.9
NB	14.6	13.3	16.3	15.9	16.2	13.2	14.7	18.0	14.3
BA	1073.0	1021.2	747.6	868.2	687.6	789.3	733.6	831.1	695.3
TH	25.4	24.9	25.2	23.7	28.4	20.9	23.2	33.0	15.5
LA	66.2	57.1	57.4	55.0	55.7	55.4	64.1	110.9	57.9
CE	119.0	112.2	119.9	121.7	117.4	109.7	130.0	198.7	119.9
ND	44.8	43.5	47.1	46.5	45.1	41.6	46.2	62.7	45.7
SM	8.0	7.3	6.7	6.4	7.6	5.2	7.6	8.5	5.1
Y	20.8	19.6	22.1	22.1	22.5	20.0	16.4	19.3	20.6
TIO2CR	0.916	0.891	1.061	1.029	1.037	0.893	0.962	0.404	0.884
TIO2W	0.905	0.891	1.058	1.021	1.035	0.908	0.960	0.399	0.881
	C28a22	C29a32	C30a33	C31a31	C33a33	C34a32	C35a40	C36a31	C37a33
SI02	69.98	62.45	65.37	63.37	65.95	62.68	63.67	63.46	64.63
AL203	15.21	16.18	15.74	16.01	15.83	15.20	16.58	16.34	15.84
FE203	3.19	5.26	4.31	4.94	4.03	5.66	4.19	4.78	4.72
MGO	1.66	2.54	2.17	2.88	2.42	3.68	1.66	2.92	2.80
CAO	1.70	4.09	3.92	3.47	4.20	1.58	2.66	3.30	3.14
NA20	1.91	3.69	3.46	3.32	4.41	2.89	1.89	3.81	3.61
K20	5.372	4.130	3.576	4.597	1.720	5.889	8.041	4.123	3.714
TIO2	0.419	0.975	0.818	0.847	0.696	0.918	0.792	0.887	0.885
MNO	0.049	0.065	0.052	0.045	0.053	0.042	0.059	0.044	0.044
P205	0.149	0.334	0.297	0.297	0.241	0.328	0.204	0.297	0.318
TOTAL	99.64	99.72	99.71	99.77	99.55	99.86	99.74	99.94	99.70
LOI	3.21	3.17	2.09	2.90	2.52	3.26	4.35	2.62	2.08
NI	13.4	61.4	52.6	56.7	31.9	41.8	15.4	39.5	62.4
CR	29.3	105.2	99.8	100.2	62.0	59.4	16.0	81.4	108.1
V	50.4	98.0	85.1	87.3	70.9	98.6	73.5	95.8	89.0
SC	7.8	14.6	12.8	13.0	8.8	14.0	9.3	14.4	13.4
CU	7.1	16.5	20.8	15.4	21.0	17.5	3.9	11.4	24.5
ZN	65.4	108.9	120.0	116.8	60.2	256.5	74.0	145.9	99.1
SR	127.5	358.1	447.9	340.6	958.4	136.1	146.0	328.4	425.0
RB	242.8	152.9	151.9	160.7	65.6	156.8	269.2	145.4	163.1
ZR	199.5	299.6	261.9	271.7	227.9	296.2	385.9	262.4	276.5
NB	12.3	16.6	13.5	13.9	11.8	13.9	17.8	13.7	13.9
BA	804.9	658.6	697.0	666.6	1534.8	804.6	1205.3	747.0	668.4
TH	27.9	20.3	24.9	24.1	17.2	19.8	30.2	19.5	22.4
LA	56.3	57.3	55.6	53.7	55.1	55.8	77.8	52.9	56.7
CE	111.6	119.8	114.4	115.6	102.9	115.5	149.8	106.3	118.6
ND	44.2	44.0	43.1	42.0	40.9	45.5	56.1	40.6	44.9
SM	6.3	5.5	7.1	7.5	7.8	7.6	7.2	5.3	6.3
Y	19.6	21.2	17.0	20.1	16.3	20.1	24.7	20.7	18.1
TIO2CR	0.517	1.006	0.862	0.875	0.748	0.953	0.841	0.935	0.934
TIO2W	0.496	1.000	0.848	0.884	0.727	0.945	0.853	0.932	0.929

TABLE B17

	C38232	C40222	C41219	C43232	C44231	C45230	C46233	C47222	C48222
SI02	61.68	68.42	78.31	63.15	63.28	63.56	63.85	65.59	51.72
AL203	16.02	14.95	12.48	16.05	15.58	15.58	15.79	15.57	15.58
FE203	5.90	3.41	0.52	5.13	4.94	4.78	4.75	3.95	5.41
MGO	3.93	2.29	0.13	3.78	3.77	3.51	3.50	2.67	3.88
CAO	4.28	1.78	0.13	3.48	4.00	4.32	3.62	2.78	4.13
NA2O	3.50	3.82	3.55	3.44	3.44	3.26	3.37	3.75	3.88
K2O	3.215	4.340	4.857	3.400	3.659	3.498	3.728	4.246	3.525
TIO2	1.009	0.636	0.133	0.907	0.857	0.852	0.830	0.756	0.946
MNO	0.085	0.063	0.001	0.091	0.084	0.076	0.074	0.064	0.098
P2O5	0.372	0.248	0.025	0.301	0.304	0.302	0.294	0.275	0.354
TOTAL	99.99	99.85	100.34	99.78	99.93	99.75	99.72	99.55	99.52
LOI	1.99	1.71	2.69	0.65	1.48	1.27	1.65	2.89	1.11
NI	72.8	40.9	4.3	74.7	76.2	55.5	68.1	44.8	68.1
CR	106.4	70.5	4.5	134.0	131.5	107.0	113.3	69.9	125.6
V	107.6	67.0	3.1	103.7	92.1	38.1	89.4	76.5	95.0
SC	13.7	9.6	0.6	14.5	13.2	11.5	12.3	10.8	13.9
CU	31.8	18.2	3.5	19.6	24.1	25.9	19.5	23.9	26.5
ZN	74.5	65.2	83.3	127.5	84.2	65.3	71.4	69.7	76.2
SR	689.2	241.1	61.7	530.4	502.0	457.5	486.1	360.0	482.5
RB	85.3	200.7	195.5	137.6	147.8	137.1	133.3	175.8	141.1
ZR	298.7	187.2	128.6	260.8	265.2	256.3	263.9	247.0	257.0
NB	15.7	17.2	20.6	13.7	13.8	14.4	14.3	16.3	15.0
BA	754.8	566.5	130.0	896.3	372.5	745.5	819.8	780.9	714.5
TH	17.5	29.2	39.6	21.8	21.1	23.7	23.2	25.4	19.8
LA	59.7	57.4	45.2	57.9	56.6	52.2	50.7	57.4	53.6
CE	126.3	110.5	92.6	115.7	111.6	109.5	107.7	119.1	110.8
ND	48.5	43.1	34.4	43.2	43.6	40.7	42.5	45.9	43.5
SM	6.0	5.4	5.3	6.0	5.6	7.0	5.0	4.6	7.7
Y	21.5	21.3	20.0	19.5	19.5	19.8	18.4	20.7	21.8
TIO2CR	1.051	0.714	0.137	0.902	0.853	0.860	0.833	0.799	0.972
TIO2W	1.036	0.711	0.150	0.912	0.858	0.854	0.824	0.817	0.949
	C4924	C50214	C51214	C52222	C54233	C55240	C57240	C58222	C59229
SI02	64.24	62.34	62.57	67.58	54.89	65.01	66.69	63.90	69.45
AL203	15.81	15.76	15.70	15.39	15.79	15.53	15.79	16.11	15.33
FE203	4.39	5.08	5.02	3.46	4.36	4.37	5.24	4.47	2.75
MGO	2.62	3.54	3.38	2.31	2.79	2.17	1.21	2.83	2.13
CAO	3.20	4.62	4.31	2.37	4.35	2.65	0.77	2.32	1.12
NA2O	4.00	3.63	3.70	3.65	4.79	2.34	3.64	3.92	3.34
K2O	4.380	3.372	3.600	4.371	1.504	5.828	5.516	4.805	5.301
TIO2	0.794	0.901	0.899	0.547	0.837	0.710	0.770	0.809	0.482
MNO	0.085	0.098	0.087	0.068	0.076	0.052	0.048	0.077	0.036
P2O5	0.270	0.288	0.296	0.226	0.276	0.257	0.196	0.301	0.174
TOTAL	99.77	99.63	99.55	100.07	99.65	99.90	99.87	99.55	100.10
LOI	0.56	0.27	0.38	1.41	3.19	3.57	1.57	1.63	1.75
NI	39.3	62.9	67.8	36.3	34.4	59.8	13.9	29.6	27.6
CR	66.8	116.6	118.9	59.7	63.9	85.4	14.7	49.8	50.9
V	75.0	87.5	90.9	57.9	80.2	74.5	63.3	84.3	45.7
SC	10.8	12.3	12.1	8.2	10.3	10.4	7.5	9.5	6.3
CU	19.8	29.6	26.2	21.6	19.6	12.3	9.1	18.6	9.3
ZN	77.3	69.5	69.9	50.8	62.6	132.3	115.1	74.7	68.0
SR	440.7	497.8	468.4	421.0	839.6	207.4	279.1	566.0	238.9
RB	165.7	110.9	152.0	188.4	58.9	191.4	203.3	166.0	256.9
ZR	295.2	266.0	277.0	214.6	282.2	259.0	385.9	330.6	203.1
NB	16.5	12.7	13.8	15.5	14.7	15.7	17.9	15.5	11.5
BA	799.0	743.0	715.5	717.3	738.2	733.3	1183.3	1153.5	707.7
TH	25.7	22.3	21.5	27.0	23.3	24.9	31.5	20.0	27.4
LA	58.4	53.3	56.2	55.1	60.0	55.6	59.6	66.9	50.1
CE	116.2	106.9	115.2	107.0	115.7	113.1	142.7	138.1	95.6
ND	44.1	41.3	42.8	41.4	40.2	43.0	51.8	51.3	36.2
SM	7.5	7.3	7.8	4.6	5.9	6.9	8.9	8.2	5.2
Y	22.0	19.4	19.3	20.3	20.3	19.5	23.5	20.8	13.7
TIO2CR	0.790	0.939	0.916	0.634	0.871	0.762	0.828	0.778	0.514
TIO2W	0.803	0.945	0.904	0.535	0.663	0.749	0.823	0.788	0.535

TABLE B17

	C60233	C61232	C62222	C64225	SA1248	SA2248	SA5248	SA621	SA7248
SI02	63.41	65.85	64.21	61.63	57.28	55.10	57.00	54.51	55.75
AL203	16.43	16.09	15.30	16.14	16.28	16.86	16.92	15.92	16.71
FE203	4.57	4.02	4.42	4.88	6.58	7.57	6.97	8.66	7.58
MGO	3.38	2.67	2.94	3.72	5.74	5.70	6.50	9.67	6.71
CAO	1.29	1.13	3.50	4.53	5.89	4.53	5.45	4.25	5.26
NA20	4.17	4.07	3.73	3.52	3.54	3.45	3.33	2.80	3.42
K20	4.747	4.343	4.032	3.736	2.080	2.016	1.736	1.842	2.157
T102	0.869	0.882	0.807	0.915	1.291	1.377	1.022	1.247	1.306
MNO	0.079	0.053	0.080	0.085	0.069	0.040	0.040	0.038	0.071
P205	0.339	0.321	0.292	0.351	0.424	0.434	0.193	0.304	0.343
TOTAL	99.28	99.43	99.32	99.61	100.18	99.07	99.17	99.33	99.31
LOI	2.29	2.48	0.52	1.33	2.77	2.57	2.99	3.66	3.32
NI	69.5	34.3	52.6	92.8	188.0	171.9	190.2	286.0	198.3
CR	118.4	68.9	91.5	108.0	379.2	390.4	354.5	519.6	402.8
V	91.3	77.4	72.3	90.4	122.1	118.7	123.3	150.1	121.5
SC	13.0	11.8	10.0	12.4	21.6	25.3	26.4	28.1	23.1
CU	4.0	7.7	21.6	66.6	17.7	18.8	25.1	26.0	14.4
ZN	89.8	105.5	65.9	95.1	111.6	138.0	268.7	124.9	169.3
SR	511.5	384.7	463.3	645.9	522.9	498.9	473.1	642.2	532.9
RB	144.3	151.2	183.2	130.5	55.0	53.3	47.9	49.9	53.0
ZR	262.6	294.8	248.6	283.0	281.4	292.8	173.0	219.7	261.3
NB	12.9	13.9	15.5	13.9	18.3	20.0	8.0	13.0	14.4
BA	969.5	739.6	695.4	981.5	540.9	491.2	400.9	464.4	519.3
TH	15.7	23.3	24.6	16.2	5.8	2.9	4.1	5.8	6.8
LA	56.7	52.4	53.0	57.9	37.7	38.9	20.5	34.8	33.3
CE	111.7	112.4	112.4	117.9	80.5	79.6	45.0	57.3	65.6
ND	44.4	44.1	42.2	46.0	35.8	36.1	21.4	28.5	30.1
SM	4.6	6.6	7.2	7.2	4.3	5.8	4.5	6.0	5.5
Y	17.1	18.6	20.4	20.6	27.8	30.3	19.7	24.7	24.1
T102CR	0.932	0.924	0.778	0.929	1.242	1.279	0.977	1.093	1.246
T102W	0.919	0.915	0.788	0.939	1.286	1.340	1.024	1.165	1.307
	SA821	SA9248	SA1021	SA1121	SA12244	SA1326	SA1421	SA1526	SA1626
SI02	56.07	53.95	54.63	54.78	64.84	67.63	60.66	64.98	59.15
AL203	16.40	15.55	15.31	16.93	17.23	17.53	15.81	17.15	20.25
FE203	5.79	9.13	7.10	7.85	4.91	5.29	6.21	4.76	6.09
MGO	2.99	7.31	4.24	6.04	2.70	1.41	5.08	3.93	6.69
CAO	10.55	7.05	11.35	7.74	0.94	0.53	5.82	1.06	3.22
NA20	3.49	3.21	2.87	2.86	4.50	4.10	3.03	5.03	2.20
K20	2.095	1.615	2.217	2.210	3.399	2.243	1.667	1.685	0.764
T102	1.291	1.196	1.113	1.139	0.761	0.733	0.940	0.756	0.940
MNO	0.133	0.119	0.125	0.072	0.074	0.045	0.079	0.050	0.029
P205	0.423	0.361	0.288	0.240	0.179	0.162	0.198	0.166	0.207
TOTAL	99.23	99.49	99.25	99.85	99.52	99.68	99.49	99.57	99.54
LOI	6.83	6.82	9.51	9.50	3.00	2.80	3.58	2.99	8.03
NI	171.3	241.1	278.1	277.2	27.2	30.2	203.0	22.6	61.4
CR	379.2	378.5	459.9	552.7	39.5	75.5	439.6	39.8	69.1
V	118.9	114.7	146.2	182.1	84.5	93.9	123.0	71.1	121.5
SC	21.1	22.0	22.9	26.3	12.6	15.9	23.9	14.3	19.8
CU	23.1	135.5	24.9	15.2	7.4	14.2	21.5	14.7	6.6
ZN	80.6	92.4	64.5	105.5	89.9	37.7	63.1	64.1	157.0
SR	459.7	317.0	771.7	392.7	135.8	354.5	429.0	370.7	115.4
RB	53.6	20.7	52.4	42.0	66.8	44.6	44.6	44.2	21.9
ZR	284.2	234.7	204.4	186.5	187.5	177.8	161.9	194.9	184.7
NB	19.7	15.0	15.1	9.4	10.0	8.7	8.0	9.8	11.3
BA	463.7	345.7	519.0	416.2	826.3	117.6	425.2	514.4	95.3
TH	6.3	8.6	3.3	4.8	1.9	5.0	2.4	5.9	8.9
LA	37.4	27.2	28.3	28.6	30.2	21.6	23.0	21.7	17.1
CE	76.0	58.6	65.6	50.1	53.2	74.5	41.2	46.7	43.1
ND	37.8	26.8	31.8	26.2	34.4	21.5	20.4	21.2	21.6
SM	4.7	4.1	6.7	5.4	6.0	3.1	4.4	3.0	3.6
Y	28.9	29.8	21.9	23.3	44.7	16.1	19.8	21.7	18.2
T102CR	1.326	1.202	1.149	1.140	0.748	0.719	0.864	0.769	0.984
T102W	1.351	1.219	1.160	1.129	0.761	0.722	0.910	0.761	0.977

TABLE B17

	SA17251	SA18213	SA19248	SA2031	SA2126	NI1222	NI2244	NI3244	NI5216
SI02	60.62	63.52	58.68	53.75	71.76	62.99	69.60	67.61	66.64
AL203	16.53	17.71	16.69	16.83	13.53	15.80	15.78	15.88	15.48
FE203	5.98	5.27	6.71	7.59	3.96	5.81	2.92	3.69	3.81
MGO	2.86	2.58	6.34	7.36	1.00	0.77	0.57	0.85	3.36
CAO	7.31	3.49	1.07	7.33	2.65	0.76	2.38	2.80	2.53
NA20	3.35	4.36	5.04	3.24	4.93	1.00	3.62	3.77	3.63
K20	1.851	1.857	3.444	1.397	1.194	10.713	4.187	3.881	3.278
TIO2	0.860	0.786	0.894	1.159	0.417	0.741	0.451	0.526	0.555
MNO	0.110	0.056	0.087	0.094	0.083	0.023	0.008	0.020	0.058
P205	0.295	0.185	0.188	0.260	0.117	0.423	0.155	0.193	0.159
TOTAL	99.77	99.79	99.13	99.61	99.83	100.03	99.67	99.22	99.50
LOI	7.29	4.30	3.48	2.59	3.98	1.29	1.04	1.33	1.85
NI	83.0	32.2	174.3	259.1	34.3	58.9	21.9	26.0	44.8
CR	225.0	63.0	335.0	518.8	50.3	227.4	54.4	73.6	85.9
V	114.2	104.0	134.5	161.4	47.8	107.8	53.8	64.4	78.5
SC	18.3	17.3	21.0	26.7	7.7	13.7	6.5	9.8	10.8
CU	15.1	11.6	38.3	9.9	14.9	51.5	12.1	9.2	18.2
ZN	80.4	71.1	167.7	80.2	35.0	13.5	17.2	17.6	60.8
SR	675.9	281.9	354.7	719.7	148.5	608.8	616.6	824.8	307.2
RB	55.7	46.1	66.4	33.2	34.8	130.4	99.0	92.5	90.9
ZR	261.3	156.2	173.0	171.5	149.7	280.9	143.3	135.2	178.5
NB	12.5	10.6	8.9	9.3	10.0	11.9	7.8	8.2	11.5
BA	680.1	491.5	1244.0	588.0	182.9	1644.7	1324.0	1455.1	707.2
TH	12.0	8.2	1.9	0.9	8.9	14.7	10.1	8.6	14.2
LA	39.8	17.7	20.3	25.8	25.9	55.4	23.7	28.8	27.1
CE	87.7	36.8	55.8	55.8	51.0	128.5	50.9	53.6	58.5
ND	39.7	18.7	24.4	28.4	20.9	57.7	21.8	24.1	25.0
SM	6.8	2.9	3.8	4.9	3.0	10.2	2.8	3.0	0.4
Y	24.1	18.3	20.2	25.9	12.6	20.9	11.6	11.0	16.1
TIO2CR	0.897	0.783	0.319	1.128	0.441	0.744	0.453	0.509	0.569
TIO2W	0.900	0.779	0.327	1.134	0.440	0.766	0.463	0.522	0.581
NI6216	NI8216	NI1035	NI11313	NI12219	NI13220	AR1213	AR2201	AR3219	
SI02	66.54	67.96	65.89	59.36	57.18	64.96	67.95	53.33	63.95
AL203	15.44	15.84	16.65	16.50	15.82	15.64	15.30	16.34	15.24
FE203	3.78	3.31	4.74	6.01	3.83	4.27	3.31	7.07	4.04
MGO	2.75	1.76	2.58	4.24	2.07	1.87	1.05	7.99	1.42
CAO	3.48	2.29	1.25	6.27	3.43	4.82	1.86	6.25	5.83
NA20	3.91	4.78	5.25	3.08	3.41	3.44	4.83	2.96	5.48
K20	2.920	3.042	1.725	2.555	3.675	2.727	3.671	3.841	3.363
TIO2	0.540	0.548	0.837	1.015	0.530	0.631	0.554	1.371	0.510
MNO	0.060	0.063	0.051	0.099	0.037	0.069	0.033	0.069	0.055
P205	0.159	0.147	0.291	0.325	0.152	0.242	0.193	0.719	0.264
TOTAL	99.59	99.73	99.27	99.46	100.13	99.67	99.75	99.95	100.13
LOI	1.26	1.45	2.44	1.37	1.46	1.30	1.29	5.60	4.64
NI	47.6	14.3	5.0	58.5	53.8	19.4	20.8	238.6	43.8
CR	89.8	18.5	4.7	78.7	115.8	9.5	73.0	339.7	69.7
V	73.0	64.3	100.5	135.5	78.4	93.8	56.8	147.2	61.1
SC	11.7	8.1	9.5	17.4	12.1	11.4	9.7	21.8	10.1
CU	23.0	7.4	2.4	26.9	18.5	9.8	11.3	14.7	22.8
ZN	54.9	81.9	79.1	64.2	52.8	50.3	26.7	160.1	30.5
SR	344.8	363.9	726.0	620.8	366.5	453.2	735.3	1260.8	704.6
RB	89.9	96.2	48.2	59.4	83.5	58.2	74.9	113.7	56.5
ZR	177.6	171.8	241.1	188.6	159.4	177.4	175.1	258.9	208.2
NB	11.7	12.0	14.3	10.2	9.4	9.4	10.0	12.8	12.9
BA	721.8	1004.5	741.0	814.6	893.5	752.4	1481.5	1893.3	1516.4
TH	14.3	10.7	11.7	9.8	12.5	9.9	11.3	8.3	16.4
LA	29.7	26.7	50.2	31.0	31.7	29.0	40.3	46.9	45.5
CE	60.1	55.5	91.2	71.2	65.0	53.5	72.6	117.8	105.4
ND	22.5	24.0	37.7	29.8	24.9	26.2	31.1	54.5	44.8
SM	1.6	5.0	6.5	7.2	2.3	4.5	3.5	6.1	2.2
Y	16.0	16.1	20.1	17.6	13.1	13.2	14.3	18.0	15.3
TIO2CR	0.565	0.581	0.833	1.035	0.558	0.673	0.587	1.376	0.561
TIO2W	0.559	0.569	0.853	1.030	0.555	0.655	0.576	1.386	0.536

TABLE B17

	AR5319	AR6044	AR7019	AR8013	AR9013	AR10013	AR11022	NG1011	NG2012
SI02	66.96	66.79	67.25	63.19	67.71	58.77	69.28	53.87	59.18
AL203	15.55	16.38	16.42	15.44	15.80	15.76	14.29	16.31	16.35
FE203	4.43	3.75	3.50	4.30	3.50	5.58	4.39	8.73	7.68
MGO	2.05	2.22	1.36	3.21	1.63	1.42	1.03	5.70	2.68
CAO	1.56	1.12	1.49	1.96	2.05	1.74	2.55	7.38	4.41
NA20	4.46	6.13	5.14	5.16	4.68	2.30	3.78	3.51	4.28
K20	3.665	2.373	3.489	3.778	3.313	10.777	3.458	2.028	2.718
TIO2	0.654	0.565	0.548	0.555	0.542	0.795	0.758	1.689	1.604
MNO	0.053	0.058	0.033	0.066	0.041	0.056	0.084	0.102	0.101
P205	0.242	0.212	0.167	0.265	0.220	0.304	0.152	0.495	0.505
TOTAL	99.62	99.58	99.40	99.52	99.49	99.49	99.78	99.81	99.52
LOI	1.44	1.36	1.04	2.47	1.44	2.69	0.47	1.22	1.35
NI	42.7	42.5	24.7	50.7	29.7	27.6	6.3	90.1	29.3
CR	121.1	92.4	17.7	74.0	81.0	114.6	6.0	157.3	42.6
V	89.8	73.9	59.7	84.2	95.4	50.1	42.2	135.5	132.0
SC	12.7	9.7	8.6	12.4	9.8	11.1	11.7	20.5	20.0
CU	18.0	10.2	12.0	23.7	17.7	12.3	12.0	24.7	14.3
ZN	37.0	56.3	30.8	68.6	32.4	25.8	49.8	84.3	80.3
SR	832.0	749.6	914.3	782.6	798.1	159.5	153.9	625.0	499.1
RB	76.6	47.6	71.2	58.2	67.3	113.8	96.4	50.3	76.4
ZR	228.1	146.4	141.7	205.4	162.3	204.3	373.7	309.2	372.4
NB	12.2	8.1	8.8	10.2	9.7	11.2	19.0	20.6	24.6
BA	1713.4	1075.5	1889.0	2209.6	1914.9	3637.3	917.6	689.5	880.7
TH	20.1	10.2	4.8	9.7	7.5	1.7	14.3	12.1	16.5
LA	45.3	26.8	23.0	36.5	31.7	18.7	43.2	52.0	67.4
CE	99.5	59.6	48.4	82.5	65.4	46.1	88.3	116.7	132.2
ND	43.9	26.9	23.7	34.9	30.4	23.9	40.6	50.1	63.8
SM	5.8	5.3	5.0	6.0	5.4	9.1	9.2	10.2	10.8
Y	18.8	12.6	13.6	18.6	13.1	20.6	50.1	37.1	44.0
TIO2CR	0.673	0.588	0.575	0.557	0.527	0.861	0.725	1.404	1.422
TIO2W	0.667	0.588	0.569	0.567	0.537	0.882	0.734	1.547	1.534
	NG3022	SH1052	SH2052	SH3052	SH4011	SH5021	SH6021	SH7013	SH8013
SI02	64.94	69.27	65.46	66.79	52.51	67.27	66.78	59.62	59.78
AL203	15.78	14.43	14.33	13.91	14.97	16.27	16.59	14.92	14.97
FE203	4.59	5.23	7.06	7.03	13.21	4.03	3.98	9.77	8.63
MGO	0.83	0.32	1.24	1.21	3.97	0.35	0.21	3.12	2.74
CAO	4.79	0.23	1.25	0.66	7.74	0.24	0.22	3.46	4.08
NA20	2.71	4.89	4.43	3.16	3.47	4.59	4.26	3.96	3.33
K20	5.404	4.197	3.845	5.204	1.517	5.458	7.137	2.470	3.550
TIO2	0.732	0.535	1.133	1.097	1.855	0.447	0.461	1.601	1.558
MNO	0.083	0.063	0.163	0.175	0.284	0.020	0.029	0.318	0.353
P205	0.246	0.103	0.307	0.300	0.286	0.085	0.087	0.343	0.457
TOTAL	100.09	99.27	99.21	99.54	99.81	99.75	99.76	99.57	99.45
LOI	3.72	0.67	1.42	1.43	0.58	0.70	0.73	1.57	1.30
NI	16.1	3.7	4.4	5.6	11.8	5.8	4.9	4.5	18.1
CR	35.4	2.9	4.5	4.0	8.0	3.9	2.4	2.0	10.5
V	81.2	4.5	39.0	36.7	360.3	14.7	13.4	183.2	131.0
SC	11.3	11.9	15.3	15.5	38.5	10.3	12.6	28.9	23.2
CU	6.7	2.3	4.3	9.0	14.0	1.7	2.1	14.5	17.7
ZN	44.8	86.4	324.7	283.1	111.8	44.2	14.5	381.4	317.2
SR	310.2	162.7	256.3	224.1	434.5	164.5	169.7	322.3	476.9
RB	214.2	108.7	90.1	123.0	30.5	140.7	172.3	59.0	99.5
ZR	307.8	406.0	422.9	408.7	182.1	696.6	702.3	280.6	278.3
NB	18.9	23.0	24.2	23.3	13.3	20.5	20.2	15.2	17.7
BA	1117.8	1647.1	1767.0	2798.2	904.3	1044.9	1234.8	778.9	1410.6
TH	26.5	8.7	8.8	6.0	9.8	13.2	13.7	6.6	7.4
LA	64.9	51.6	59.8	42.0	29.0	18.1	46.3	34.4	47.0
CE	128.0	108.6	117.5	89.0	59.6	45.6	89.7	75.5	91.3
ND	48.0	48.5	53.4	47.1	27.8	19.7	40.3	34.6	42.8
SM	6.8	6.2	8.1	9.2	5.9	3.2	5.6	5.5	5.6
Y	22.1	46.0	48.2	49.7	31.4	30.3	35.3	35.9	38.6
TIO2CR	0.723	0.570	1.158	1.115	1.927	0.440	0.449	1.657	1.594
TIO2W	0.758	0.569	1.175	1.130	1.944	0.460	0.466	1.656	1.592

TABLE B17

	SH9213	SH1025	SH11219	SH12252	SH13252	SH14219	SH15211	SH16220	SH17221
SI02	59.22	60.87	78.02	69.20	70.00	61.91	55.54	54.26	74.42
AL203	14.98	15.14	11.43	14.15	14.37	15.83	16.58	16.93	13.51
FE203	8.83	8.01	2.10	5.56	4.83	5.15	8.96	8.55	2.18
MGO	3.00	2.28	0.18	0.20	0.23	0.52	4.29	4.06	0.14
CAO	4.42	2.32	0.05	0.32	0.25	3.66	3.35	8.40	0.22
NA20	3.49	5.95	0.12	4.63	3.37	3.28	5.32	2.77	1.10
K20	3.080	2.539	8.573	4.591	5.769	7.802	3.670	2.905	8.233
TIO2	1.549	1.526	0.091	0.775	0.535	0.942	1.381	1.423	0.177
MNO	0.203	0.216	*	0.083	0.148	0.081	0.066	0.143	0.038
P205	0.441	0.535	0.010	0.163	0.104	0.250	0.353	0.367	0.017
TOTAL	99.20	99.38	100.57	99.59	99.61	99.42	99.51	99.81	100.03
LOI	1.40	1.27	0.58	0.58	0.74	2.77	0.91	0.93	0.75
NI	13.7	3.4	5.0	4.8	5.2	7.4	18.8	41.3	4.6
CR	10.5	3.2	4.1	5.5	3.6	6.9	6.6	24.5	4.8
V	126.8	84.6	4.4	11.1	5.7	33.6	186.5	211.9	1.0
SC	22.8	20.8	*	12.7	13.0	14.1	20.0	23.6	0.3
CU	18.3	3.2	5.0	3.6	3.2	5.7	15.0	36.3	1.3
ZN	249.0	421.3	24.3	42.6	17.3	23.2	39.2	71.6	18.8
SR	431.2	403.0	24.0	174.1	115.9	278.3	363.8	667.3	75.9
RB	77.7	55.6	245.1	144.9	144.6	142.0	155.2	47.0	159.6
ZR	276.6	287.5	331.9	487.8	403.0	441.0	240.9	218.3	406.0
NB	17.5	17.6	25.9	25.2	22.1	26.3	17.0	17.3	37.7
BA	1035.5	1620.9	1457.7	1707.4	2557.4	2542.1	1310.0	1806.8	790.2
TH	6.7	3.1	18.2	12.0	4.2	4.8	5.3	4.2	17.6
LA	45.3	48.1	12.4	45.9	56.0	71.3	37.1	43.4	82.1
CE	94.3	98.8	37.6	124.6	137.5	142.1	74.5	90.1	171.3
ND	43.5	47.5	15.4	44.6	54.2	52.6	33.7	39.1	59.1
SM	8.1	7.4	3.3	7.7	7.2	10.7	7.6	8.3	10.7
Y	38.1	41.3	48.4	41.8	38.7	41.3	27.0	30.6	44.2
TIO2CR	1.539	1.521	0.103	0.789	0.555	0.896	1.344	1.411	0.182
TIO2W	1.564	1.531	0.114	0.789	0.571	0.914	1.335	1.443	0.195
	SH18220	SH19220	SH20219	SH22220	SH23212	SH24211	SH25211	SH27211	SH28219
SI02	52.69	53.04	67.50	51.91	50.01	51.41	49.86	58.11	72.27
AL203	17.02	16.91	15.33	16.45	18.92	17.35	16.29	15.59	13.33
FE203	12.75	11.69	5.05	10.93	8.07	11.18	10.38	8.32	4.30
MGO	3.91	5.77	0.42	4.12	7.61	3.84	8.52	4.65	0.23
CAO	4.74	4.99	0.54	5.44	10.28	5.66	9.60	5.00	0.06
NA20	3.73	3.55	4.93	3.30	2.81	3.14	2.93	3.90	2.99
K20	1.980	1.014	4.734	4.746	0.593	4.023	0.571	2.548	6.684
TIO2	1.947	1.748	0.534	1.784	0.811	1.900	1.038	0.929	0.314
MNO	0.254	0.213	0.078	0.166	0.113	0.155	0.251	0.333	0.037
P205	0.401	0.308	0.113	0.434	0.104	0.459	0.135	0.157	0.019
TOTAL	99.42	99.24	99.22	99.28	99.32	99.12	99.57	99.74	100.22
LOI	2.73	3.08	0.89	1.35	2.18	2.73	2.75	1.71	0.51
NI	49.7	66.9	3.4	19.2	143.1	22.2	195.3	73.4	6.0
CR	44.9	101.8	2.6	4.4	239.3	4.1	351.2	155.6	3.0
V	263.3	251.4	5.0	234.0	143.2	255.7	203.0	159.3	2.4
SC	27.2	36.5	15.1	22.3	25.7	27.6	31.6	28.9	0.5
CU	7.7	5.3	1.1	34.7	25.8	44.6	36.5	16.3	3.2
ZN	246.6	291.1	370.5	102.7	67.1	139.6	170.0	473.1	62.0
SR	633.6	462.0	281.9	721.0	468.2	576.9	308.4	318.2	33.9
RB	59.7	26.4	108.6	93.3	16.5	91.3	33.1	80.4	221.5
ZR	228.1	173.1	588.5	270.0	68.7	275.1	108.7	202.5	393.0
NB	17.2	12.3	21.4	18.6	5.0	19.5	8.8	18.2	34.6
BA	1198.1	792.2	3185.3	1690.2	331.3	2015.3	141.3	769.6	421.2
TH	0.5	2.8	4.3	5.2	0.4	3.5	*	11.4	13.2
LA	35.0	24.0	63.3	49.0	5.4	48.1	10.3	33.0	70.6
CE	67.5	48.4	129.1	97.3	15.2	100.1	12.1	61.4	165.7
ND	33.1	23.6	58.4	44.9	8.3	46.4	8.3	26.2	54.8
SM	7.4	4.7	9.2	8.1	2.6	9.8	3.6	2.3	10.0
Y	32.9	30.0	40.3	34.6	15.4	34.1	23.1	31.2	47.0
TIO2CR	1.787	1.590	0.570	1.549	0.783	1.771	1.029	0.992	0.337
TIO2W	1.861	1.648	0.581	1.693	0.804	1.810	1.047	0.994	0.342

TABLE B17

	SH29a4	SH30a10	SH31a11	SH32a11	SH33a19	SH34a19	SH35a19	SH36a11	SH37a11
SI02	56.50	56.85	54.02	57.25	76.20	74.90	66.57	51.28	51.73
AL203	15.73	15.65	18.82	15.70	12.91	12.76	15.89	17.45	15.69
FE203	8.19	8.32	10.41	7.78	1.76	2.63	4.39	9.42	10.37
MGO	5.20	5.09	2.88	5.36	0.11	3.08	0.84	5.80	6.75
CAO	7.52	7.20	2.50	8.17	0.10	0.05	1.05	8.97	7.48
NA20	3.21	3.09	6.44	2.97	3.64	1.75	6.12	3.53	4.26
K20	2.011	2.121	1.959	1.649	5.130	3.130	3.589	1.144	1.303
TI02	0.973	0.994	1.075	0.767	0.166	0.186	0.571	1.600	1.452
MNO	0.129	0.138	0.568	0.206	0.011	0.028	0.171	0.393	0.232
P205	0.155	0.161	0.167	0.090	0.018	0.015	0.152	0.292	0.270
TOTAL	99.62	99.62	98.83	99.94	100.04	100.59	99.33	99.89	99.53
LOI	0.49	0.33	2.12	1.59	0.65	0.43	1.41	1.42	4.67
NI	67.0	69.2	146.6	136.5	4.7	4.2	3.8	59.4	110.0
CR	151.9	152.5	228.4	341.3	3.4	3.2	3.5	61.8	211.2
V	123.5	137.5	172.1	161.8	1.3	0.2	8.4	245.6	211.5
SC	23.3	24.5	38.4	32.9	*	*	11.4	34.6	32.1
CU	12.4	11.5	30.9	14.4	7.5	9.9	1.3	67.4	13.2
ZN	84.3	96.3	1246.5	111.1	60.0	29.2	1235.3	577.5	402.1
SR	411.1	396.1	750.5	256.7	69.2	38.9	139.1	466.3	403.5
RB	72.8	63.5	95.3	49.0	159.2	222.8	76.7	23.1	48.8
ZR	170.4	186.3	123.0	99.2	344.0	851.2	515.8	167.7	156.2
NB	18.0	18.4	11.4	9.3	38.8	28.2	22.6	11.5	12.3
BA	747.5	759.6	1106.6	398.0	630.9	710.2	845.1	714.5	453.6
TH	9.9	10.1	3.5	5.3	22.8	17.4	14.3	0.7	1.4
LA	31.1	32.3	21.0	18.5	69.6	36.8	94.4	22.7	23.0
CE	57.5	65.5	40.4	34.4	116.7	80.5	179.1	52.5	47.5
ND	23.7	26.2	18.2	13.7	53.1	33.0	67.3	27.0	23.9
SM	5.8	4.1	*	3.3	9.7	3.5	7.2	3.9	3.3
Y	29.5	31.6	25.3	26.1	56.4	46.2	42.6	28.7	25.0
TI02CR	0.811	0.953	0.888	0.775	0.184	0.192	0.600	1.668	1.328
TI02W	0.868	0.977	0.943	0.799	0.193	0.207	0.596	1.681	1.368

	SH38a1	SH39a12	SH40a52	SH41a52	OR1a12	OR2a12	OR3a12	OR4a12	OR5a22
SI02	50.89	53.61	63.36	64.36	50.47	52.23	48.20	51.44	49.98
AL203	15.65	16.07	14.69	14.57	20.28	19.23	16.26	19.86	15.74
FE203	12.55	9.04	6.97	6.84	7.11	5.97	8.57	7.15	10.48
MGO	4.82	5.84	1.96	1.98	1.51	3.04	9.84	4.45	9.71
CAO	7.11	6.45	2.49	2.07	10.75	7.79	9.79	7.49	8.02
NA20	5.10	3.68	4.70	4.51	3.04	3.20	3.44	5.37	2.83
K20	1.123	2.599	3.576	3.925	4.089	1.545	1.492	1.556	1.179
TI02	1.495	1.226	1.240	1.203	1.421	1.167	1.255	1.241	1.232
MNO	0.315	0.603	0.234	0.172	0.076	0.132	0.127	0.133	0.091
P205	0.267	0.236	0.320	0.307	0.779	0.709	0.560	0.734	0.191
TOTAL	99.32	99.35	99.54	99.93	99.53	100.01	99.55	99.42	99.47
LOI	2.87	2.02	0.95	1.21	7.07	2.92	1.61	3.42	3.15
NI	60.8	43.1	9.3	9.2	46.4	53.5	196.8	32.3	264.3
CR	43.3	50.5	10.1	10.8	48.6	72.5	284.0	17.1	408.5
V	222.3	211.7	99.0	97.0	170.5	150.5	198.7	166.7	186.1
SC	32.3	35.0	19.3	17.4	23.4	23.4	29.3	19.8	31.1
CU	10.4	52.6	17.5	8.5	10.5	40.1	50.0	44.6	61.2
ZN	667.9	861.5	517.2	237.1	141.0	55.6	51.5	49.6	73.6
SR	479.8	527.2	541.9	485.7	1165.5	1316.7	1178.9	1266.0	330.7
RB	45.0	80.3	100.3	107.5	98.2	14.6	25.9	19.5	29.5
ZR	153.9	192.0	282.1	297.3	166.4	208.8	148.8	195.7	96.2
NB	12.4	11.8	16.6	16.2	57.8	32.5	43.3	42.2	15.3
BA	557.2	1139.0	1389.4	1569.0	2741.7	1952.7	1471.2	2395.9	523.6
TH	2.2	2.4	7.1	6.7	2.4	2.0	6.6	*	*
LA	20.5	24.9	40.5	39.1	61.9	51.0	66.6	56.1	14.8
CE	41.8	55.9	88.1	85.1	119.0	112.3	112.8	102.4	23.5
ND	21.0	26.2	40.8	39.7	48.7	49.9	42.2	45.1	10.4
SM	3.2	3.8	9.0	8.2	4.8	6.5	7.3	5.7	4.4
Y	26.7	29.7	34.6	32.7	24.6	23.0	25.6	24.0	22.5
TI02CR	1.411	1.268	1.177	1.171	1.572	1.248	1.359	1.280	1.148
TI02W	1.454	1.262	1.199	1.185	1.545	1.215	1.324	1.287	1.210

TABLE B17

	OR6822	OR7211	OR8211
SiO2	49.81	49.67	49.23
Al2O3	14.76	15.02	16.58
Fe2O3	11.41	11.32	9.24
MgO	6.00	7.73	6.76
CaO	5.80	10.12	10.63
Na2O	1.90	2.83	3.05
K2O	6.427	1.302	2.854
TiO2	2.445	1.348	1.268
MnO	0.082	0.147	0.077
P2O5	0.463	0.235	0.224
TOTAL	99.13	99.72	100.01
LOI	5.80	3.98	8.84
NI	38.3	93.3	104.0
CR	47.8	189.6	269.7
V	326.1	217.8	270.5
SC	34.9	33.6	45.4
CU	131.0	136.1	79.1
ZN	106.1	63.2	59.0
SR	384.8	351.6	349.6
RB	154.6	25.5	63.1
ZR	214.1	103.8	99.5
NB	52.7	17.3	16.7
BA	2967.2	824.9	577.6
TH	*	*	1.0
LA	35.7	16.8	19.0
CE	73.5	33.4	34.5
ND	34.6	16.3	16.4
SM	8.7	4.6	4.0
Y	42.2	26.8	24.2
TiO2CR	2.733	1.216	1.302
TiO2W	2.773	1.292	1.320

APPENDIX C : ELECTRON MICROPROBE TECHNIQUES

All mineral analyses were performed on the Cambridge Instruments electron probe microanalyzer of the Grant Institute of Geology. A wavelength dispersive system (WDS) was used for silicate and apatite analyses, and for the analysis of Zr and Nb in oxide minerals. Most oxide minerals were analyzed using a Link Systems energy dispersive system (EDS), however.

C1 : WAVELENGTH DISPERSIVE SYSTEM

All analyses were performed using a gun potential of 20 kV. A nominal probe current of 30 nA was used for the major elements, but to provide higher count rates for the minor elements a 60 nA current was used. The current was frequently monitored using a Faraday cage. Beam diameter was about 1 μ m. Analytical conditions, standards used and approximate precision are given in Table C1. A vacuum-deposited carbon film provided a conductive coating, and standards and samples were coated simultaneously. Samples were stored in a dessicator prior to analysis. In general, counting times were divided into a number of 10 or 20 s counts to allow detection of any changes in count rate due to volatilization, burning or pulse height depression. Volatilization was only observed for K, and this element was therefore analysed first for all minerals. Deep burning of the specimen was only encountered during the analysis of apatite on basal sections: this was readily overcome by restricting analysis to prism sections.

Dead time correction and conversion to apparent concentrations were carried out using the computer program APPCONC, written by D.J. Humphries. Apparent concentrations used were in general calculated relative to averages of standard counts measured before and after each set of analyses, but on rare occasions refer to only one set of standards, where significant drift in standard count rates occurred. Corrections for matrix absorption, atomic number and enhancement (ZAF) were made using the iterative computer program PROBE, written by D.J. Humphries, based on the program of Duncumb and Jones (1969).

C2 : ENERGY DISPERSIVE SYSTEM

An EDS method with a nominal 6 nA probe current was used for some of the oxide minerals. 100 s livetimes were used on a Si(Li) detector: precision is a little worse than for WDS analyses. Apparent concentrations were calculated relative to a cobalt metal standard, and full calibration is only necessary at infrequent intervals. These calculations and ZAF corrections were made on an on-line Data General computer, using a program written by Statham (1975).

TABLE C1 : Analytical conditions used in wavelength dispersive electron microprobe analysis.

Element & line	Crystal	Background offset $2\theta^0$	Peak time	Back- ground time	Typical conc ⁿ . $\pm 2\sigma$	Standard
Si K_{α}	RAP	+1.5	40	20	55 $\pm$ 0.3%	Wollastonite
Al K_{α}	RAP	+1.5	40	20	30 $\pm$ 0.15%	Synthetic Corundum
Fe K_{α}	LiF	$\pm$ 2.0	40	20	11 $\pm$ 0.16%	Metal
Mg K_{α}	RAP	+1.5	40	20	30 $\pm$ 0.2%	Synthetic Periclase
Ca K_{α}	PE	$\pm$ 2.0	40	20	13 $\pm$ 0.1%	Wollastonite
Na K_{α}	RAP	+1.5	{ pl 50 px 30	20	5 $\pm$ 0.1%	Jadeite
K K_{α}	PE	$\pm$ 1.75	{ pl 50 px 30	20	0.2 $\pm$ 0.015%	Orthoclase
Ti K_{α}	LiF	$\pm$ 2.0	40	20	0.3 $\pm$ 0.04%	Rutile or metal
Mn K_{α}	LiF	$\pm$ 2.0	20	20	0.2 $\pm$ 0.06	Metal
Cr K_{α}	LiF	$\pm$ 2.0	20	20	0.35 $\pm$ 0.06%	Metal
Ni K_{α}	LiF	$\pm$ 2.0	100	80	600 $\pm$ 180 ppm	Metal
Zr L_{α}	PE	$\pm$ 1.0	160	160	1420 $\pm$ 140 ppm	Metal
Nb L_{α}	PE	$\pm$ 1.0	320	320	150 $\pm$ 80 ppm	Metal
Sr L_{α}	PE	+1.0	100	80	1350 $\pm$ 160 ppm	Celestite
Ba L_{α}	Qz	$\pm$ 2.0	100	120	450 $\pm$ 200 ppm	Barytes
P K_{α}	PE	$\pm$ 2.0	80	80	42 $\pm$ 0.16%	Apatite
La L_{α}	Qz	+1.0	100	80	1120 $\pm$ 230 ppm	Synthetic Standards: Drake and Weill, (1972)
Ce L_{α}	Qz	$\pm$ 1.0	80	80	1130 $\pm$ 300 ppm	
Nd L_{α}	Qz	+1.0	80	80	470 $\pm$ 270 ppm	
Sm L_{α}	Qz	+0.75	100	80	300 $\pm$ 220 ppm	
Y L_{α}	PE	$\pm$ 2.0	100	80	410 $\pm$ 120 ppm	

Table C2 : Average core compositions of O.R.S. mineral phases.

Average analyses for each mineral type in a rock have been computed using the program MEANFILE (Appendix D), and tabulated using the program MINTAB, written by A.M. Graham.

Analysis numbers (first line) are referred to in the text of the thesis; the analysis name is the rock in which the mineral was analysed. N.B. two analyses are frequently given for the same rock in the same table; these may refer to phenocryst and xenocryst compositions, for example, or most commonly to coexisting ortho- and clinopyroxene.

The number in parentheses is the number of individual analyses incorporated in the average.

Tables are in the order olivine - pyroxene - plagioclase - amphibole - biotite - spinel - ilmenite - apatite. FeO refers to total iron as FeO ; Fe_2O_3 in spinels has been recalculated assuming R304.

The low totals for many analyses are mainly due to the non-analysis of minor elements, in particular H_2O , F and Cl, but also including elements such as Zn and V in oxide minerals, and Ba in biotites. The minor elements analysed for these minerals are quoted in Table C4.

AVERAGE CORE COMPOSITIONS OF O-R-S. OLIVINES

TABLE C2

	1	2	3	4
	MT45	OC72	OC152	OR3
	(5)	(4)	(5)	(3)
SiO2	40.37	36.28	39.42	39.39
TiO2	0.00	0.02	0.03	0.00
Al2O3	0.05	0.05	0.06	0.04
Cr2O3	0.05	0.00	0.05	0.01
FeO	14.45	34.70	17.38	16.17
MnO	0.21	0.66	0.30	0.31
MgO	45.72	29.03	42.79	44.66
NiO	0.26	0.07	0.22	0.20
CaO	0.16	0.13	0.16	0.23
TOTAL	101.28	100.93	100.41	101.00
MOLE PERCENT ENDMEMBERS				
FO	84.9	59.9	81.4	83.1
FA	15.1	40.1	18.6	16.9

AVERAGE CORE COMPOSITIONS OF O.R.S. PYROXENES

TABLE C2

	1	2	3	4	5	6	7	8
	L26	L73	L51	L113*	L113	L68*	L79	L50
	(3)	(3)	(5)	(2)	(3)	(2)	(4)	(4)
SI02	50.65	50.19	51.91	53.33	51.91	52.32	51.59	50.63
TIO2	0.70	0.77	0.46	0.29	0.56	0.61	0.77	0.71
AL2O3	3.73	4.72	2.40	0.64	2.94	1.32	2.65	4.10
CR2O3	0.00	0.71	0.32	0.01	0.02	0.02	0.06	0.68
FE0	6.40	5.60	5.94	6.29	6.24	6.53	7.93	5.09
MNO	0.16	0.15	0.16	0.21	0.13	0.22	0.23	0.10
MGO	15.12	15.83	17.04	15.58	15.89	15.92	15.14	16.32
CA0	21.76	20.63	19.57	21.47	20.06	20.91	20.80	20.40
NA2O	0.39	0.49	0.41	0.57	0.53	0.42	0.44	0.59
K2O	0.00	0.00	0.02	0.03	0.05	0.02	0.01	0.03
TOTAL	98.91	99.08	98.24	98.33	98.33	98.28	99.64	98.65
MOLE PERCENT ENDMEMBERS								
EN	44.0	46.8	49.5	45.1	47.0	46.0	43.8	48.2
FS	10.4	9.3	9.7	10.2	10.3	10.6	12.9	8.4
WO	45.5	43.9	40.8	44.7	42.7	43.4	43.3	43.3
	9	10	11	12	13	14	15	16
	L50*	L121	L128	L146	GC1	GC25	GC26 *	GC29
	(1)	(2)	(3)	(4)	(5)	(4)	(2)	(3)
SI02	53.36	51.26	51.17	50.54	50.99	51.43	53.31	51.96
TIO2	0.25	0.74	0.78	0.95	0.99	0.80	0.27	0.63
AL2O3	0.39	2.22	2.15	3.97	1.99	3.31	0.38	2.60
CR2O3	0.00	0.15	0.14	0.44	0.06	0.15	0.02	0.04
FE0	7.43	9.55	9.20	6.30	8.38	7.67	10.08	7.72
MNO	0.19	0.21	0.19	0.16	0.27	0.19	0.30	0.26
MGO	15.76	14.79	15.05	15.39	15.34	15.37	14.51	15.18
CA0	20.97	19.54	19.57	21.12	20.00	20.44	20.62	20.69
NA2O	0.40	0.53	0.51	0.42	0.49	0.39	0.37	0.44
K2O	0.03	0.03	0.00	0.01	0.00	0.00	0.00	0.01
TOTAL	98.79	99.03	98.78	99.30	98.51	99.83	99.87	99.53
MOLE PERCENT ENDMEMBERS								
EN	45.0	43.3	43.9	45.1	44.6	44.7	41.5	44.2
FS	11.9	15.7	15.1	10.4	13.7	12.5	16.2	12.6
WO	43.1	41.1	41.0	44.5	41.8	42.8	42.4	43.2
	17	18	19	20	21	22	23	24
	BN2	MT45	MT10	MT10	MT42	S44	S12	S13
	(4)	(7)	(3)	(1)	(8)	(5)	(5)	(4)
SI02	51.54	51.62	54.73	52.10	51.67	55.11	52.48	51.35
TIO2	0.46	0.75	0.29	0.74	0.80	0.25	0.67	1.05
AL2O3	2.49	3.05	1.65	2.39	2.96	1.52	2.13	1.83
CR2O3	0.06	0.41	0.35	0.69	0.40	0.42	0.26	0.06
FE0	9.63	5.67	11.36	6.30	5.86	10.32	7.72	9.67
MNO	0.26	0.12	0.23	0.13	0.10	0.21	0.22	0.26
MGO	13.90	16.17	29.18	16.67	16.17	30.60	17.48	15.07
CA0	20.43	21.51	1.97	20.10	21.43	1.75	18.44	19.43
NA2O	0.63	0.28	0.00	0.37	0.29	0.00	0.32	0.38
TOTAL	99.40	99.59	99.77	99.49	99.70	100.19	99.73	99.30
MOLE PERCENT ENDMEMBERS								
EN	40.9	46.5	78.9	48.1	46.4	81.3	49.9	43.6
FS	15.9	9.1	17.2	10.2	9.4	15.4	12.3	16.0
WO	43.2	44.4	3.8	41.7	44.2	3.3	37.8	40.4

* = Augite forming reaction rim to quartz ?phenocrysts

AVERAGE CORE COMPOSITIONS OF O.R.S. PYROXENES

TABLE C2

	25	26	27	28	29	30	31	32
	S52	S52	S28	S41	OC22	OC13	OC17	OC27
	(3)	(3)	(5)	(5)	(5)	(5)	(7)	(1)
SI02	52.69	51.59	51.77	51.63	50.90	50.32	50.51	49.72
TI02	0.47	0.52	0.75	0.73	0.80	0.82	0.91	1.01
AL203	1.81	1.91	2.42	1.35	3.14	2.47	2.53	4.00
CR203	0.01	0.03	0.24	0.00	0.00	0.00	0.04	0.00
FE0	19.52	9.70	7.57	11.78	7.25	11.80	11.39	8.04
MNO	0.43	0.29	0.20	0.39	0.24	0.39	0.32	0.21
MGO	23.39	16.04	16.98	13.71	15.78	13.98	15.07	14.85
CA0	1.99	18.48	18.45	19.44	20.17	18.70	17.38	20.35
NA20	0.00	0.38	0.37	0.36	0.47	0.52	0.54	0.45
K20	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
TOTAL	100.32	99.35	98.78	99.39	98.75	99.01	98.70	98.63

MOLE PERCENT ENDMEMBERS

EN	65.4	46.1	49.2	40.0	45.9	41.1	44.4	43.7
FS	30.6	15.7	12.3	19.3	11.8	19.4	18.8	13.3
WO	4.0	38.2	38.4	40.7	42.2	39.5	36.8	43.0

	33	34	35	36	37	38	39	40
	OC15	OC15	OC23	OC7	OC25	OC43	OC98	OC98
	(4)	(4)	(4)	(6)	(5)	(3)	(5)	(3)
SI02	50.72	54.40	50.73	50.87	51.74	50.39	54.07	51.28
TI02	0.75	0.23	0.79	0.68	0.47	0.83	0.36	0.72
AL203	3.71	2.09	2.91	2.10	1.94	3.64	1.29	2.36
CR203	0.47	0.17	0.11	0.19	0.00	0.03	0.15	0.27
FE0	6.55	11.71	9.43	12.93	9.09	9.11	13.82	9.35
MNO	0.16	0.22	0.26	0.42	0.42	0.36	0.32	0.27
MGO	16.12	29.30	14.67	13.23	14.79	14.30	27.59	15.94
CA0	20.04	1.56	19.58	18.14	20.29	19.86	1.97	18.33
NA20	0.39	0.05	0.50	0.55	0.44	0.53	0.00	0.55
K20	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01
TOTAL	98.94	99.73	99.00	99.13	99.19	99.04	99.59	99.07

MOLE PERCENT ENDMEMBERS

EN	47.1	79.2	43.1	39.5	42.9	42.5	75.1	46.4
FS	10.8	17.8	15.5	21.6	14.8	15.2	21.1	15.3
WO	42.1	3.0	41.4	38.9	42.3	42.4	3.8	38.3

	41	42	43	44	45	46	47	48
	OC67	OC67	OC72	OC123	OC123	OC86	OC54	OC84
	(3)	(4)	(4)	(4)	(5)	(2)	(7)	(3)
SI02	51.43	53.55	51.02	52.24	55.48	49.33	51.44	55.48
TI02	0.43	0.13	1.13	0.58	0.18	1.15	0.38	0.19
AL203	2.59	0.43	2.42	2.50	2.05	6.34	2.08	1.89
CR203	0.05	0.01	0.28	0.25	0.66	0.06	0.15	0.44
FE0	8.70	19.70	8.12	6.33	9.47	6.53	9.20	10.27
MNO	0.34	0.80	0.24	0.18	0.24	0.14	0.34	0.18
MGO	14.41	23.90	15.00	16.50	30.82	15.24	14.61	30.26
CA0	20.78	1.12	20.48	20.42	1.32	19.48	20.52	1.60
NA20	0.45	0.00	0.45	0.35	0.00	0.59	0.54	0.00
K20	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	99.20	99.65	99.16	99.42	100.23	98.87	99.27	100.32

MOLE PERCENT ENDMEMBERS

EN	42.1	66.8	43.8	47.5	83.1	46.3	42.3	81.4
FS	14.3	30.9	13.3	10.3	14.3	11.1	15.0	15.5
WO	43.6	2.3	42.9	42.2	2.6	42.6	42.7	3.1

AVERAGE CORE COMPOSITIONS OF O.R.S. PYROXENES

TABLE C2

	49	50	51	52	53	54	55	56
	OC84	OC93	OC93	OC103	OC103	OC109	OC108	OC152
	(5)	(5)	(4)	(3)	(5)	(4)	(2)	(5)
SiO ₂	51.04	51.56	53.65	55.90	52.01	53.51	51.91	50.51
TiO ₂	0.82	0.80	0.44	0.15	0.63	0.40	0.74	0.89
Al ₂ O ₃	3.69	2.18	1.30	1.67	3.63	2.81	2.76	3.86
Cr ₂ O ₃	0.44	0.16	0.09	0.37	0.59	0.05	0.02	0.47
FeO	7.81	8.57	17.32	8.87	6.24	14.99	8.72	5.93
MnO	0.18	0.20	0.38	0.19	0.18	0.30	0.27	0.15
MgO	15.72	15.98	25.11	30.90	17.15	27.06	15.05	15.67
CaO	19.25	19.43	1.83	1.89	18.94	1.43	20.42	21.55
Na ₂ O	0.49	0.35	0.00	0.00	0.47	0.00	0.42	0.30
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	99.44	99.25	100.12	99.95	99.85	100.54	100.30	99.33
MOLE PERCENT ENDMEMBERS								
EN	46.3	46.0	69.5	83.0	50.1	74.1	43.5	45.4
FS	12.9	13.8	26.9	13.4	10.2	23.0	14.1	9.7
WO	40.8	40.2	3.6	3.6	39.7	2.8	42.4	44.9
	57	58	59	60	61	62	63	64
	OC131	OC140 *	OC140	PE15	PE24	PE25	PE26	PE15
	(3)	(2)	(1)	(6)	(4)	(5)	(3)	(4)
SiO ₂	51.90	53.07	52.06	55.58	51.92	54.34	51.78	55.01
TiO ₂	0.80	0.39	0.93	0.19	0.50	0.31	0.86	0.23
Al ₂ O ₃	2.15	0.71	1.80	1.44	2.77	2.26	2.14	1.74
Cr ₂ O ₃	0.40	0.03	0.03	0.30	0.64	0.37	0.38	0.33
FeO	7.87	19.68	9.80	9.48	5.18	11.93	7.45	11.26
MnO	0.23	0.61	0.35	0.21	0.14	0.23	0.22	0.25
MgO	16.45	22.68	14.94	30.82	16.77	28.74	16.02	29.21
CaO	19.24	2.24	19.48	1.60	20.78	1.75	20.05	1.82
Na ₂ O	0.38	0.00	0.44	0.06	0.34	0.11	0.36	0.06
K ₂ O	0.01	0.00	0.02	0.00	0.00	0.02	0.01	0.00
TOTAL	99.44	99.41	99.87	99.67	99.05	100.07	99.28	99.91
MOLE PERCENT ENDMEMBERS								
EN	47.4	64.2	43.4	82.7	48.4	78.3	46.3	79.3
FS	12.7	31.3	16.0	14.3	8.4	18.2	12.1	17.1
WO	39.9	4.6	40.7	3.1	43.2	3.4	41.6	3.6
	65	66	67	68	69	70	71	72
	PE41	PE41	AY4	AY13	AY27	AY12	AY12	AY35
	(7)	(4)	(5)	(3)	(5)	(3)	(2)	(5)
SiO ₂	52.80	55.45	55.06	53.44	52.23	54.28	52.34	51.89
TiO ₂	0.41	0.23	0.25	0.28	0.62	0.27	0.49	0.35
Al ₂ O ₃	1.98	1.21	1.59	1.27	2.23	1.45	2.13	1.63
Cr ₂ O ₃	0.45	0.16	0.30	0.20	0.55	0.23	0.31	0.11
FeO	5.99	11.20	10.78	15.71	6.83	13.10	7.33	23.18
MnO	0.16	0.29	0.25	0.34	0.20	0.30	0.24	0.50
MgO	17.20	29.69	29.39	25.90	17.05	27.85	16.81	20.54
CaO	20.35	1.76	1.96	1.95	19.09	2.03	19.27	1.69
Na ₂ O	0.27	0.00	0.00	0.00	0.36	0.00	0.31	0.00
K ₂ O	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
TOTAL	99.52	100.00	99.58	99.11	99.19	99.54	99.22	99.89
MOLE PERCENT ENDMEMBERS								
EN	48.9	79.7	79.8	71.7	49.3	76.0	48.3	59.1
FS	9.3	16.9	16.4	24.4	11.1	20.0	11.8	37.4
WO	41.6	3.4	3.8	3.9	39.6	4.0	39.8	3.5

* = ?xenocrysts

AVERAGE CORE COMPOSITIONS OF O.R.S. PYROXENES

TABLE C2

	73	74	75	76	77	78	79	80
	AY35	AY38	C54	C54	C51	C51	C33	C33
	(3)	(6)	(6)	(4)	(4)	(6)	(7)	(5)
SiO ₂	51.53	51.41	52.87	51.21	53.23	51.63	52.82	51.00
TiO ₂	0.55	0.90	0.34	0.70	0.39	0.63	0.37	0.78
Al ₂ O ₃	1.53	2.02	1.18	1.85	1.29	2.24	1.25	2.07
Cr ₂ O ₃	0.01	0.04	0.06	0.07	0.03	0.08	0.06	0.15
FeO	12.21	11.74	20.24	10.44	17.84	8.93	20.12	11.34
MnO	0.35	0.33	0.50	0.29	0.43	0.24	0.49	0.30
MgO	13.69	14.88	23.00	14.20	24.94	15.04	22.99	14.20
CaO	19.06	17.73	1.49	19.68	1.58	19.99	1.61	18.73
Na ₂ O	0.37	0.38	0.07	0.47	0.06	0.47	0.03	0.46
TOTAL	99.31	99.44	99.76	98.91	99.79	99.24	99.74	99.04

MOLE PERCENT ENDMEMBERS

EN	40.0	43.5	64.9	41.5	69.1	43.7	64.9	41.7
FS	20.0	19.3	32.0	17.1	27.7	14.6	31.9	18.7
WO	40.0	37.2	3.0	41.3	3.1	41.7	3.3	39.6

	81	82	83	84	85	86	87	88
	C62	C62	C7	C7	C48	C58	OR3	SH23
	(3)	(2)	(5)	(5)	(4)	(5)	(4)	(5)
SiO ₂	53.94	53.52	51.02	53.15	52.20	52.17	49.43	51.78
TiO ₂	0.19	0.12	0.87	0.41	0.41	0.35	1.37	0.39
Al ₂ O ₃	0.52	0.56	2.27	1.25	1.33	1.56	5.71	3.68
Cr ₂ O ₃	0.02	0.01	0.07	0.02	0.02	0.01	0.18	0.77
FeO	19.75	7.95	10.10	17.88	8.88	8.24	6.46	6.05
MnO	0.62	0.35	0.31	0.44	0.32	0.52	0.18	0.17
MgO	24.02	13.99	14.80	24.75	14.58	14.72	14.06	17.18
CaO	1.08	22.90	19.31	1.77	20.97	20.99	21.95	19.11
Na ₂ O	0.03	0.53	0.45	0.06	0.43	0.51	0.63	0.32
K ₂ O	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.00
TOTAL	100.18	99.93	99.21	99.73	99.15	99.12	99.98	99.45

MOLE PERCENT ENDMEMBERS

EN	66.9	40.1	43.1	68.6	42.1	42.8	42.0	50.1
FS	30.9	12.8	16.5	27.8	14.4	13.4	10.8	9.9
WO	2.2	47.1	40.4	3.5	43.5	43.8	47.2	40.0

	89	90
	SH9	SH30
	(5)	(1)
SiO ₂	51.41	51.31
TiO ₂	0.75	0.24
Al ₂ O ₃	1.52	0.82
Cr ₂ O ₃	0.01	0.00
FeO	12.91	13.06
MnO	0.48	0.49
MgO	14.25	13.11
CaO	17.78	18.87
Na ₂ O	0.32	0.33
K ₂ O	0.01	0.00
TOTAL	99.44	98.23

MOLE PERCENT ENDMEMBERS

EN	41.6	38.5
FS	21.1	21.5
WO	37.3	39.9

AVERAGE CORE COMPOSITIONS OF O.R.S. PLAGIOCLASE

TABLE C2

	1	2	3	4	5	6	7	8
	L73	L68*	L95	L50	L50*	L121	L128	GC3
	(3)	(3)	(3)	(2)	(3)	(4)	(5)	(4)
SI02	51.35	63.01	55.76	56.31	60.40	55.83	56.59	54.01
TIO2	0.09	0.14	0.07	0.05	0.02	0.10	0.11	0.03
AL2O3	29.48	20.84	27.36	26.55	23.91	26.75	26.10	27.71
CR2O3	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.01
FeO	0.48	0.34	0.47	0.41	0.20	0.61	0.66	0.49
MNO	0.00	0.00	0.05	0.00	0.00	0.00	0.02	0.00
MGO	0.16	0.03	0.09	0.07	0.03	0.10	0.15	0.06
CAO	13.33	3.21	10.37	9.42	6.26	9.67	9.16	10.77
NA2O	3.86	6.25	5.32	5.79	7.00	5.64	5.92	4.76
K2O	0.21	4.69	0.47	0.56	1.26	0.55	0.63	0.72
TOTAL	98.95	98.51	99.98	99.13	99.10	99.22	99.35	98.56
MOLE PERCENT ENDMEMBERS								
AB	33.9	56.3	46.8	51.0	62.0	49.3	52.0	42.6
AN	64.9	16.0	50.4	45.8	30.7	47.5	44.4	53.2
OR	1.2	27.8	2.8	3.2	7.4	3.2	3.7	4.2
	9	10	11	12	13	14	15	16
	GC6	GC26	GC29	GC30	BN2	BN3	BN7	MT4
	(3)	(1)	(5)	(5)	(3)	(3)	(4)	(4)
SI02	60.31	54.57	53.93	56.62	53.78	55.14	56.45	52.28
TIO2	0.03	0.04	0.02	0.01	0.05	0.03	0.03	0.05
AL2O3	24.14	27.78	28.47	26.56	28.50	27.47	26.90	29.03
FeO	0.00	0.56	0.45	0.29	0.67	0.39	0.34	0.56
MGO	0.07	0.06	0.06	0.04	0.21	0.07	0.06	0.11
CAO	5.63	11.01	11.53	9.20	10.61	10.23	9.33	12.60
NA2O	7.81	4.93	4.71	5.98	4.71	5.59	6.00	4.17
K2O	0.69	0.44	0.30	0.44	0.44	0.29	0.33	0.28
TOTAL	98.69	99.38	99.47	99.14	98.97	99.19	99.44	99.09
MOLE PERCENT ENDMEMBERS								
AB	68.7	43.6	41.8	52.7	43.4	48.9	52.8	36.8
AN	27.3	53.8	56.5	44.8	54.0	49.5	45.3	61.5
OR	4.0	2.6	1.7	2.6	2.6	1.6	1.9	1.6
	17	18	19	20	21	22	23	24
	MT45	MT10	S44	S33	S8	S12	S13	S52
	(4)	(3)	(5)	(4)	(5)	(4)	(3)	(5)
SI02	50.67	53.52	54.41	52.02	52.93	54.14	56.28	54.22
TIO2	0.07	0.07	0.06	0.06	0.15	0.09	0.14	0.10
AL2O3	29.92	28.44	27.86	29.80	28.54	28.40	26.65	28.16
FeO	0.69	0.51	0.55	0.33	0.68	0.55	0.48	0.70
MGO	0.15	0.19	0.12	0.17	0.19	0.18	0.09	0.19
CAO	14.09	11.97	11.30	13.36	11.84	11.61	9.64	11.13
NA2O	3.36	4.59	5.01	3.64	4.45	4.73	5.64	4.85
K2O	0.20	0.30	0.34	0.16	0.32	0.66	1.35	0.76
TOTAL	99.15	99.59	99.66	99.74	99.09	100.35	100.27	100.11
MOLE PERCENT ENDMEMBERS								
AB	29.8	40.4	43.7	33.9	39.7	40.9	47.6	42.2
AN	69.0	57.8	54.4	55.2	58.4	55.4	44.9	53.5
OR	1.2	1.8	1.9	1.0	1.9	3.7	7.5	4.3

* = xenocryst

AVERAGE CORE COMPOSITIONS OF O.R.S. PLAGIOCLASE

TABLE C2

	25	26	27	28	29	30	31	32
	S28	S41	S50	OC22	OC13	OC17	OC27	OC15
	(3)	(1)	(5)	(2)	(4)	(5)	(3)	(2)
SiO ₂	53.30	69.03	52.08	53.51	57.67	55.51	55.13	52.47
TiO ₂	0.05	0.00	0.05	0.05	0.08	0.10	0.09	0.07
Al ₂ O ₃	27.70	19.28	28.66	27.82	25.37	26.50	26.91	28.34
FeO	0.56	0.01	0.49	0.71	0.53	0.62	0.65	0.73
MgO	0.16	0.00	0.10	0.07	0.06	0.09	0.08	0.25
CaO	11.82	0.36	12.57	11.30	8.17	9.83	9.88	12.15
Na ₂ O	4.65	11.41	4.17	4.57	6.24	5.50	5.43	4.40
K ₂ O	0.31	0.04	0.23	0.41	0.93	0.64	0.61	0.29
TOTAL	98.55	100.13	98.45	98.46	99.06	98.78	98.78	98.71

MOLE PERCENT ENDMEMBERS

AB	40.9	98.1	36.8	41.2	54.9	48.4	48.1	39.0
AN	57.3	1.7	61.8	56.4	39.7	47.8	48.4	59.4
OR	1.8	0.2	1.3	2.4	5.4	3.7	3.5	1.7

	33	34	35	36	37	38	39	40
	OC15*	OC23	OC7	OC25	OC2	OC43	OC88A	OC88B
	(1)	(2)	(4)	(3)	(4)	(4)	(3)	(7)
SiO ₂	56.12	53.77	56.75	58.16	55.83	55.11	55.47	53.15
TiO ₂	0.08	0.06	0.11	0.06	0.11	0.05	0.03	0.03
Al ₂ O ₃	26.49	28.15	26.37	25.47	26.33	27.19	27.49	29.12
FeO	0.91	0.46	0.40	0.38	0.51	0.46	0.37	0.43
MgO	0.08	0.08	0.05	0.05	0.09	0.05	0.03	0.16
CaO	9.38	11.23	9.29	8.22	9.75	10.09	10.17	12.92
Na ₂ O	5.90	4.92	5.81	6.51	5.58	5.48	5.63	3.73
K ₂ O	0.70	0.24	0.76	0.55	0.65	0.32	0.28	0.23
TOTAL	99.66	98.91	99.54	99.40	98.85	98.76	99.48	99.76

MOLE PERCENT ENDMEMBERS

AB	51.1	43.6	50.8	57.0	49.0	48.6	49.2	33.8
AN	44.9	55.0	44.8	39.8	47.3	49.5	49.2	64.8
OR	4.0	1.4	4.4	3.2	3.8	1.9	1.6	1.4

	41	42	43	44	45	46	47	48
	OC98	OC67	OC72	OC123	OC86	OC54	OC84	OC93
	(4)	(7)	(6)	(1)	(6)	(6)	(5)	(5)
SiO ₂	56.30	52.14	55.86	53.11	53.41	55.39	53.81	54.71
TiO ₂	0.10	0.03	0.09	0.07	0.04	0.02	0.08	0.08
Al ₂ O ₃	25.76	29.34	26.66	27.92	27.98	27.94	28.78	27.73
FeO	0.94	0.53	0.33	0.85	0.38	0.39	0.47	0.66
MgO	0.12	0.08	0.04	0.15	0.08	0.04	0.09	0.09
CaO	9.11	12.49	9.79	12.05	11.64	10.45	11.64	10.63
Na ₂ O	5.90	4.26	5.86	4.45	4.71	5.38	4.69	5.17
K ₂ O	0.53	0.20	0.35	0.30	0.26	0.32	0.34	0.52
TOTAL	98.89	99.08	98.99	98.91	98.49	99.93	99.91	99.60

MOLE PERCENT ENDMEMBERS

AB	52.0	37.7	51.0	39.3	41.7	47.3	41.4	45.4
AN	44.3	61.1	47.0	58.9	56.8	50.8	56.7	51.6
OR	3.7	1.2	2.0	1.8	1.5	1.8	2.0	3.0

* = Groundmass composition

AVERAGE CORE COMPOSITIONS OF J.R.S. PLAGIOCLASE

TABLE C2

	49	50	51	52	53	54	55	56
	OC103	OC108	OC128	OC152	OC131	OC140	PE16	PE26
	(4)	(4)	(5)	(5)	(3)	(6)	(4)	(4)
SiO ₂	53.90	52.72	64.54	50.30	54.38	51.81	53.74	53.35
TiO ₂	0.08	0.06	0.01	0.05	0.07	0.06	0.06	0.07
Al ₂ O ₃	28.43	29.53	21.80	30.03	27.40	29.52	27.89	28.73
FeO	0.59	0.49	0.15	0.82	0.65	0.52	0.41	0.44
MgO	0.16	0.07	0.00	0.09	0.16	0.07	0.17	0.11
CaO	11.70	12.56	3.05	13.99	11.03	12.98	11.55	11.86
Na ₂ O	4.60	4.17	9.06	3.45	5.04	4.04	4.72	4.63
K ₂ O	0.38	0.22	0.98	0.25	0.43	0.25	0.35	0.32
TOTAL	99.83	99.84	99.60	99.01	99.17	99.27	98.90	99.53
MOLE PERCENT ENDMEMBERS								
AB	40.6	37.1	79.5	30.5	44.1	35.5	41.6	40.6
AN	57.2	61.6	14.8	68.0	53.4	63.0	56.3	57.5
OR	2.2	1.3	5.7	1.5	2.5	1.5	2.0	1.9
	57	58	59	60	61	62	63	64
	PE12	PE15	PE19	PE3A	PE8	PE41	AY4	AY13
	(2)	(5)	(3)	(4)	(6)	(6)	(2)	(5)
SiO ₂	56.81	52.94	60.39	54.68	52.14	53.23	53.42	55.03
TiO ₂	0.02	0.03	0.00	0.05	0.07	0.05	0.07	0.11
Al ₂ O ₃	26.50	28.53	23.84	27.75	29.46	28.58	28.25	26.99
FeO	0.27	0.48	0.17	0.43	0.42	0.58	0.61	0.53
MgO	0.03	0.15	0.01	0.05	0.18	0.17	0.30	0.11
CaO	9.06	12.00	5.79	10.48	12.96	12.10	12.08	10.65
Na ₂ O	6.06	4.44	7.84	5.29	4.02	4.49	4.57	5.42
K ₂ O	0.42	0.29	0.61	0.32	0.20	0.29	0.29	0.41
TOTAL	99.19	98.97	98.65	99.05	99.46	99.50	99.60	99.24
MOLE PERCENT ENDMEMBERS								
AB	53.4	39.4	68.5	46.8	35.5	39.5	40.0	46.8
AN	44.1	58.9	27.9	51.3	63.3	58.8	58.4	50.9
OR	2.4	1.7	3.5	1.8	1.2	1.7	1.7	2.3
	65	66	67	68	69	70	71	72
	AY27	AY12	AY35	AY38	C54	C51	C33	C62
	(6)	(5)	(4)	(3)	(4)	(6)	(8)	(5)
SiO ₂	54.87	54.17	56.01	50.46	56.07	55.85	55.27	57.01
TiO ₂	0.09	0.07	0.07	0.05	0.06	0.04	0.06	0.05
Al ₂ O ₃	27.34	28.29	27.13	30.77	25.92	26.90	26.99	26.43
FeO	0.49	0.50	0.40	0.42	0.54	0.44	0.54	0.27
MgO	0.12	0.14	0.08	0.14	0.09	0.03	0.07	0.02
CaO	10.80	11.05	9.96	14.15	9.49	9.38	10.11	8.83
Na ₂ O	5.24	4.90	5.46	3.19	5.52	5.99	5.50	7.18
K ₂ O	0.42	0.42	0.56	0.21	0.80	0.23	0.61	0.25
TOTAL	99.36	99.55	99.67	99.39	98.50	98.85	99.15	100.04
MOLE PERCENT ENDMEMBERS								
AB	45.6	43.4	48.2	28.6	48.9	52.9	47.9	58.7
AN	52.0	54.1	48.6	70.1	46.5	45.8	48.6	39.9
OR	2.4	2.4	3.3	1.3	4.7	1.3	3.5	1.4

AVERAGE CORE COMPOSITIONS OF O.R.S. PLAGIOCLASE

TABLE C2

	73	74	75	76	77	78	79	80
	C52	C7	C48	C58	OR3	SH23	SH9	SH30
	(4)	(5)	(4)	(4)	(2)	(4)	(4)	(6)
SI02	58.47	56.05	59.05	57.27	47.43	51.01	56.69	51.88
TIO2	0.03	0.09	0.07	0.05	0.03	0.02	0.08	0.07
AL2O3	25.56	26.63	25.14	25.91	32.59	30.27	26.01	29.39
FE0	0.30	0.55	0.42	0.37	0.42	0.35	0.65	0.61
MGO	0.03	0.08	0.06	0.05	0.06	0.21	0.10	0.10
CA0	7.95	9.54	9.35	8.24	16.55	14.04	9.25	12.85
NA20	7.64	5.60	5.14	6.16	2.09	3.44	5.91	3.93
K20	0.47	0.77	0.27	0.79	0.15	0.09	0.52	0.30
TOTAL	100.45	99.32	99.52	98.84	99.31	99.44	99.20	99.13
MOLE PERCENT ENDMEMBERS								
AB	61.9	49.2	49.0	54.9	18.4	30.6	52.0	35.0
AN	35.6	46.3	49.3	40.5	80.7	68.9	45.0	63.3
OR	2.5	4.4	1.7	4.6	0.9	0.5	3.0	1.7

AVERAGE CORE COMPOSITIONS OF O.R.S. AMPHIBOLES

	1	2	3	4	5	6	7	8
	GC3	GC29	GC30	BN2	BN3	BN3*	BN7	BN7*
	(3)	(3)	(4)	(1)	(3)	(1)	(3)	(1)
SI02	41.76	42.44	46.65	41.82	43.58	53.25	43.28	52.27
TIO2	2.39	3.60	1.97	2.00	2.85	0.18	2.64	0.27
AL2O3	10.97	11.27	7.31	12.36	10.06	2.93	10.71	3.66
CR2O3	0.04	0.01	0.02	0.02	0.03	0.05	0.03	0.07
FE0	11.65	11.14	11.99	13.90	11.21	10.08	11.16	12.60
MNO	0.12	0.11	0.31	0.17	0.13	0.83	0.14	0.67
MGO	14.16	14.23	14.87	12.62	14.60	16.60	14.73	14.73
NIO	0.00	0.03	0.03	0.00	0.00	0.00	0.00	0.00
CA0	11.19	11.25	11.18	10.93	11.40	12.55	11.17	12.03
NA20	2.48	2.47	1.75	2.45	2.19	0.40	2.42	0.50
K20	0.71	0.89	0.67	0.63	0.59	0.07	0.68	0.28
TOTAL	95.48	97.46	96.74	96.91	96.66	96.94	96.97	97.09
	9	10	11	12	13			
	S41	OC23	OC25	OC67	C62			
	(2)	(3)	(2)	(5)	(1)			
SI02	49.05	40.45	41.24	42.26	53.99			
TIO2	1.08	3.17	3.31	2.72	0.25			
AL2O3	2.59	13.38	12.15	11.53	1.88			
CR2O3	0.00	0.05	0.01	0.05	0.00			
FE0	20.11	11.84	11.25	11.50	7.37			
MNO	0.55	0.17	0.18	0.16	0.33			
MGO	10.35	13.40	14.25	14.09	19.48			
CA0	8.14	10.92	11.03	11.15	11.63			
NA20	4.02	2.68	2.93	2.18	0.28			
K20	0.97	0.50	0.59	0.85	0.04			
TOTAL	96.88	96.56	96.85	96.51	95.26			

* = Actinolitic amphibole pseudomorphing clinopyroxene

AVERAGE CORE COMPOSITIONS OF O.R.S. BIOTITES

TABLE C2

	1	2	3	4	5	6	7	8
	L113	L139	BN3	OC72	OC128	PE28	PE4	PE12
	(3)	(3)	(2)	(3)	(3)	(1)	(2)	(2)
SiO2	39.17	36.33	36.42	37.27	36.04	32.84	35.22	38.07
TiO2	6.37	4.59	4.17	5.63	4.10	2.69	4.11	4.73
Al2O3	12.00	14.29	13.54	12.80	14.57	16.04	15.71	13.60
Cr2O3	0.01	0.00	0.01	0.00	0.00	0.03	0.02	0.01
FeO	6.67	13.11	16.53	16.10	18.97	27.34	20.71	11.62
MnO	0.06	0.09	0.36	0.07	0.67	0.33	0.35	0.26
MgO	20.41	16.11	12.99	13.91	12.29	5.27	9.08	16.68
CaO	0.03	0.05	0.60	0.00	0.00	0.12	0.01	0.03
Na2O	0.76	0.79	0.08	0.27	0.65	0.75	0.56	0.52
K2O	8.92	8.28	8.87	9.27	8.63	7.57	8.37	9.09
TOTAL	94.40	93.66	93.57	95.34	95.93	93.04	94.13	94.61
	9	10	11	12	13	14		
	PE19	C62	C52	C48	C58	C65		
	(2)	(3)	(1)	(1)	(3)	(3)		
SiO2	37.01	38.81	37.87	37.34	37.04	37.78		
TiO2	4.29	4.84	5.29	6.23	6.35	4.84		
Al2O3	14.83	12.04	12.70	12.93	13.46	14.28		
Cr2O3	0.00	0.02	0.04	0.04	0.02	0.05		
FeO	11.09	11.66	10.76	14.11	11.42	12.23		
MnO	0.24	0.09	0.10	0.18	0.07	0.09		
MgO	17.23	17.24	17.59	15.04	16.42	15.83		
CaO	0.01	0.00	0.00	0.00	0.01	0.02		
Na2O	0.93	0.13	0.32	0.24	0.82	0.59		
K2O	8.63	9.43	9.40	9.02	6.76	8.75		
TOTAL	94.27	94.26	94.08	95.13	94.37	94.52		

AVERAGE CORE COMPOSITIONS OF O.R.S. SPINELS

TABLE C2

	1	2	3	4	5	6	7	8
	L51	L68	L68	L79	L95	L121	L128	L146
	(3)	(2)	(1)	(1)	(1)	(2)	(3)	(2)
SiO2	0.45	0.53	0.50	0.13	0.59	1.62	0.93	0.13
TiO2	15.73	7.54	5.50	12.66	12.05	10.20	13.55	7.03
Al2O3	1.01	0.90	1.37	2.38	2.10	0.70	1.33	1.52
Cr2O3	0.49	0.94	0.00	0.64	0.25	1.61	1.39	0.75
Fe2O3	32.77	48.34	52.63	37.94	39.14	39.84	34.18	51.25
FeO	43.55	36.06	35.73	40.44	41.84	37.83	39.07	35.13
MnO	0.49	0.20	0.00	0.28	0.09	2.08	3.93	0.19
MgO	0.15	0.34	0.00	0.30	0.08	0.09	0.07	1.03
CaO	0.20	0.27	0.00	0.05	0.05	0.23	0.18	0.10
Na2O	0.04	0.04	0.00	0.06	0.00	0.13	0.00	0.00
K2O	0.07	0.06	0.00	0.05	0.03	0.07	0.04	0.04
TOTAL	94.95	95.22	95.72	94.34	96.22	94.33	94.67	97.18
	9	10	11	12	13	14	15	16
	GC29	GC30	BN3	BN7	S13	OC22	OC27	OC15
	(4)	(2)	(2)	(1)	(2)	(2)	(1)	(1)
SiO2	0.00	0.00	0.62	0.43	0.41	0.05	0.33	0.14
TiO2	9.79	4.19	0.37	5.01	18.01	3.31	13.77	7.96
Al2O3	2.09	1.51	0.21	0.16	2.39	1.05	2.92	0.87
Cr2O3	0.56	0.38	0.42	0.23	1.30	0.13	0.01	1.00
Fe2O3	45.39	57.87	66.31	56.59	27.62	59.89	35.81	49.63
FeO	39.44	34.41	30.48	35.40	44.61	32.38	40.07	36.26
MnO	0.05	0.40	1.56	0.10	2.53	0.11	3.47	0.31
MgO	0.13	0.00	0.09	0.05	0.00	0.71	0.07	0.80
ZnO	0.00	0.00	0.00	0.00	0.96	0.00	0.00	0.00
CaO	0.03	0.00	0.09	0.10	0.00	0.04	0.00	0.05
TOTAL	97.48	98.78	100.14	98.07	97.83	97.69	96.45	97.02
	17	18	19	20	21	22	23	24
	OC23	OC7	OC43	OC88A	OC98	OC67	OC72	OC54
	(2)	(1)	(5)	(2)	(4)	(3)	(3)	(3)
SiO2	0.95	0.35	0.00	0.00	0.00	0.00	0.00	0.39
TiO2	14.97	20.07	14.44	9.73	15.20	9.70	9.22	12.34
Al2O3	1.81	2.23	0.98	1.63	2.00	2.29	1.56	1.33
Cr2O3	0.36	0.06	0.05	0.00	1.40	0.00	0.25	0.22
Fe2O3	32.62	22.82	37.57	45.81	32.60	45.85	47.79	40.94
FeO	42.97	43.54	36.77	37.15	41.16	36.93	38.04	39.08
MnO	1.62	4.94	5.22	0.39	2.50	0.61	0.15	1.43
MgO	0.08	0.04	0.07	0.96	0.08	0.85	0.56	0.48
ZnO	0.00	0.00	0.06	0.00	0.06	0.20	0.00	1.20
CaO	0.26	0.07	1.08	0.00	0.14	0.34	0.08	0.04
TOTAL	95.52	94.24	96.34	95.63	95.15	96.77	97.67	97.45

AVERAGE CORE COMPOSITIONS OF O.R.S. SPINELS

	25	26	27	28	29
	OC128	OC152	PE3A	C7	C48
	(5)	(6)	(5)	(1)	(1)
SiO2	0.46	0.31	1.60	0.00	0.00
TiO2	2.30	8.56	10.44	14.13	0.93
Al2O3	2.70	2.90	1.29	1.31	0.00
Cr2O3	0.00	5.41	0.03	0.51	0.79
Fe2O3	57.87	43.26	41.37	35.47	64.50
FeO	30.62	34.57	41.14	42.25	31.06
MnO	1.84	9.45	0.10	0.00	0.00
MgO	0.36	2.92	0.00	0.00	0.00
ZnO	0.05	0.35	0.75	0.30	0.00
CaO	0.00	0.37	0.13	0.00	0.30
TOTAL	96.21	98.60	96.85	93.96	97.28

AVERAGE CORE COMPOSITIONS OF D.R.S. ILMENITES

TABLE C2

	1	2	3	4	5	6	7	8
	L51	L113	L79	L145	S13	OC22	OC72	OC54
	(1)	(2)	(1)	(1)	(1)	(1)	(3)	(1)
SiO2	0.21	0.21	0.02	0.10	0.31	0.00	0.00	0.38
TiO2	49.75	37.37	47.09	45.47	48.42	39.55	49.30	43.51
Al2O3	0.35	0.50	0.45	0.12	0.00	0.11	0.07	0.28
CR2O3	0.13	0.00	0.00	0.11	0.16	0.05	0.00	0.00
FeO	43.63	50.12	48.18	45.05	48.01	53.83	47.68	49.12
MnO	0.34	0.47	0.34	0.55	0.58	0.57	0.81	0.70
MgO	0.72	4.09	0.47	3.78	2.11	2.65	1.29	0.68
CaO	0.34	0.35	0.09	0.09	0.00	0.04	0.16	0.13
Na2O	0.06	0.06	0.00	0.00	0.00	0.00	0.00	0.00
K2O	0.06	0.06	0.03	0.04	0.00	0.00	0.00	0.00
TOTAL	95.50	93.84	96.59	95.31	99.59	96.81	99.31	94.80
	9	10	11	12	13	14	15	16
	OC128	OC152	C54	C51	C52	C52	C7	C48
	(1)	(1)	(2)	(1)	(1)	(1)	(3)	(3)
SiO2	0.34	0.00	0.81	0.00	0.00	0.04	0.00	0.00
TiO2	34.02	46.92	46.29	45.22	45.98	48.06	48.39	45.38
Al2O3	1.28	0.00	0.23	0.08	0.04	0.05	0.13	0.00
CR2O3	0.00	0.42	0.29	0.21	0.05	0.05	0.11	0.12
FeO	55.42	43.80	46.85	50.91	50.23	44.99	47.48	49.34
MnO	2.30	0.52	0.45	2.18	2.06	4.77	0.66	2.98
MgO	0.00	5.48	3.17	0.19	0.15	0.15	1.12	0.15
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.17	0.10
CaO	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.16
TOTAL	93.36	97.14	98.17	98.79	98.51	98.10	98.06	98.23
	17							
	C65							
	(1)							
TiO2	38.87							
Al2O3	0.48							
CR2O3	0.29							
FeO	53.95							
MnO	0.33							
MgO	0.60							
ZnO	0.31							
TOTAL	94.83							

AVERAGE CORE COMPOSITIONS OF O.R.S. APATITE

TABLE C2

	L113	L139	GC3	BN3	OC88A	C7	C51
	(2)	(4)	(3)	(2)	(3)	(2)	(2)
CaO	53.61	54.41	54.68	54.86	54.63	54.43	54.69
P ₂ O ₅	40.81	41.91	41.10	41.44	41.66	41.59	41.10
Total*	94.42	96.32	95.78	96.30	96.29	96.02	95.79
La	780	1090	877	1090	813	1650	1720
Ce	1570	1925	1737	1855	1283	3290	3825
Nd	950	1115	1107	1045	873	1635	1960
Sm	340	360	377	365	303	355	420
Y	185	173	390	275	390	635	560
Sr	1710	2258	1673	1740	940	675	300

* = Total does not include trace elements, or Si, Fe, F, Cl etc. (undetermined)

O.R.S. GARNET COMPOSITIONS

	1	2	3	4	5	6	7
	1PE28	1PE28	2PE28	2PE28	3PE28	4PE28	4PE28
	(R)	(C)	(C)	(R)		(C)	(R)
SiO ₂	36.31	36.61	36.96	36.45	37.09	36.95	36.60
TiO ₂	0.10	0.04	0.19	0.16	0.25	0.26	0.03
Al ₂ O ₃	20.39	20.35	20.18	20.52	20.16	20.28	20.41
FeO	35.16	34.72	35.17	35.64	35.07	35.06	35.99
MnO	5.87	6.67	3.20	4.43	2.86	2.89	5.61
MgO	1.33	1.26	1.29	2.18	1.42	1.46	1.13
CaO	0.49	0.41	3.42	0.30	3.79	3.75	0.41
K ₂ O	0.01	0.01	0.01	0.01	0.01	0.01	0.01
TOTAL	99.66	100.06	100.42	99.69	100.65	100.66	100.18
PYR	6.2	6.0	5.5	9.7	6.0	6.1	5.2
ALM	92.1	92.6	84.0	89.3	82.6	82.6	93.4
GRD	1.6	1.4	10.5	1.0	11.4	11.3	1.4

CORE-RIM PAIRS OF STRAITON PYROXENES

	1	2	3	4	5	6	7	8
	2AY35	2AY35	5AY35	5AY35	3AY35	3AY35	5AY38	5AY38
	(C)	(R)	(C)	(R)	(C)	(R)	(C)	(R)
SiO ₂	51.87	53.66	52.06	52.31	51.43	52.03	51.56	51.88
TiO ₂	0.27	0.54	0.26	0.31	0.53	0.77	0.83	0.95
Al ₂ O ₃	1.25	0.98	1.02	0.89	1.68	1.62	1.79	2.04
Cr ₂ O ₃	0.04	0.08	0.07	0.02	0.03	0.14	0.02	0.13
FeO	23.31	16.06	24.02	23.44	12.07	9.29	12.91	10.00
MnO	0.48	0.35	0.56	0.55	0.36	0.22	0.36	0.31
MgO	20.93	25.57	20.29	20.58	13.61	16.19	14.32	15.50
CaO	1.50	2.11	1.63	1.64	19.42	18.26	17.27	18.78
Na ₂ O	0.00	0.00	0.00	0.00	0.37	0.27	0.45	0.33
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	99.65	99.36	99.92	99.75	99.51	98.78	99.52	99.93
MOLE PERCENT ENOMEMBERS								
EN	59.7	70.8	58.1	58.9	39.6	46.9	42.1	44.8
FS	37.3	25.0	38.6	37.7	19.7	15.1	21.3	16.2
WO	3.1	4.2	3.3	3.4	40.6	38.0	36.5	39.0

TABLE C3 : Electron microprobe analyses of phenocrysts showing important zoning. (see sections 6.1, 6.2).

(C) refers to core analysis, (R) to rim.

TABLE C4 : Average electron microprobe analyses (ppm.) for trace elements in minerals of Table C2. * = not detected.

PYROXENE ^o = orthopyroxene, ^c = clinopyroxene.

	5	12	18	19	20	21	22	27	80	83	84	87
	L113	L146	MT45	MT10 ^o	MT10 ^c	MT42	S44	S28	C33	C7 ^c	C7 ^o	OR3
Ni			398	630	730	443	808	203		*	258	238
Zr	*	*							*	7200	*	

PLAGIOCLASE ^x = xenocryst

	4	5	10	11	14	16	17	18	19	20	25
	L50	L50 ^x	GC26	GC29	BN3	MT4	MT45	MT10	S44	S33	S28
Sr	2425	1440	3160	3306	3635	1510	1400	1247	1342	1110	1220
Ba			400	438							
	52	66	67	68	71	74	77	78	79	80	
	OC152	AY12	AY38	AY35	C33	C7	OR3	SH23	SH9	SH30	
Sr	1290	1087	817	990	1390	1417	2270	750	1187	1012	

AMPHIBOLE

SPINEL

		Sr	Ba	Zr		8	9	26	28
2	GC29	1530	920	*		L146	GC29	OC152	C7
					Zr	*	*	140	*
					Ni				480

BIOTITE

	1	2	4	5
	L113	L139	OC72	OC128
Ba	2965	10280	1020	6565
Sr	420	*	190	145
Zr	140		140	140

ILMENITE

	1	2	4	5	10	15	17
	L51	L113	L146	S13	OC152	C7	C65
Zr	2050	2065	1610	1370	2400	1940	720
Nb				190			
Ni					690		

APPENDIX D : DATA HANDLING COMPUTER PROGRAMS

The large quantity of analytical data generated in the course of this research required the use of a comprehensive package of data handling programs. The majority of the programs used have been written by the author in IMP (ERCC, 1974) and all take as input the norminput file output of the XRF data processing programs or the 'punchfile' output of the PROBE program (Appendix C), which are in a similar free format (Fig. B11). The programs written are summarized briefly here: more comprehensive program documentation is available at the Grant Institute.

D1 : ABSTRACT

Source file : ATOMS ; Object file : ATOMY

This is a manipulative program allowing the rapid extraction of groups of related analyses from the input file, and the creation of an output file containing the selected analyses in the same format. Analysis groups output may be determined by a particular group of characters in the analysis title e.g. 'PLG', or '@11' or by specifying the silica range required in the output analyses.

D2 : MEANFILE

Source file : ATOMS ; Object file : ATOMY

This program calculates arithmetic means of groups of analyses in the input data, and outputs the means as a file in norminput format. The groups of analyses averaged are chosen through having identical analysis titles, or through being all the same mineral type from the same rock. For example, PXC10C23@16, PXC30C23@16, PXC5<C>0C23@16 would be included in an average PXC90C23@16, but not PLG10C23@16 or PXC10C23@36. Rim analyses (those containing the sequence <R>) may be included in the mean if so required. All analyses quoted in Table C2 were generated using this program, not including <R> compositions in the average.

D3 : RATCALC

Source file : ANALABS ; Object file : ANALTABY

This program calculates mean, median, range, quartiles and interquartile mean for element/oxide concentrations and ratios. Output is to the interactive terminal. Quartiles quoted in Chapter 9 were generated using this program.

D4 : ANALTAB

Source file : ANALABS ; Object file : ANALTABY

This program generated Table B17; negative input is replaced by an asterisk and input of 0.00001 is interpreted as not determined 'n.d.'.

D5 : ATOM

Source file : ATOMS ; Object file : ATOMY

This program recalculates mineral analyses as atomic constituents; minerals are identified by the presence of one of OLI, PXO, PXC, AMP, BIO, GNT, PLG, KSP, SPI, ILM as the first three letters in the analysis title. Spinel and ilmenites have ferric iron recalculated on an R304 and R203 basis, respectively. In addition to file or line printer

output, the atomic constituents may be retained in core storage after termination of the program by use of the option PRELOAD. These may then be used as input for VARPLOT (section D7).

D6 : NORMS

Source file : NORMS ; Object file : NORMY

This program calculates the CIPW norms of input analyses using a user-selected iron oxidation ratio. Norms are not recast to 100% and should have the same total as the input analysis oxides. Output may again be retained in core storage, as for ATOM.

D7 : VARPLOT

Source files : GRAPHS, PLOTS ; Object files : GRAPHY, PLOTY

This program has been used to create all the variation diagrams presented in this thesis. It may create a wide variety of variation diagrams using the input analyses, and many arithmetic combinations of these including logs and reciprocals. It may also use data on atomic or normative constituents of the input, previously created in core storage using ATOM or NORMS. If this facility is used, then the input to VARPLOT should contain the same samples in the same order as was used in the input for ATOM or NORMS. A range of triangular diagrams, including the pyroxene quadrilateral, may also be plotted.

Symbols on graphs may correspond to differences in initial lettering in the sample names. For example, the file required to produce Table B17 could be used to generate different symbols for all L-samples, all GC-samples etc. Alternatively, symbols may correspond to the number following the '@' symbol in the sample name. While this is frequently described as a 'phenocryst assemblage' in the text, any division may be used, and the 'phenocryst assemblages' corresponding to the 52 numbers currently permissible are given in Table D1. If the required name is not present, it is possible to allocate a temporary name to a number by use of the facility CHANGE ASSEMB. Symbol keys may be placed on graphs at user-specified positions and arrowed lines may be drawn between bulk rock-groundmass pairs, or between core-rim pairs for phenocryst mineral compositions.

The program is mainly located in the source file PLOTS, but uses routines from the file GRAPHS, and uses the basic plotting routines of the ERCC Graphpack (ERCC, 1977).

TABLE D1 : "Phenocryst Assemblages" corresponding to the number after the '@' symbol in rock names.

1 Ol	27 Cpx+Pl
2 Opx	28 Ol+Opx+Pl
3 Cpx	29 "Trachyte"
4 Pl	30 Coarse granular Opx+Cpx+Pl
5 Opx+Pl	31 Fine granular Opx+Cpx+Pl
6 Opx+Pl+Hb	32 Hyalopilitic Opx+Cpx+Pl
7 Ol+Cpx	33 Vitrophyric Opx+Cpx+Pl
8 Opx+Cpx	34 Cumulate
9 Ol+Opx+Cpx	35 (a default code)
10 Ol+Opx+Cpx+Pl	36 Xenocryst
11 Ol+Pl	37 Groundmass
12 Ol+Cpx+Pl	38 Ol+Hb+Pl
13 Opx+Cpx+Pl	39 Wehrlite
14 Opx+Cpx+Pl+Bi	40 "Mica-felsite"
15 Cpx+Hb+Bi	41 Harzburgite
16 Cpx+Opx+Pl+Hb	42 Websterite
17 Pl+Bi	43 Dunite
18 "Trachyandesite"	44 Opx+Pl+Hb+Bi
19 Acid Lava	45 Ol+Cpx+Hb+Pl
20 Aphyric Lava	46 Ol+Opx+Cpx+Hb
21 Ignimbrite	47 Ol+Hb
22 Intrusive Rock	48 Ol+Opx
23 Groundmass	49 Ol+Opx+Pl+Hb
24 Opx+Cpx+Pl+Hb+Bi	50 Opx+Hb
25 Hornfelsed Lava	51 Ol+Cpx+Pl+Bi
26 Ol+Cpx+Bi	52 Pl+Kspar+Opx+Cpx