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GEOCHEMICAL METHODS FOR PROVENANCE STUDIES OF STEATITE

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Abstract

The aim of archaeology is the reconstruction of past cultures and the processes behind cultures. Conclusive evidence of cultural contacts between distinct groups of peoples is of great importance. It has long been realised that the study of the raw materials utilised for artifacts that were then moved far from their place of origin is vital in identifying these contacts and this study is concerned with the investigation of one such material - steatite.

Steatite is a soft talcose rock that is easily carved even with stone, bone or metal tools. It also has a low coefficient of thermal expansion. These physical properties have resulted in steatite being used as a raw material for the production of many domestic and decorative items throughout the world from prehistoric times until the present. However, the geological formation process has only occurred in a limited number of locations, and hence steatite sources have a relatively restricted geographical distribution. Thus steatite can be seen to fulfil a number of the basic requirements for provenancing, namely limited geographical distribution and extensive utilisation in the past. As a lithic material the physical production techniques do not affect the physical and chemical nature of the material, which may be a considerable problem with characterisation of other archaeological material, eg. ceramics, metal and glass. Thus by characterisation of source material, steatite artifacts of unknown provenance may be compared and their ultimate origin established. However, the formation of steatite is a complex process that often results in a source body that is inhomogeneous, making simple characterisation techniques inadequate.

This study seeks to establish differences between source regions and between individual quarries. If a unique pattern in measurable properties can be established, by comparing artifacts to sources, their origin may be established. Hence it is important to identify all the recognisable potential sources that may have been utilised by peoples in the past. It is considered that all regonisable sources of steatite in Britain have been noted, their geological background investigated, and fieldwork undertaken to procure samples. A considered geochemical approach was undertaken in order to characterise these sources. The problem was approached from two different angles in order to identify the simplest operational method that worked; i) trace element analysis and identification of characteristic elements by a structured statistical approach, ii) the utilisation of elements and isotopic ratios that were considered appropriate on geochemical grounds for discriminating between sources.

These different approaches required the development of several analytical programmes. ICP-MS enabled 68 elements to be analysed. By a structured statistical analysis of this data, using both univariate/bivariate and multivariate methods, the capability of these elements to discriminate between sources was assessed. Additionally, more precise ICP-MS analyses were obtained of elements that were considered effective at source characterisation. ICP-MS was also utilised in order to analyse the ultra-trace REE concentrations of most steatite. Several isotope techniques were also evaluated, $^{87}Sr/^{86}Sr$ ratios and $^{40}Ar/^{39}Ar$ ratios. Twenty-one artifacts, from the National Museums of Scotland, were also analysed for selected trace elements and REE, enabling artifact-source comparison.

Initial difficulties with sample preparation and pre-concentration of ultra-trace elements have been successfully overcome allowing the achievement of high quality analyses. The results of the multi-elemental study have enabled an assessment of the potential of ICP-MS in archaeological studies. The structured statistical approach is suggested as a model for the assessment of the large complex data set produced by ICP-MS. This statistical approach made possible the identification of elements that demonstrated great potential in separating source regions. Although all the regions could not be separated, elements identified were able to discriminate Lewisian sources, a result with important implication for the study of pre-Viking utilisation. This was later confirmed and enhanced by more precise analysis. This study has also established the existence of considerable differences in chondrite normalised REE patterns between individual source quarries, and minimal intra-source variation in these patterns. These REE results are extremely promising as they may enable artifacts to be provenanced to individual quarries. $^{87}Sr/^{86}Sr$ ratios have confirmed the proposed model that suggests the $^{87}Sr/^{86}Sr$ ratios are dependent on the interaction of the fluid and surrounding host lithologies. $^{87}Sr/^{86}Sr$ ratios have demonstrated that Dalradian and ophiolite hosted sources may be separated. This has important implication for the resolution of sources in Shetland, the most important steatite production region in Britain. Other techniques including Ar and Pb isotopic ratios, demonstrate great promise, but further work is required before their full potential can be ascertained.

The results obtained from analysis of artifacts, both trace element and REE, for the first time conclusively establish steatite artifact origin. Hence important new light has been shed on the problem of resource use and movement in the Iron Age in Scotland, a period in which there is little conclusive evidence for cultural contacts.

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CHAPTER 1 : THE IMPORTANCE OF STEATITE AS A MATERIAL FOR ARCHAEOLOGICAL STUDIES IN THE NORTHERN ATLANTIC REGION.

1.1 Introduction

The aim of archaeology is the reconstruction of cultural history, the reconstruction of past life styles and the processes behind cultures and explanations of them (Binford 1968). Thus conclusive evidence of cultural contacts between distinct groups of peoples in prehistory is of great importance. The development of absolute dating techniques has reduced dependence on such links for chronological purposes and has helped to demonstrate the inadequacy of the conventional diffusionist picture built up by Worsaae, Montelius and Childe (Renfrew 1973). However, these contacts are still the essential basis when the origins and relationship of a culture are being studied. In the past cultural contacts have been demonstrated by typological similarities of artifacts. It was assumed that the description and classification of the data would make it explain itself. Data were fitted into preconceived models, often an invasion/diffusion scenario (Binford 1968). However many typological comparisons are open to various interpretations and discussion; thus it is extremely difficult to be certain of any direct contact by this method alone. As Renfrew (1973) states

> *In the absence of direct contacts, this (the extension of known chronology) had to be done on the basis of similarities between monuments and finds of Europe and those of the east Mediterranean, interpreted in the light of diffusionist assumptions. Without the assumption that finds of Europe were related to those in the Aegean and Near East, no chronological relationship was possible; and without assuming the direction of influence it was not possible to say which was earlier.*

It has long been realised that the study of the raw materials utilised for artifacts which were then moved far from their place of origin is of great importance in studying these cultural contacts (Harbottle 1982). Now more attention is being paid to the precise characterisation of such source materials and the determination of the properties of the materials that distinctively identify their specific source. By the extension of these methods it may be possible to assign a source to a given archaeological specimen. This provenancing evidence is far more conclusive proof of contact between the source region and where the artifact was found than typological studies, even though the nature of such contact may still be open to debate. To date obsidian is perhaps the most successful material studied in this way. Obsidian has been used throughout the world for the production of blades, scrapers and projectile points. Earliest studies concentrated on utilisation of Mediterranean sources, that are relatively restricted in number

(Cann *et al* 1969). This is fundamental to most provenance studies as all possible sources must be eliminated before a positive provenance can be established with confidence. The fact that obsidian sources are often quite uniform internally while source-to-source variations are substantial has enabled later studies to refine the techniques and variables used for source characterisation. Examples of these studies can be found in Gale 1981, Grutuze *et al* 1993, Longworth & Warren 1979, Randle *et al* 1993, William-Thorpe *et al* 1979, 1984. Thus obsidian can be seen to meet the basic requirements of provenancing studies, i.e. that there are a limited number of geographically distinct sources, and that the material was traded and is now found far from its origin source. The Mediterranean studies have allowed the documentation of trade and thus cultural implications can be made.

In contrast to material such as obsidian, initial provenance studies of ceramic (reviews by Harbottle 1976, Wilson 1978) and glass artifacts (Sanderson *et al* 1984) encountered fundamental problems associated with the raw material. As many authors have recognised in order to establish provenance of all relevant sources of the raw material used for production of artifact must be identified and characterised (Peacock 1970, Harbottle 1976, Jones 1986, Cherry & Knapp 1991). When the raw material is relatively common and widespread in its distribution the identification, let alone the characterisation, of all sources that may relate even to a particular site is often a challenging undertaking. Thus if the maximum information is to be gained from provenance studies the distribution extent of the raw material must be considered a critical factor.

Lithic and ceramic materials are of particular importance in provenance studies as they are usually the only finds that have not been severely affected by the processes of degradation (Hodges 1964). The use of petrological and geochemical techniques in characterising source materials is now widespread. Geochemical techniques rely on certain elements or combinations of elements being able to produce a unique "fingerprint" for individual sources. Thus by comparing an artifact of unknown provenance to these source "fingerprints", the object may be assigned a specific origin. This technique requires that every source, whether it be a single outcrop or a broader regional area, has a unique and identifiable composition so that any differences in the fingerprinting parameters between the potential sources are greater than any variation within a single source area, within any errors. Trace elements have been successfully utilised as mentioned above in the case of obsidian (Renfrew *et al* 1968, Cann *et al* 1969). The fact that obsidian sources are often quite uniform internally, at least over the ancient production areas, while source-to-source variations are substantial has resulted in an opportunity for precise provenancing which in turn has allowed the documentation of this early exchange. Many methods have been used in obsidian analysis. These have been summarised by Longworth & Warren 1979 and Harbottle 1982.

Attempts to provenance ceramic materials initially have in general proved less successful. Various assumptions were used that correlate the *chemical type* that occurs to the greatest extent with a *local ware*. However, the picture becomes problematic when the dominant composition changes through time within a site. More recently various authors have overcome this problem by both the chemical characterisation of the composition of natural clays close to the site of interest and by physical description of these sources (this is not the place for a comprehensive review therefore a selected list of references is given: Adan-Dayewitz & Perlman 1985, Barlow & Idziak 1989, Day 1989, Gillings 1989, Jones 1986, Jones & Vagnetti 1991 Schubert 1988 Whitbread 1986). However, the chemical analysis of clays in provenance studies faces some problems in determining the relationship between the clay and the pottery. Firstly the raw material, the clay, is physically and chemically altered by the manufacturing process and post depositional changes. In a sense ceramics can be viewed as metamorphosed sedimentary rocks, whose main ingredients are clays to which tempering materials are sometimes added. This technological transformation of the raw material, coupled with potential re-working and mixing of older items, is also a problem with other materials such as metals, glass and faience. Secondly, as stated above there are considerable problems associated with the identification and analysis of the large number of potential sources associated with most sites. However, these problems may be mitigated by integrated petrological and chemical approaches. Gillings' (1989) study of Roman pottery from southern Scotland is a excellent example of this multiple approach. Also more recent studies of glass have characterised detrital material found on production centres thus enabling positive correlations to be established with artifacts (again selective references are given: Djingova *et al* 1992, Heyworth 1991 and Kuleff *et al* 1975.

The raw materials used in the production of ceramics, metals and glass are combinations of a number of distinct components that are physically and chemically altered by the technology of their production. This is an implicit problem with such materials, since the raw material is fundamentally different from the finished product, the artifact. Therefore any variation recorded in the finished artifact may be a combination of both raw material variation and technology variation. The deliberate alteration of a material such as copper by the addition of tin, arsenic, lead and zinc to form bronze or brass alloys does often follow a "recipe" that is itself characteristic of a particular temporal period or cultural region. However, if more than simple artifact grouping is required a characterisation parameter that is not affected by the production process, such as Pb isotopes in metal provenance (Gale 1989) must be sought. Clearly such changes do not present a problem for lithic materials that are unaltered during artifact production and are the product of a single raw material.

Steatite or soapstone is a soft talcose rock that is readily carved with stone, bone or metal tools. It also has a low coefficient of thermal expansion. These physical properties have resulted in steatite being utilised as a raw material for the production of many domestic and decorative objects throughout the world from prehistoric times until the present. However, the complex nature of steatisation, the geological formation process, has only occurred in a limited number of locations, and hence steatite sources have a relatively restricted geographical distribution. Thus steatite can be seen to fulfil a number of the basic requirements for provenancing to be useful, limited geographical extent of sources and extensive utilisation in the past. As a lithic material the physical production techniques do not affect the physical and chemical nature of the material. By characterisation of source material, artifacts of unknown provenance may be compared and their ultimate origin established. However, the formation of steatite is a complex process that often results in a source body that is inhomogeneous, making simple characterisation techniques such as hand identification, mineral phases identification and major element analysis inadequate. The identification and development of a suitable technique or range of techniques that can characterise steatite sources is a particular challenge.

If the challenges can be overcome these methods will prove important in conclusively demonstrating cultural contacts between peoples in the past. This is particularly important to island communities, especially in the North Atlantic, where steatite is not present as a raw material, yet remains abundant on archaeological sites. Clearly the material must have been imported and thus by establishing the origin of the steatite a picture may be gained of the nature of the social and economic contacts of these communities.

1.2 The General Geological Description and Formation of Steatite

This section will briefly discuss the geological formation of steatite. A more detailed discussion of the paragenesis of steatite can be found in section 2.1. Steatite or soapstone is a general term used to describe metamorphic rocks that are composed primarily of talc, hydrous magnesium silicate, but which may contain varying quantities of other minerals, carbonate, amphibole, magnetite and chlorite. Steatite deposits form as a result of regional or contact metamorphism due to the metasomatic alteration of an original parent body. These parent bodies are normally ultrabasics, such as serpentinites, peridotites, dunites and pyroxenites, or in some rarer cases the original deposit may be a carbonate sedimentary rock.

1.3 The Use of Steatite in Prehistory and Early Historic Periods

In any provenancing study it is important to recognise the nature and extent of utilisation of the artifacts derived from the raw material of interest. This section will briefly outline the extent and the uses of steatite in prehistory, primarily for the area of greatest interest to this study, in northern Britain and the wider north Atlantic region. There are no drawings in this section as it was considered that these are more appropriate within the site reports, refered to within the text, and previous typological studies such as Lossius (1977) and Buttler (1985).

1.3.1 The use of steatite in the British Isles

Steatite has been used in Britain since Neolithic times. The earliest known use of steatite was in Shetland where a number of vessel fragments were recovered from the Neolithic site at the Scord of Brouster (Whittle *et al* 1986). In Shetland other limited use of steatite as a raw material is known from this period (Calder 1963, Roberts 1965). Hedges & Parry (1980) also recovered some Neolithic material in layers that gave radiocarbon dates of 3285-3085 cal B.C. (2σ) on a site at Sumburgh Airport, Shetland. Some trade or movement of steatite must have occurred during this early period, as vessels have been found in Orkney where steatite is known not to occur naturally (Grant 1939, Marwick 1951).

The use of steatite was not confined to the manufacture of vessels and other domestic objects. It was also used as a ceramic temper. Fojut (1981) suggested that steatite temper would allow a high gloss finish if the object were polished. Buttler (1984) has suggested that the inclusion of steatite dust in the clay could act as a lubricant and allow the clay to be worked in a drier state, and thus reduce drying time before firing. This would also allow larger vessels to be manufactured.

In the Bronze Age steatite vessels seemed to become more common. Steatite vessels and steatite-tempered pottery are known from Jarlshof (Curle 1932, Hamilton 1956) and Clickhimin (Hamilton 1968), and from other sites in Shetland; Quaff (Johnston 1900), Nissetter (Callander 1933), Little Asta (Corrie 1932), Whalsay (Calder 1963) and at Tongs, Burra Isle (Hedges 1986). The small scale trade or movement of steatite continued, with vessels found on Fair Isle and Orkney. These finds have been for the most part from funerary contexts. Steatite vessels seem to have been used alongside ceramics as containers for cremated remains, either in cist burials, as on Quandale, Rousay (Grant 1937) or associated with secondary use of Neolithic sites, such as at the chambered tomb of Taversoe Tuick on Rousay (Henshall 1963) and Cuween Hill, Mainland Orkney (Charleson 1902). Other steatite finds include fragments of an urn at Geord of Nears, Rousay (Grant 1933), and from other sites; at Blows, Deerness (Grant 1933, Marwick 1939), Trumland, Brodgar (Callander 1933), Rousay (Craw 1934), and Fair Isle (Callander 1933). Øvrevik (1985) has suggested that the relatively large amount of steatite found in funerary contexts from Orkney was imported especially for this purpose. However, recently evidence for the domestic use of steatite on Orkney in this period has come to light; some vessel fragments were found on the house site of Tofts Ness (Smith forthcoming). It has also been suggested that fragments found in the structure known as the *Potter's Workshop* on the Calf of Eday (Calder 1939) may have been Bronze Age, although there is confusion over the exact date of the structure. The small number of domestic sites of this period that have been excavated, compared with the relatively large number of known cists and other funerary sites, has tended to emphasise the evidence for the use of steatite vessels of this period in a funerary context. However, as Smith (forth) points out, Tofts Ness lies close to a large funerary complex, and it is conceivable that the steatite vessels were imported as high value goods, probably not for everyday use, but to be kept as prestige items in a domestic context, later being utilised in a funerary setting.

A speculative Bronze Age date has been suggested for three stone cups from a cairn in Aberdeenshire (Callander 1916). If this is an accurate age it would suggest that steatite was being transported even at this early stage, as there are no known outcrops of steatite in this area. However, Steer (1956) suggests that many of the stone cups are in fact Iron Age, although the typology is in the Bronze Age. These typological similarities are probably debatable and stone cups are rarely found associated with Bronze Age sites.

Steatite was also utilised during the Bronze Age as a raw material for metal working moulds. The ease of carving and its thermal properties probably made it a material that was much sought after. Moulds have been found on Fetlar (Corrie 1932). Tylecote (1962) provides a reference to finds of moulds from Britain and Ireland.

Throughout the Iron Age, vessels and small objects continued to be manufactured in Shetland (Steer 1958, Hamilton 1968, Close-Brooks 1974). The trade or exchange of steatite to Orkney continued and is reflected in a number of finds from various sites, e.g. Calf of Eday (Calder 1937, 1939) and finds from Knowe of Rowiegar are considered to be part of the iron age occupation of the site (Davidson & Henshall 1989). Steatite also continued to be used as a temper in the Iron Age being found at Jarlshof and Bu (Hedges 1987). However its use seems to decline thereafter (Calder 1939, Small 1967, Hamilton 1968, Buttler 1984).

Steatite items are also found far from local source, at this time, as can be seen from finds of a loom weight from Braidwood, Midlothian, which was thought to be 1st century AD. (Stevenson 1948), and from Hownam Rings, Roxburgh, 3rd century AD. (Piggott 1948). They are however similar in style to loom weights found in the Viking layers at Jarlshof, Saevar Howe and Brough of Birsay. There are also a number of fragments of cups and a lamp from the late iron age site of Carlungie, Angus (Wainwright 1963).

Steatite is associated with a number of brochs. These tend to be brochs close to sources of steatite. In Shetland steatite is associated with the sites at Clickhimin and Jarlshof (Hamilton 1956, 1968); on Orkney, with Midhowe, Rousay (Grant 1934), Okstrow, Birsay (Callander 1933) and Broch of Burrain, North Ronaldsay (MacGregor 1974). The exact phase of the production and use of these objects is uncertain; they are generally considered to be pre-Viking, but the possibility of their introduction on to sites during the later use of brochs by Viking settlers cannot be discounted. Steatite has also been found at a number of brochs on the Scottish mainland and the Western Isles. The brochs in Glenelg, Dun Telve (Curle 1916) and Dun Troddan (Curle 1921), have produced much steatite. Other examples include Dun Beag, Skye (Callander 1921), Dun an Iardhard, Skye (Macleod 1915), Caisteal Grugaig (Wallace 1897), Lochalsh, Carn Liath, Golspie and Clachtoll, Stoer (Young 1962). It is difficult to be certain that the steatite is not from later Viking occupation of these brochs. The more recently excavated broch at Dun Mor Vaul, Tiree (MacKie 1974) revealed no steatite. A cup found at Cinn Trolla, Kintradwell is ascribed to the Iron Age.

Thus there is ample evidence for the use of steatite on prehistoric sites in northern Britain. However, the main point to note is that steatite vessels as compared to ceramic wares are rare in all periods prior to the Viking colonisation of Northern Britain from the eighth century AD onwards. In terms of the number of artifacts recovered, the most abundant, Pre-Viking, use occurred as a temper for pottery or as spindle whorls and beads (Buttler 1984). However trade in steatite during prehistory, especially in the Northern Isles, may have been more significant than previously thought, as the number of well-excavated sites from this period is relatively limited. Nowhere is there any evidence for a large scale steatite industry comparable to that of Norse Shetland.

During the Viking Period the Norse settlers imposed their cultural traditions over large parts of the North Atlantic region, including their preference for steatite. Pottery is virtually unknown from most Viking age sites in Scotland, the Faeroes, Iceland and Greenland. The only site with any quantity of ceramics is Udal, South Uist (Crawford 1974). The effect of the Viking colonisation in Shetland was a massive expansion of the steatite industry (Buttler 1984). The single most important use of steatite in Norse Shetland was as a substitute for pottery, continuing the aceramic tradition of the Vikings. In the later Norse period native and imported pottery gradually replaced steatite vessels. Steatite was the most common find from the Viking levels at Jarlshof (Hamilton 1956), although Hamilton suggested a transition from steatite to water-worn pebble loomweights by the late 9th century. On other Viking sites (Curle 1982, Hedges 1983) this transition from steatite to other materials was also observed. Further sites in Viking Shetland that have produced steatite include a farmstead built over the remains of a Broch Period hut at Underhoull. Small (1967) considered this to be 9th century, but the finds are difficult to date and in a reassessment Underhoull has been assigned an 11th century date (Bigelow 1984). Steatite is less common on Orcadian and mainland sites than those on Shetland, but nevertheless is still used (Hedges 1983). It occurs in Viking levels in Orkney. There are many loomweights, spindle whorls, vessel fragments and high quality worked vessels from Saevar Howe, Birsay, Orkney (Hedges 1983), also spindle whorls (Curle 1982), a considerable number of vessels from Brough of Birsay (Morris 1982, Hunter 1986), Birsay Bay (Morris 1990) and from Brough of Deerness (Morris & Emery 1986). A number of vessels and moulds were recovered from Lavacroon, Orphir (Batey & Freeman 1986). Hunter (1986) suggested that the steatite from early Norse contexts may have come from Norway, whereas in later phases, more local quarries would be utilised. However, in the absence of objective provenancing methods this remains an interesting speculation. It is marked that from a number of recently excavated sites in Orkney that span Pictish and Viking Periods, Pool (J. R. Hunter. pers comm), Saevar Howe and the Brough of Birsay, that there is no steatite prior to the Viking levels. At the Brough of Birsay there is a notable decline in its use at the end of the Norse Period. However, not all Viking sites have produced steatite. Buckquoy, which has a settlement record from the 1st millennium AD. to the late Norse Period, did not produce any steatite (Ritchie 1977). Ritchie (1974) has argued for considerable integration of the native and Norse during the colonisation, perhaps reducing the settlers' use of steatite in some instances.

Methods and tools used in Shetland for quarrying were similar to those in Norway (Buttler 1989). However, it is apparent that the industry in Norway was organised on a more professional level than Shetland quarrying. Buttler (1984) suggested that working in Shetland was probably carried out during the winter by men who were crofters and fishermen at other times of the year. In Norway quarrying was more likely to have been a summer activity, with quarrymen living at some of the more remote quarries and concentrating on the production of finely made vessels for a wide distribution.

The typological system devised for Norwegian steatite vessels (Lossius 1977) apparently cannot be applied to most artifacts from Shetland (Buttler 1989). Most steatite vessels found in Shetland tend to be plain, lacking any detail suitable for classification.

Steatite is relatively common on Viking sites even outwith the Northern Isles, being found at Dornoch (PSAS 84), Drimore Machair, South Uist (MacLaren 1974), A Cheardach Mhor, Drimore, South Uist (Young and Richardson 1960) Freswick, Caithness (Curle 1939, Batey 1987). It has also been found associated with Viking graves such as Cruach Mhor, Islay (Gordon 1990).

The major problem in making any statements about the Viking utilisation of steatite on sites in northern Britain is the lack of well excavated sites of the period. Udal on South Uist is the only early Viking site with substantial quantities of ceramics, where it is claimed that local pottery was adopted by settlers (Crawford 1974). Steatite is also found far from any potential sources as can be seen from finds from Clifford Street, York.

1.3.2 The use of steatite in the North Atlantic region

In Scandinavia steatite has been utilised as a raw material since the Stone Age. It was used in the Neolithic Period for manufacturing carving tools, amulets, spindle-whorls, loomweights and as temper in pottery, and in the Bronze Age as a raw material for metalworkers' moulds. However, it was not until the pre-Roman Iron Age that vessels were first manufactured (Skjølsvold 1961, 1969, Møllerup 1959). These vessels generally appear to have copied the form of the contemporary pottery and differ from later Viking Period bowls (Skjølsvold 1961, Pilo 1989). Little is known about the organisation of these early steatite industries. They were relatively extensive in comparison to earlier periods (Skjølsvold 1969), but appear to have been on a much smaller scale than the later Norse industry. It has been suggested that the pre-Roman Iron Age industry was totally separate from the later Viking industry (Møllerup 1959).

In the Norse Period, the steatite industry flourished (Skjølsvold 1976) and steatite wholly supplanted ceramic pottery for several centuries (Hougen 1969). Quarrying was both extensive and intensive, with over one hundred quarries known in Norway. It is probable that there was a professional craft industry in steatite vessel manufacture during this period in addition to local production for domestic use (Skjølsvold 1961). Finds of steatite vessels and other artifacts are much more frequent from this period than from earlier times. The rapid increase in the use of steatite was first thought to occur with the start of the Viking Age. Tools found in a number of quarries have given early Viking Period radiocarbon dates, suggesting extensive use of steatite in this early Viking phase (Skjølsvold 1976), but closer examination has shown that it was more gradual, with steatite dominating the later Viking Period. Evidence from the quarries in Lesjafellene strongly suggests a professional production centre was present in the summer and autumn (Skjølsvold 1976). However, little is known about the social structure of these craftsmen. In the late Norse Period and the Middle Ages ceramics became more widely used, while steatite declined. Medieval steatite vessels differ in form from those of the early Viking Period. In towns steatite does not appear to be common later than the 18th century, however its utilisation continued until the late 19th and 20th centuries in rural areas.

The dominance of steatite over pottery during the Viking Period throws up a number of problems. Why should the use of pottery die out in areas where ceramics were used for thousands of years? Steatite has a number of advantages over ceramics, i) superior thermal properties, ii) durability and iii) does not affect the flavour of contents. However ceramics have the advantage of being considerably lighter. It is unclear which was cheaper or which was more easily manufactured. Buttler (1990) has suggested that steatite may have become more fashionable during the Viking Period resulting in its eventual dominance. An interesting speculation is that steatite's dominance may have developed in areas with limited fuel supplies, steatite production being less energy intensive than ceramics.

The small number of finds from Jutland/Denmark, where steatite is known not to occur naturally, suggests that the steatite trade between Norway/Sweden and Norway/Denmark was limited. At Hedeby steatite artifacts are limited to the later part of the Viking Period and are not common, although trade certainly did occur (Resi 1979). As in Denmark steatite does not occur naturally on the Faeroe Islands, although it has been found from settlement sites on these islands (Dahl 1970). At the early Viking Age farm settlement of Toftanes over 700 objects were found, mostly vessel fragments (Hansen 1990). The Faeroes had close links with the Isle of Man and Shetland, and the steatite may have been imported along these trade links.

Steatite was also widely used by the settlers and later inhabitants of Iceland (Eldjárn 1950). Domestic objects made of steatite, presumably imported, are known from the Viking Age settlement of Hvitárholl (Magnússon 1972). There are no steatite sources in Iceland, and hence all the steatite must have been imported, most likely from Norway or Shetland.

Steatite is also known from Greenland, where it does occur naturally (Bøggild 1953). It was utilised in prehistory by the native Eskimos and by later Norse settlers (Rousell 1941). Buildings close to steatite quarries, and presumably related, have been excavated and are considered to be Norse (Bøggild 1953).

A steatite spindle whorl, found at L'Anse aux Meadows, near the northern tip of Newfoundland, is considered to be Norse and is taken as evidence for the early settlement of North America (Ingstad 1970, Allen *et al* 1978).

1.3.3 Quarry evidence for prehistoric use of steatite in Britain

In any provenancing investigation an understanding of the extent and scale of production is important. However, little hard evidence is available for production centres in Great Britain. This section will detail the evidence for working from quarry sites. Lithic material such as steatite has the advantage over other source material in provenancing studies in that the quarries for the raw material are not subject to rapid erosion and so often contain direct evidence of exploitation. It should be noted that Buttler (1984) observed that recently worked steatite surfaces rapidly discolour. The locations of all these quarries can be found in section 1.4.1.

i) Shetland

Place names provide some evidence that several sources of steatite were exploited in Norse and prehistoric periods. In Shetland several locations incorporate the element *cleber*, which is from the old Norsk *kle-berg* or *loom weight stone*. Examples of this can be seen in names such as Cleber Geo (Fethaland and Hillswick Ness) and Clibberswick. Buttler (1984) suggests that *Clammel* which is peculiar to Unst and Fetlar is a derived form of the same root, and seen in such names as Clammel Knowes and Clemmil Geo.

More direct evidence of use can be seen in quarry sites in the working of the rock faces. The age and nature of the working seen is difficult to determine but it is generally assumed that bosses, the classic roughed out shapes that would have contained vessels since removed, are Viking (Buttler 1984).

The geos at Cross Geo, Clibberswick on Unst show signs of working. Both of these geos have been quarried, although more extensively in the north geo. The north face of Cross Ness, the promontory separating the two geos, is covered with bosses left after vessel removal. There is some evidence for quarrying in the southern geo, but this is not as extensive as in the north geo. Buttler (1984) excavated part of the area around the quarry faces and revealed buildings that he concluded were associated with the final stage of vessel manufacture.

At Clammel Knowes there is now a large hole in the centre of the zoned talc body. On the down side of the slope there is a large spoil heap containing many fragments of steatite. There is no direct evidence of exploitation on the rock face as most has been removed and vegetation has grown across the rest. However the removal of such large quantities of material coupled with the spoil heap suggests that intensive quarrying took place. Spence (1899) also refers to Clammel Knowes as a steatite quarry.

The zoned bodies at Gorsendi Geo and on Houllans Ness show a limited number of bosses and were possible workings for smaller objects. This was probably the case for the other sources on the west coast of Unst, Wick of Collaster, Clay Geo Ness of Collaster and Fiska Wick.

The large body at Queyhouse has been extensively quarried for talc since the early part of this century. This recent working has unfortunately removed any possible traces of prehistoric usage.

Steatite firebricks were cut at Uyeasound until recently (Buttler 1984), and there are no signs of ancient working which may have been removed by this activity. However small objects may have been cut from this source and other steatites on Unst, between Belmont and Head of Mula, Mu Ness and The Taing.

On Hesta Ness on Fetlar there are numerous signs of industry. In Scarpi Geo a large area of the cliff has been worked with many bosses remaining from intensive production. In the early part of this century talc was commercially extracted at [HP 662 927]. Blast marks are still evident. Bosses with chisel marks similar to those recognised as prehistoric occur near this gully.

The eastern face of Clemmil Geo, Hubie, is covered with many bosses of all shapes and sizes. The strong foliation of the steatite may have made vessel manufacture difficult. However the working that is apparent shows that the bosses tend to be elongate and arranged parallel to the foliation. This foliation may have made the steatite easier to remove from the outcrop. Steatite was cut here for firebricks and whitening stones until recently (Howat pers coms). The steatite mass at Dammins is relatively close and has much evidence of working, a face 400m by 100m having numerous bosses within it. Between these two areas there are number of mounds of what appears to be spoil material from vessel production.

On mainland Shetland there is a large quarry at Cleber Geo, Fethaland. The large geo contains much evidence of working and, although part of the face has since collapsed, many bosses are still visible. There is also a considerable amount of spoil left in the quarry. Below the largest face a step has been cut on the hillside that may have been used as an area for the final finishing of the vessels.

Close to the quarry at Cleber Geo another area which has been intensively quarried is the cliff at Breibister. Further south at Head of Calasta there are two steatite bodies which both show limited evidence of working. However the steatite here is fissile and may not have been suitable. At Orra Wick, Lunning, on the shore 50 metres east of the stream, an outcrop contains a number of clear bosses and a roughout for a large vessel which has not been detached. However, working here has been on a small scale.

At Cleber Geo, Hillswick Ness the pink steatite in the middle of the cliff shows some signs of use. Working was probably limited by the awkward access to the cliff. However the steatite is considered to be of good quality.

Southern Mainland Shetland contains a number of worked steatite quarries, the largest being at Cunningsburgh, Dunrossness. Here the hillside from Vestinore in the north to the Knowe of Wilga in the south contains many worked steatite outcrops. The quarry area has been surveyed for the Scottish Development Department, Historic and Ancient Buildings (Ritchie 1981). The main area is around the Catpund Burn. This area was first described by Hamilton (1956, appendix II). Working is visible in and by the stream from just above the road to well above the fence line. A small excavation was carried out at Catpund Burn where over 500 vessel fragments were recorded (Smith 1989). A prehistoric house sited just to the north of the quarry area may have been related to quarrying (Calder 1963). South of the main quarry area spoil heaps and small worked outcrops run to the foot of Knowe of Wilga. To the north of Catpund Burn for a distance of about 700 m there are steatite outcrops that show occasional signs of working. The largest worked outcrop is 200 m south west of Vestinore croft. Another area of spoil heaps lies to the north of the burn and to the east of the road. On the coast at HU 428 275 there is an area of worked steatite showing bosses from the production of vessels of various shapes.

Further south, on the shore at The Berg, Hoswick, Dunrossness, a steatite body contains numerous bosses, some of these being below the high tide mark.

ii) Mainland Britain

Various quarries on mainland Britain have been worked in the past. However, many of the best steatite sources have been quarried comparatively recently and hence may have obliterated any sign of prehistoric working. The quarry at Shinness on the north side of Loch Shin was used to produce lime and it seems unlikely that steatite was ever quarried here. Near Ardintoul in Glenelg a band of talc schist has been worked and produced 500-600 tons between 1931 and 1933 (Wilson and Phemister 1946). The other smaller talc-carbonate bodies have been used locally as rubbing stones to whiten hearths, but it is unclear how much, if any, working took place in prehistory. The talc deposit on Eilean Glas has also been worked on a small scale, but the age of this extraction is unclear. There is a relatively large quarry at Damshead which produced material in the earlier part of this century. At Corrycharmaig in Glen Lochay the serpentinite, in which there are various steatite lenses, has been worked for chromite (Wilson & Cadell 1884). However the trial pits appear separate from the working that occurs at one of the steatite lenses. Talc has been known and worked in the vicinity of Inellan and Toward. It has been worked at the junction of the two streams north of Toward Taynuill, where 183 tons was produced in 1828-29 (Wilson and Phemister 1946).

The steatite in Cornwall has been worked in historic times. Gew-graze the "soap-rock" was worked intermittently about the start of the 19th century. About 12 tons was quarried annually (Straham *et al* 1945).

The working at the Shetland quarries is assumed to be from the Norse Period, because no evidence of clearly pre-Norse quarrying has been found (Buttler 1984). All artifacts and broken roughouts recovered from spoil heaps have been of Norse type. Attempts have been made to relate the shapes of bosses on the exposed surfaces to the sequence of vessel known from excavation (Hamilton 1956). However this may not be wholly reliable as boss shape is not necessarily a function of the vessel produced from it and gradation changes in sites are not clear (Buttler 1984). In addition, the worked face that is preserved today represents only the last stage of use of an outcrop.

1.3.4 Summary

In summary it is apparent that within the Northern Atlantic region steatite has been used from the Neolithic Period until recently. However, it was not until the Viking Period, with the colonisation of many areas in this region by Norse settlers, that steatite's use became both intensive and extensive. The Viking preference for steatite over ceramics, cultivated in Scandinavia, a region with extensive steatite sources, was introduced to new areas with the Viking colonisation. Thus in many areas steatite wholly supplanted a ceramic tradition that was subsequently lost.

In the colonised regions ceramics, both local and imported, eventually regained their position as the dominant material of vessel manufacture by the latter part of the Norse Period. This transition away from steatite appears to have occurred later in Scandinavia, presumably as steatite was more readily available, fashionable and therefore was still able to compete with the increasing accessibility of imported pottery with the rise of the Hanseatic trade network that took over in the rest of the North Atlantic region.

1.4 Steatite as a Potential Resource in Prehistory and Early Historic Times.

The identification of the raw material sources is the first stage in any provenance study. This section will briefly give details of the locations in which steatite was available to be used as a raw material by peoples in the past. The first section will detail potential quarry sites in Great Britain, the second section in the broader north Atlantic region relevant to charting of Viking expansion and colonisation A more detailed geological description of each individual quarry may be found in section 2.3.

The recognition of quarry or raw material sites is a considerable problem in any form of provenance study. This is pertinent if sources are to be assigned unique signatures, as no two sources can have a similar source characteristics if a unique provenance is to be established. In certain cases sources may have been worked to extinction in prehistory thus there identification may be difficult. Also caution must be exercised when assumptions are made about working of quarry sites. As Buttler (1985) observed relatively recent working may appear to be prehistoric and more recent working may obliterate previous exploitation evidence. There has been considerable work on the characterisation of British stone axes and their relationship to sources (Clough & Cummins 1979, 1988). Clough and Cummins have described 24 different rock types that are used in the manufacture of stone axes, however, as yet only * production centres have been identified and only 4 excavated.

Clearly this represents a problem for a provenancing problem such as steatite. However, as steatite is a relatively sparse raw material, unlike the multitude of lithics that are used for stone axes and marble in its broadest sense, most of its sources are more readily identified.

It is apparent that the centres of stone axe production changed through time as well as the scale production and the subsequent distribution, now reflected in the artifact distribution pattern

(Smith 1979). This change in emphasis is also apparent from flint working which appears to have declined on the south coast of England whilst expanded in East Anglia during the Neolithic (Mercer 1981).

The nature of the axe trade is considered by many to be purely a commercial operation. However, Bradley & Edmonds (1988) have suggested that this social organisation imposed by our current society may not be relevant to this Neolithic culture. The movement of stone axes has been studied from the distribution of the finished products. Discussion of this evidence has attempted to identify different forms of exchange systems, through the analysis of the dispersal of products around their sources, it seems possible to suggest some of the agencies involved (Renfrew 1975). Such techniques have been applied in stone axe studies (Chappell 1987), but other research suggests that this approach can be dangerous, since computer simulations show that different fall-off pattern can be created by exactly the same process (Hodder & Orton 1976). Bradley & Edmonds (1988) have also suggested that artifacts may change the function though time and space, practical work object to symbolic/ritual object for example and cite examples of grouping of exotic axes found in areas of abundant raw materials. This would clearly affect both the production and the related distribution, the change being opaque in the archaeological record.

1.4.1 Steatite as a potential resource in Great Britain

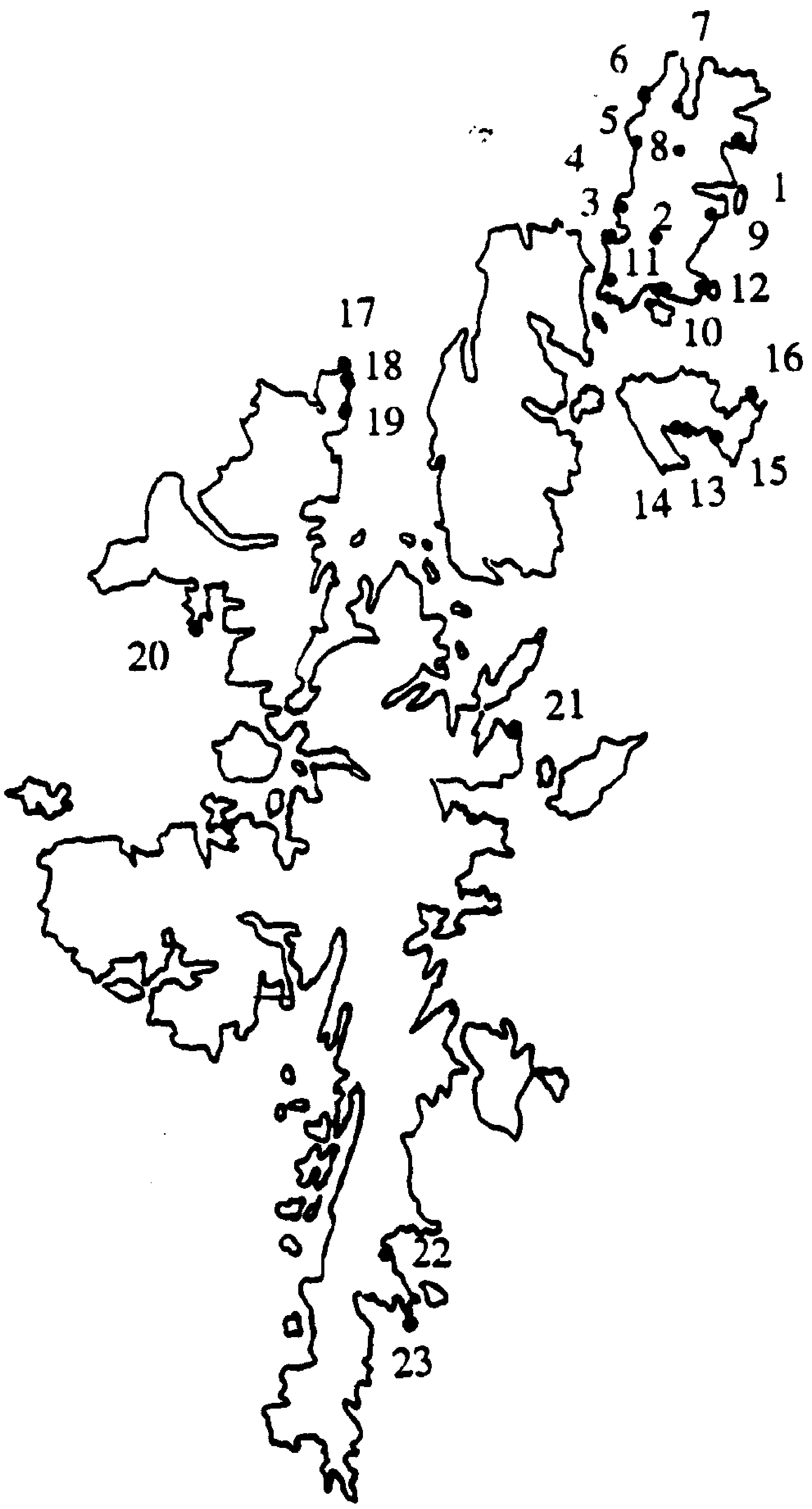
The information in this section was compiled from visits to all the localities and from various sources in the literature, principally Wilson & Phemister (1946), who listed potential talc deposits as part of the Economic Wartime Pamphlet, Heddle (1901) who listed many localities in his *Mineralogy of Scotland*, and Ritchie (1984), who described many of the same quarries, and Buttler (1984) who listed most of the Shetland sources. Grid references refer to the centre of the body or the point where steatite alteration is found.

i) Shetland

Locations of all the source localities in Shetland are shown in figure 1.1.

Unst

On Unst there are many places where small talc bodies are found. However, there are large deposits on the cliffs at Cross Geos, Clibberswick [HP 652 122], small outcrops of steatite occurring to the north as far as The Taing [HP 653 146]. At Clammel Knowes [HP 586 064] a mound exists where most of the talc deposit has been removed in the past. The quarry at Queyhouse near Burra Firth [HP 614 123] is a steatite deposit which has been commercially quarried since the early part of this century. East of Gorsendi Geo, especially around the point where the coast turns south in Lunda Wick [HP 565 044], there are numerous small talc bodies,



1. Cross Geo, Clibberswick
2. Clammel Knowes
3. Gorsendi Geo, Lund
4. Houllans Ness
5. Wick of Collaster
6. Ness of Collaster
7. Fiska Wick
8. Queyhouse
9. Wick of Hagadale
10. Uyeasound
11. Belmont
12. Scolla Wick
13. Clemmil Geo, Hubie
14. Dammins, Hubie
15. Leagarth
16. Hesta Ness
17. Cleber Geo, Fethaland
18. Pundy Geo, Breibister
19. Head of Calasta
20. Cleber Geo, Hillswick Ness
21. Orra Wick
22. Cunningsburgh
23. The Berg

Figure 1.1 Locations of steatite sources in Shetland.

the best exposures being on the beach and foreshore. These small talc deposits are apparent in many other places along the west coast of Unst, on Houllans Ness [HP 567 054], Wick of Collaster [HP 596 077], Clay Geo, Ness of Collaster [HP 576 077], and Fiska Wick [HP 614 156]. They tend to be small deposits in the order of 5 metres across or less. On the east coast there are also numerous small deposits the largest being at Wick of Hagadale [HP 641 106]. There are a few small bodies on the south coast, at Uyeasound [HU 599 011], small shears between Belmont and the Head of Mula [HU 566 996], and Scolla Wick [HP 634 007]. On Unst the only deposits of any notable size are at Clibberswick, Clammel Knowes and Queyhouse. Other deposits are smaller, but nevertheless are still potential sources that could have been exploited in prehistory.

Fetlar

Fetlar has a similar geology to Unst and therefore also has many small steatite deposits. The largest bodies that show alteration to steatite are as follows. On Hesta Ness there are several outcrops of steatite along the east side of the Wick of Gruting. The largest of this group of outcrops is on the top and half way down the cliffs at Scarpi Geo [HU 664 927]. There are also smaller deposits at [HU 662 927] where there is a narrow gully in the cliff, and large deposits in two areas around Hubie. Firstly, at Clemmil Geo [HU 620 905] SW of Hubie a geo has been cut into the less resistant steatite, which occurs on both sides of the geo and on the top of the small cliffs. Secondly, four hundred metres west of Clemmil Geo is an area of steeply sloping outcrop about one hundred metres long. This is the large outcrop at Dammins [HU 618 903]. There is another potential source of steatite on the beach at Leagarth [HU 627 905] where there is a thin talc schist band surrounded by chlorite schist.

Mainland Shetland

As on Unst and Fetlar there are numerous small steatite deposits on mainland Shetland. The larger deposits are as follows. At Cleber Geo, Fethaland, North Roe [HU 378 943] the top of the cliff above the large geo is formed from a large steatite body. To the SE at Breibister [HU 377 938] there are two smaller yellowish steatite bodies within the cliff. Further to the south at Head of Calasta [HU 377 878] there are two smaller steatite exposures in the face of the small cliff. The west coast of mainland at Cleber Geo, Hillswick Ness [HU 276 749] contains a small pink steatite body in the middle of the cliff, however access to the cliff is awkward. On the east coast of Mainland at Orra Wick, Lunning [HU 505 670], there is a small steatite outcrop on the shore some 40 m east of the stream.

Southern Mainland contains a number of steatite bodies the largest being at Cunningsburgh, Dunrossness [HU 425 271]. This covers a large area from Vestinore in the north to the Knowe of Wilga in the south and extends on to the beach north of the Catpund Burn and some 500 m west of the road up the Catpund Burn. It consists of many separate outcrops of steatite. To the south of Cunningsburgh there is another steatite body at The Berg, Hoswick [HU 426 228]. The deposit forms the tip of the point and extends into the intertidal zone.

ii) Mainland Scotland

Locations of all the source localities in Mainland Scotland are shown in figure 1.2.

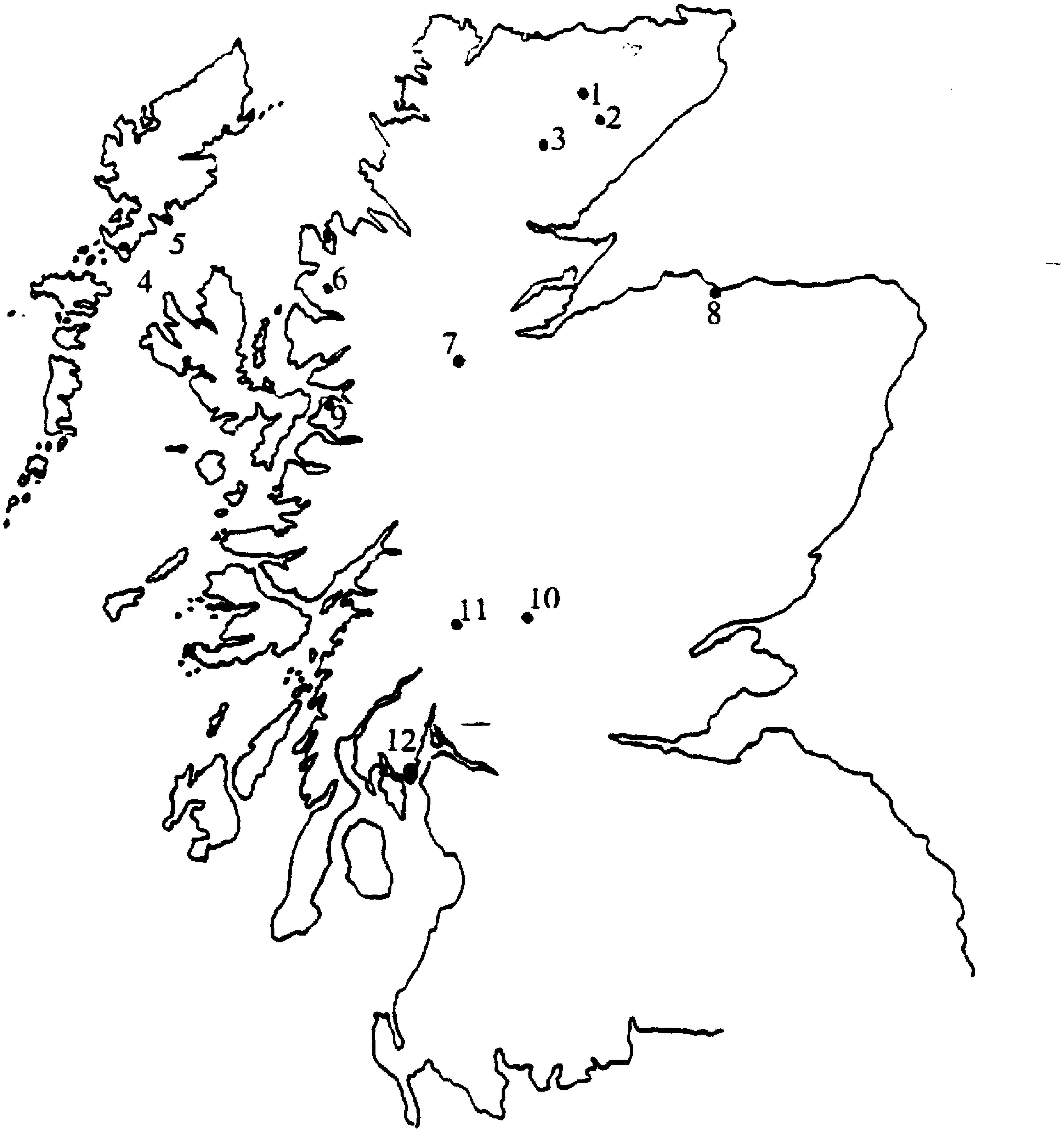
In Sutherland there are a number of small ultrabasic outcrops which show some alteration to talc. At Allt Dionach-caridh [NC 556 422] there is a small outcrop in the bank of the burn, however only a very small alteration zone of the ultrabasic mass is present and so working is most unlikely. Further south there are number of small ultrabasic bodies that have been partially altered to talc, olivine, anthophyllite and chlorite around Altnaharra, Druim Klibreck [NC 605 352], River Mudale [NC 554 358], Grumore [NC 600 369] and Meall a'Bhrollaich [NC 588 368]. At Shiness steatite occurs as nodules within the limestone in a small quarry on the north shore of Loch Shin [NC 552 139].

On Harris there are a number of ultrabasic bodies which have been altered to form rocks with some talc content. A line of these occurs within the well-exposed rock along Loch Langavat. The largest is at Scara Ruadh [NG 056 884], and similar bodies to the west occur at Dun Borve [NG 034 940], Loch-na-h-Uamba [NG 046 918] and Rubha Sgeir nan Sgarbh [NF 025 950]. Also on Harris there are two small ultrabasic bodies at Grose-Cleit [NG 143 942] and Uaval Beag [NG 143 942], although the extent of the talc alteration is limited. On Scalpay of East Loch Tarbet, Harris, there is a small sill-like exposure on the narrow isthmus joining Scalpay to Eilean Glas [NG 246 948].

In Wester Ross a talc and chlorite rock is thought to exist on the north east side of Beinn Dearg Bheag (Clough *et al* 1913), but no sign of this exposure could be found when visited. To the south in the Sheildaig Forest there is a small body 1000 m south of the head of Loch na h'Oidhche [NG 895 628].

In Glen Urquhart there is a serpentinite mass 1000 m^2 in extent, occurring on the north side of Glen Urquhart [NH 763 354]. A number of altered bodies exist by the side of the road to Kiltarlity at the junction with the road to Gartallt.

A large belt of serpentinite around Portsoy extends 8 km SSW from the coast, 700 m west of Portsoy to Mains of Badenyouchers. At its northern end there is a quarry at Damshead [NJ 575 636], 400 m north west of Damshead farm.



1. Allt na Dionach-caridh
2. Druim Klibreck
3. Shiness
4. Scara Rubha
5. Eilean Glas
6. Loch na h'Oidhche
7. Glen Urquhart
8. Portsoy
9. Glenelg
10. Bolfracks Hill, Aberfeldy
11. Toward/Inellan
12. Corrycharmaig

Figure 1.2 Location of steatite sources on mainland Scotland

In the Glenelg district there are number of serpentinite and talc bodies. On the shore near Ardintoul [NG 934 245] a 2 m thick band of talc schist occurs. Other small ultrabasic bodies in this district that show talc alteration are as follows: in the left bank of the small burn which flows into Loch Duich 100 m south of Tigh Dhruideig, just below the confluence of the two burns about 400 m south west of Tigh Dhruideig [NG 877 244], also in Glean Beag, 3 km south-west of Glenelg, 300 m up the Allt Mor [NG 845 168], and thirdly a body which is reported to exist in the Allt Utha, which flows into the Arnisdale River about 2 km from Loch Hourn. The body is reported by Clough (1910) to be 300 yards above the Eas na Cuingid, but no trace of this body was found when the site was visited.

Near Aberfeldy, on the east side of Bolfracks Hill, 3 km south west of Aberfeldy there is a dark green sill-like body that contains alteration to talc and chlorite [NN 836 477]. To the west in Glen Lochay, there is a large serpentinite body to the west of the farm of Corrycharmaig on the south west side of the River Lochay about 5 km north west of Killin. The serpentinite forms the craggy hill of Dun Garbh Beag [NN 622 358] and is connected to the farm by a rough track.

A talc deposit is known from the vicinity of Inellan and Toward. Limited working has occurred at the junction of the two streams [NS 134 687] north of Toward Taynuill. In the eastern branch of the stream there is a 1 m wide talc vein 5 m above the confluence, 4m further up this branch another vein of talc is exposed in the stream. These veins also occur in the western stream but the exposures are more obscure. Small quantities of talc are also apparent within the serpentinite on the shore west of Toward Point. Here the serpentinite has largely been converted to dolomite fault rock, but talc does occur in small amounts.

iii) England

Locations of the known source localities in England and Wales are shown in figure 1.3.

The largest outcrops of serpentinite in Britain occur in the Lizard peninsula where it covers some 30 square km. Veins of steatite are not uncommon within the Lizard serpentinite; they are found around Kennack, Mullion [SW 666 178], the Black Head [SW 775 162], Pentreath [SW 685 135] and to the west of Kyance [SW 674 174]. These are usually small and discontinuous. The largest locality is at Gew Graze [SW 675 144] where the soap-rock is known locally. A similar outcrop occurs on the east side of Kennack, on the east side of Kyanance Cove, at a quarry 400 m west of Trezise and at the north end of Pentreath beach.

iv) Wales

There are a number of talc carbonate deposits on Anglesey. A carbonated serpentinite occurs on the beach on the west coast at Porth Delise and also at Cliperau [SH 282 845] near Llanfwrog.

A thin band of talc schist about 1.5 m thick occurs within a quarry 250 m north of Bronddel [SH 268 764] on the south-west margin of the large serpentinite mass that occurs to the north of Rhoscolyn.

1. Anglesey 2. Lizard

Figure 1.3 Location of steatite sources in England and Wales.

1.4.2 Steatite as a potential resource in the north Atlantic region

Steatite is also found in many places in the north Atlantic region where it has been extensively utilised as a raw material. This section will briefly make references to the potential quarry sites in this region.

Scandinavia

Scandinavia has large numbers of potential steatite quarries throughout the region. The Geology of Norway (1st Ed) (Holtedahl 1953) gives some of the known localities of talcose rocks in Norway. A large number of the Norwegian deposits are described by Helland (1893) in 'Tagskifere, hellar og vegstene'. Skjølsvold (1961) contains an appendix which gives the localities of ca. 150 potential quarries. This relies on the work of Helland and unpublished material from Bergen Museum. Wiik (1953) describes a number of steatite sources from the

Caledonides. Qvale & Stigh (1985) review the ultramafic rocks, the original parents to steatites, within the Scandinavian Caledonides. More detailed description of certain steatite bodies and quarries can be found in Skjølsvold (1976), Resi (1979), and Natterstad (1983).

Although, Sweden contains fewer steatite deposits than Norway, they are still relatively common. Wiik (1953) describes a few sources from the Caledonides. Du Rietz (1935) examines a great number and variety of ultrabasics from northern Sweden. Resi (1979) gives the location of seven potential quarries.

Finland although not strictly part of the North Atlantic area may have been involved in the exploitation of steatite during the Viking period. Eskola (1933), Haapala (1936), and Wiik (1953) give localities of a number of steatite bodies in the Kalelidic zone of eastern Finland, which can be followed in a zone from Lake Ladoga in the south-east to Finnish Lapland in the north-west. Park (1983) describes the bodies in the eastern Kalelides in more detail and discusses their formation.

A general account of the mineralogy of Greenland is given by Bøggild (1953). This gives a list of places where talc and steatite are known to occur. Wiik (1953) describes material from Godthaab in south-west Greenland. Soen (1962) and later Fowler *et al* (1981) describe talc bearing zoned ultramafic from Greenland that may potentially have been used as a raw material.

1.5 Steatite as a Provenancing Problem

It has long been realised that studying artifacts far from their place of origin could tell us much about cultures in the past. As has been noted in section 1.3, the favourable properties of steatite were clearly recognised by early peoples resulting in its widespread utilisation over a considerable period of time in prehistory and early history. The fact that steatite in common with most lithic material is able to withstand the processes of physical degradation that occur after an artifact has been buried means that it survives to be found on sites where it was used in the past. Another advantage of using lithic materials for provenancing is that the processes used in the production do not change the characteristics of the artifact from the raw material. Steatite's extensive use in northern Britain and Scandinavia during the Norse period is perhaps a reflection of it being a relatively cheap material, so it was generally discarded rather than repaired or reused, although reuse does occur (Hedges 1983), and this would contribute to its abundance on certain archaeological sites. It was used over a long period of time, from the Neolithic until the Viking Period/Middle Ages, so making it an important material to provenance for a number of different time periods.

The potential quarry sites for steatite, as described in section 1.4, are relatively sparse. They tend to be concentrated in local discrete source areas such as Shetland. Steatite's physical nature probably precludes it from the problem of being transported, by the action of ice, from its primary natural source to where it was used by man. Steatite is found on many archaeological sites and in many cases far from potential source quarries. This fact alone implies that steatite was either exchanged as a raw material or finished goods; or some other form of movement, such as the movement of a people with their belongings into a new area took place. The fact that steatite sources are geographically limited means that not all cultural groups would have direct access to the sources. Thus if they required the material they must have traded with the peoples that controlled the quarries. This has been suggested as a model for utilisation by Indians, Eskimos and Norse settlers in Newfoundland (Allen *et al* 1978) and may have taken place in other areas in the northern Atlantic region.

Steatite was used extensively in certain periods, such as the Viking period (Buttler 1984). As the Viking world expanded during the eighth and ninth centuries, the Vikings took their preference for steatite to these new areas, which did not necessarily contain any potential steatite quarries, or where the settlers would not have been aware of all the potential local raw materials. Thus if steatite can be provenanced it may be possible to effectively trace this Viking expansion in the north Atlantic region. As mentioned in section 1.3, steatite is not found naturally on certain islands that were colonised during the period, such as Orkney, the Faeroes and Iceland yet it is present on many Viking sites. The ability to identify the source of the steatite on Viking sites could potentially give much hard evidence of Viking cultural links during this period of change.

1.6 Methods of Archaeological Provenancing

The application of chemical analysis to archaeological problems has a long history that extends back to the late 18th century (Caley 1949). Many of the early investigators dealt with compositional characteristics of artifacts to elucidate aspects of their properties, yet as Harbottle (1982) noted, by the end of the 19th century, analysis was made as a means of documenting long-distance transportation of particular materials. The underlying approach of the determination of the chemical composition of an artifact and comparison of that profile with others and the source material has been elaborated since that time.

The method most commonly used to provenance archaeological material is that based upon characterisation of source material. This method relies on the premise that unique patterns in some measurable property may be used to identify the geographical source of artifacts.

The property of the material used to characterise source and artifacts is dependent upon the material from which the artifacts were manufactured. Therefore methods of characterisation are largely dependent on the material.

Glass objects have been characterised using minor and trace elements determined for samples by NAA (Kuleff & Djingova 1985, Sanderson *et al* 1984), XRF (Sanderson & Hunter 1982, Henderson & Warren 1981). Non-ferrous metal artifacts are commonly characterised using lead isotope ratios, (Northover & Gale 1982, McGechan-Liritzis & Gale 1988) as well as compositional and trace element concentrations (Trampuz *et al* 1991). Pottery can also be characterised using minor and trace element composition analyses; e.g. by AAS (Pollard *et al* 1982, Miriti *et al* 1990) and NAA (Perlman & Asaro 1969, Glascock 1992) (Picon 1975, reviews by Harbottle 1976, Wilson 1978) as well as structural inclusions (Bromund 1976). Some lithic materials have proved to be easily characterised due to their relatively simple nature, e.g. volcanic material used for axe heads (Clough & Cummins 1979,1988), greenstone has been characterised by petrography (Kars *et al* 1992), sandstones by petrography and electron microprobe (Newman 1992), mill stones (Williams-Thorpe & Thorpe 1988), pitchstone (Williams-Thorpe & Thorpe 1984), jet (Hunter *et al* 1993), and obsidian (Cann & Renfrew 1964, Cann *et al* 1969, Hallam *et al* 1976) using electron microprobe (Merrick & Brown 1984) and strontium isotopes (Gale 1981). However other lithics still prove difficult due to their complex nature, e.g. flint (de Bruin *et al* 1972), and marble where NAA (Mello *et al* 1988), cathodoluminescence (Barbin *et al* 1992) and stable isotopes (Herz 1992) (a general review is given by Herz (1985)) have been used.

1.7 Previous Attempts to Provenance Steatite

The earliest attempt to provenance steatite was by MacGregor (in Hamilton 1956), who made a petrographic investigation of eight of the numerous steatite finds from Jarlshof and four samples from the nearest potential quarry, Catpund Burn, Cunningsburgh. In some of the cases there were clear similarities between the artifacts and the quarry samples, but for other artifacts no good matches were observed. It was suggested that these unmatched samples originated elsewhere in Shetland. This may indeed be the case but until a detailed petrological examination of all possible quarry sites is carried out a conclusive statement of the origin of the Jarlshof material cannot be made.

Petrographic examination was also carried out on two sherds excavated in the Norse town of York (MacGregor 1982). One was found to closely resemble two of the Jarlshof sections which did not match the Cunningsburgh samples. The second was more similar to the Cunningsburgh sections, although XRD analysis showed the carbonate present to be dolomite, whereas magnesite was thought more typical of Cunningsburgh steatite. Buttler (1984) has since shown that both dolomite and magnesite are present in Cunningsburgh steatite, following from Wiik's (1953) demonstration that magnesite, dolomite and magnesite-dolomite assemblages could all be present as the carbonate in steatite. Wiik (1953) also identified, in a study of various steatite deposits throughout the world, various types of steatite assemblage, carbonate soapstone (talc-carbonate-chlorite-accessories), tremolite soapstone (talc-tremolite-chlorite-accessories) and the rare Godthaab type soapstone (talc-chlorite-accessories). Some steatites showed characteristic mineralogy, textures or accessory mineral phases. However it was noted that most steatites have very similar mineralogy and textures, thus making any discrimination of steatite deposits by petrographic means very difficult. Buttler (1984) also examined a large number of samples taken from most of the Shetland quarries. The examination of hand specimens as Buttler points out is very subjective and cannot be regarded as conclusive evidence, but has the advantage of being cheap, quick and non-destructive. From a comparison with a reference set of hand specimens, taking into account mineralogy, texture, colour and hardness, a large number of the Jarlshof finds were assigned to various quarries. This evidence is difficult to verify and did not include any of the Scandinavian source material that was undoubtedly traded (Hodges 1982). The thin sections, using both descriptive and point counting of minerals, were less easily matched than the hand specimens, most specimens appearing very similar. The mineralogy is very similar, as Wiik (1953) had observed, only the textures showing slight differences. Petrological techniques suffer from the problem of representative sampling. The fact that the thin section must give an accurate reflection of the source material is a particular problem with inhomogeneous materials such as steatite in which the minerals form clusters and bands on the outcrop scale. Clearly, as a consequence of these problems petrographic comparison of sources and artifacts is not a feasible approach to steatite provenancing.

Alfsen and Christie (in Resi 1979) attempted to provenance steatite artifacts from the Norse site of Haithabu in Denmark. Forty artifacts and nine samples from a number of Scandinavian quarries close to Haithabu where extensive quarrying had taken place were analysed for various trace elements using mass spectrometry techniques. However their method gave large errors, of the order of 15-20%. After assessing quarry variability and regional variability a group of nine trace elements that showed differences were considered for further investigation. By using cluster analysis (equal pair grouping) the different quarry sites were compared to the Haithabu material. This met with limited success and better resolution could not be achieved with cluster analysis. It is also difficult to assess the importance of each individual clustering parameter in the overall cluster analysis. However, some tentative identification of sources of the Haithabu material was made. This study emphasises a necessary prerequisite that all potential sources must be characterised before artifacts may be compared. If this is not done, as in the study of Alfsen and Christie, then no firm conclusion can be reached. The material from

Haithabu may, as Alfsen and Christie argue, be from the Scandinavian Precambrian, but they studied only a limited number of the quarries that were most accessible to Haithabu.

Kohl *et al* (1979) studied the large number of soft stone vessels that are found in SW Asia from Arabia and Mesopotamia to the Indus Valley. These contained various combinations of talc and chlorite that were extremely variable, a fact that was considered to characterise the sources. This study principally used XRD to characterise the chlorite, by measuring the peak height of various indices, which are characteristic of significant differences in internal ionic substitution and as a result different basal plate diffraction peaks. These peak heights were expressed as ratios and discrimination was attempted using multivariate statistics. This was able to produce a reasonable resolution for some of the material suggesting separate sources for the Arabian material. However the material from Iraq and Iran demonstrated significant variation in the chlorite XRD peak heights from one region, thus making any discrimination very difficult. As mentioned earlier the source of these materials are often inhomogeneous and a single mass may contain very different mineral assemblages.

Buttler (1984) also used XRD to assess the carbonate within the various steatites in Shetland. Dolomite, magnesite, both of these carbonates or no carbonate were the various criteria. However, as Wiik (1953) showed, a single steatite deposit has variations in carbonate composition and is subject to inhomogenities. Buttler demonstrated that on Shetland this is also true: e.g. Cunningsburgh showed samples with carbonates both singly and together. Buttler concluded that at best, this would provide negative information on provenance, i.e. a sample did not come from a certain quarry. Samples were also analysed for major and trace elements by XRF. Twenty five samples were taken from a number of different quarry sites in Shetland, but it was found that pellets were difficult to manufacture. This was probably as a result of the hydrous nature of steatite that contains a high content of H_2O and CO_2. Both major and trace elements were assessed for discrimination potential. Major elements were very similar in all samples, as would be expected for samples with similar mineralogical compositions as has already been argued in this chapter. Analysis of variance in all cases showed variance to be greater within the quarries than between quarries. Trace elements suffered from low concentrations, most being below detection limits for the methods used, and since no sample showed all the elements, comparison was difficult. Various ternary plots were tried but these showed no discrimination potential.

Olabanji *et al* (1991) used Proton Inducsed Gamma Emission (PIGE) analysis to study the major light elements in west African sculptures and a few local source materials. These light elements showed similar concentration in the sculptures and sources, Olabanji *et al* (1991) suggested that the sculptures were from these sources, but these elements are likely to reflect the overall mineralogy of the steatite/chlorite schist which in general will be similar, hence most steatites would give similar values. Only gross differences in mineralogy would give significant differences in these major elements, thus their interpretation must be treated with caution. These mineralogical differences would be seen in hand specimens.

In the USA Allen *et al* (1975) and Allen & Pennell (1978) initially evaluated 22 trace elements for their discrimination potential. They concluded that most trace elements showed large internal variation, but the Rare Earth Elements (REE) did not show as much internal variability within one quarry and showed differences between quarries, making them potentially useful in discriminating quarries. They assumed that where the mineralogy varies across a steatite body, this variation is reflected in the major elements and also affects the trace elements to a lesser extent as major and trace elements are preferentially concentrated in certain mineral phases. This variability can be further reduced if the REE are considered. Different formation processes for different steatite bodies were thought to result in significant variations in trace element concentrations, while different bulk chemistry was thought to produce similar REE concentration. As the different phases within steatite have similar partition coefficients, the REE would partition evenly between the talc, amphibole and chlorite. Therefore any phase differences across the steatite body would not affect the REE concentration across the body.

Steatite sources from the eastern USA were characterised using REE patterns evaluated by NAA. Quarries showed significant variations from one another allowing the raw material for artifacts to be traced to their place of origin. A clear picture of different areas of utilisation using different quarries was produced.

Allen and Pennell (1978) and later Rogers *et al* (1983) developed a computer program to match artifacts and sources. The criteria the classification was based on are as follows:

1. slope of the LREE (La-Sm)
2. slope of the HREE (Gd-Lu)
3. slope between Sm and Gd
4. Eu anomaly (Eu^*/Eu)
5. magnitude of one element, normally La

Unfortunately, they do not give more details of the classification system used and how their REE results, both intra-site and inter-site, are categorised. Various clustering procedures were also considered, but these did not produce good results.

Allen & Pennell (1978), Allen *et al* (1978) and Rogers *et al* (1983) expanded the work to characterise the various sources of Labrador and Newfoundland using this REE pattern fingerprinting technique. Much of this work on steatites from eastern North America appears very promising, however it is unfortunate that little of the REE data has been published to enable further analysis and investigation.

Buttler (1984) and Moffat and Buttler (1986) also attempted to utilise the REE patterns to provenance Shetland steatite. Using Instrumental Neutron Activation Analysis (INAA) it was found that the concentration was very low, less than 50 ppb for most HREE. This gave large errors, greater than 20% in most cases, and many of the REE were below detection limits. These factors made any comparison of results very difficult. Radiochemical Neutron Activation Analysis (RNAA) was then used as a more sensitive technique for a limited number of the original sample set. However samples from Cunningsburgh showed REE concentrations that were extremely variable. They claimed that this variation encompassed all the other samples from Shetland, making a unique signature impossible. They also suggested that the REE are not partitioned equally in different mineral phases within the steatite, as suggested by Allen and Pennell (1978), and that any differences in the REE concentration across a body may be due to differences in the steatisation processes. The body studied by Williams (1977) did not show any fractionation during steatisation only an overall depletion relative to the parent serpentinite. However as steatisation is a complex process, a large number of factors could produce a body with a very variable REE concentration as with the Cunningsburgh deposit. Examination of Moffat & Buttler's (1986) data suggests that their results may have underestimated total errors, or their accuracy may not have been as good as the authors claim. This may in part account for the intra-site results they report, hence their interpretation must be considered dubious.

1.8 Dating of Steatite Artifacts

Pennell (1977) attempted to use fission tracks to date steatite artifacts. It was thought that heat, applied to the artifact in prehistory, might anneal the existing geological tracks, so resetting the clock back to the last heating event. However, the whole rock samples have low U concentration, less than 1 ppm in all samples, while a concentration of greater than 1 ppm is more desirable. This low U concentration results in a low fission track density and so large errors. As U is concentrated in certain minerals, these minerals were assessed for fission tracks. However, no great differences in the fission track densities from archaeological and geological material were observed. The conclusions were that tracks may not be stable in the material, i.e. that they fade, and that the geological tracks may not be completely annealed by the archaeological heating event. Another problem that affects this approach was the texture of steatite, which has a variety of coarse and fine grained minerals and different fabrics.

CHAPTER 2: GEOLOGICAL BACKGROUND TO STEATITE FORMATION AND STEATITE SOURCES IN THE NORTHERN ATLANTIC REGION.

2.1 Introduction

In any provenance study it is important to consider the spatial distribution of the resource material. However, it is also relevant to understand the nature of the material and how this relates to the spatial distribution pattern. This chapter includes a detailed examination of the processes that result in the formation of steatite, principally the types that occur in Britain and Scandinavia. The geological provinces of all known British sources have been established, thus for the first time enabling an assessment of their influence on steatite provenance studies. A short section describes the main features of these tectonic environments. An extra section also briefly discusses the tectonic regions in Scandinavia, and their relationship to British tectonic environments.

The chapter is concluded by a discussion of the principal ideas behind this provenancing study as determined by the geological formation of steatite quarries. A detailed geological description of all British steatite ~~sources~~ is given in Appendix A, based upon sampling work done on these sources.

2.2 The Paragenesis of Steatite

In order to find a suitable method in any provenance study it is important to understand the nature of the material that is of interest. This section discusses the formation processes and conditions of talc and steatite development. Some differences in terminology are connected with steatite. In this study steatite is defined as a rock mainly consisting of talc. Talc, the mineral species has the idealised formula $Mg_6Si_8O_{20}(OH)_4$. Soapstone in the past has been used to describe many different forms of talc and talc-rich rocks, its use can be confusing and thus is not used in this study.

Steatites are associated with several different geological environments;
1) Hydrothermally altered ultrabasic rocks. Large steatite bodies are formed from the alteration of entire ultrabasic bodies (Hess 1933b, Wiik 1953). The occurrences of talc-rich zones around nodules of serpentine in schists have also been described by Francis (1948), Read (1934 b), Matthew's (1967), Curtis and Brown (1969), Wilson (1926) Canada, Pabst (1942) USA, Du Rietz (1935) Sweden and Wiik (1953). Metasomatic zones are also common along the contacts of ultramafic bodies in regional metamorphic terrains, Hess (1933a, b), Read (1934b),

Phillips & Hess (1936), Chidester (1962), Curtis & Brown (1969,1971) and Carswell (1974). Certain features are common to many of these zoned ultramafics. From these an idealised sequence of zones has been constructed by Read (1934 b).

Antigorite I Talc-Magnesite I Talc I Actinolite I Chlorite I Biotite I Country rock

2) Steatite is also associated with Mg-rich carbonates that have undergone decarbonatisation or silicification, Tilley (1948), Engel (1949), Wright (1950), Eskola (1933), Cooper & Field (1977), Berg (1979) and Olson (1976).

These different geological situations in which steatite may be produced indicate that several different processes interacting with different precursors occurred to enable steatite formation.

2.2.1 Mineralogical Composition of Steatite

Three different types of steatite have been recognised based on their mineralogy (Wiik 1953).

1. Carbonate steatite	(talc-carbonate-chlorite-accessories)
2. Tremolite steatite	(talc-tremolite-chlorite-accessories)
3. Chlorite steatite	(talc-chlorite-accessories)

Accessories may include- serpentine, magnetite, chromite, pyroholite and pentlandite.

1. Carbonate steatite is the most common type (Wiik 1953). This type forms through the metasomatic alteration of ultrabasic rocks. The formation of talc-rich rocks by hydrothermal alteration of ultrabasic bodies is generally described as steatisation. Hess (1933a) recognised this processes and defined it as follows;

> *Steatisation may be defined as that process of hydrothermal alteration of an ultrabasic which in its final stages results in the formation of talcose rock. It may be applied either to the processes by which soapstones (steatite) are formed or to the processes by which relatively pure concentrations of talc are formed.*

Petrological studies have demonstrated that most show typical hydrothermal textures, and relict structures are not common, although rare examples demonstrate talc pseudomorphs after olivine and pyroxene. Carbonates present include calcite, dolomite and magnesite. In the field the extent of steatisation is variable. Hess (1933b) considered there to be two types of ultrabasic steatisation, however it is more probable these types merely reflect different degrees of steatisation. In some cases the entire ultrabasic mass is altered to steatite, in others, margins and fractures are intensely locally steatised. These differences have neatly been explained in terms of simple kinetic consideration by Curtis & Brown (1969).

Naldrett (1966) considered that neither addition nor subtraction of Si, Mg, Fe, Ni, had occurred only CO_2 was introduced during steatisation. This was disproved by Curtis and Brown (1969) who demonstrated that the CO_2 metasomatism involved considerable mass transfer over metric distances. Brady (1977) has since demonstrated this to be the case and that SiO_2 and MgO + FeO + MnO are diffusion components. Calculations of the mass movements are difficult as constant volume calculations are not justified and little diffusion coefficient data are available.

2. Tremolite steatites have talc-tremolite-chlorite-anthophyllite-serpentinite assemblages. Texturally they are similar to carbonate serpentinites displaying typical hydrothermal textures. They are generally associated with the hydrothermal alteration or silicification of dolomitic sediments. Most show sharp contacts with siliceous intrusive rocks.

3. Chlorite steatites are not common (Wiik 1953). This type has a talc-chlorite-magnetite composition with accessory apatite (not seen in other steatites). Texturally they are similar to other steatites displaying typical hydrothermal textures.

2.2.2 Reactions involved in steatisation

Carbonate-steatite is the type that forms all the large steatite deposits in Britain. Therefore the following discussion of formation will concentrate on this type. As an initial material for steatisation process, Hess (1933b) suggests that talc-carbonate rocks may be formed from any ultrabasic rock type. This appears to be possible as a range of ultrabasic rock types have been cited as the precursors to steatite; dunite (Wellman 1942, Wiik 1953), pyroxenite (Wiik 1953), peridotite (Moffat & Buttler 1986), and serpentinite (Hess 1933b, Wenner & Taylor 1974, Park 1983).

Chemical changes connected with the process of steatisation involve a number of possible reactions, depending on the mineralogy of the initial precursor and the composition of the fluids introduced. Starting from forsterite, anthophyllite or serpentinite and introducing only water, and/or silica, reactions such as the following occur (Bowen & Tuttle 1949, Wiik 1953, Johannes 1969):

$$\underset{\text{forsterite}}{5\ Mg_2SiO_4} + 10\ H_2O = 0.83\ \underset{\text{talc}}{Mg_6Si_8O_{20}(OH)_4} + 0.83\ \underset{\text{serpentine}}{Mg_6Si_4O_{10}(OH)_8}$$

$$\underset{\text{forsterite}}{3\ Mg_2SiO_4} + 2\ H_2O + 5\ SiO_2 = \underset{\text{talc}}{Mg_6Si_8O_{20}(OH)_4}$$

$$\underset{\text{enstatite}}{10\ MgSiO_3} + 10\ H_2O = 0.83\ \underset{\text{talc}}{Mg_6Si_8O_{20}(OH)_4} + 0.83\ \underset{\text{serpentine}}{Mg_6Si_4O_{10}(OH)_8}$$

$$\underset{\text{anthophyllite}}{Mg_7Si_8O_{22}(OH)_2} + 3.02\ H_2O = 0.83\ \underset{\text{talc}}{Mg_6Si_8O_{20}(OH)_4} + 0.34\ \underset{\text{serpentine}}{Mg_6Si_4O_{10}(OH)_8}$$

$$\underset{\text{anthophyllite}}{Mg_7Si_8O_{22}(OH)_2} + 1.33\ H_2O + 1.33\ SiO_2 = 0.83\ \underset{\text{talc}}{Mg_6Si_8O_{20}(OH)_4}$$

$$\underset{\text{serpentine}}{Mg_6Si_4O_{10}(OH)_8} + 2\ SiO_2 = \underset{\text{talc}}{Mg_6Si_8O_{20}(OH)_4} + H_2O$$

If CO_2 and H_2O are present the following reactions occur:

$$8\ \underset{\text{forsterite}}{Mg_2SiO_4} + 2\ H_2O + 10\ CO_2 = \underset{\text{talc}}{Mg_6Si_8O_{20}(OH)_4} + 10\ \underset{\text{magnesite}}{MgCO_3}$$

$$8\ \underset{\text{enstatite}}{MgSiO_3} + 2\ H_2O + 2\ CO_2 = \underset{\text{talc}}{Mg_6Si_8O_{20}(OH)_4} + 2\ \underset{\text{magnesite}}{MgCO_3}$$

$$\underset{\text{anthophyllite}}{Mg_7Si_8O_{22}(OH)_2} + H_2O + CO_2 = \underset{\text{talc}}{Mg_6Si_8O_{20}(OH)_4} + 10\ \underset{\text{magnesite}}{MgCO_3}$$

$$\underset{\text{serpentine}}{Mg_3Si_2O_5(OH)_4} + 6\ CO_2 = 3\ \underset{\text{magnesite}}{MgCO_3} + \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + 3\ CO_2 + 3\ H_2O$$

$$2\ \underset{\text{serpentine}}{Mg_3Si_2O_5(OH)_4} + 3\ CO_2 = \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + 3\ \underset{\text{magnesite}}{MgCO_3} + 3\ H_2O$$

The hydrothermal alteration of more calcium-rich ultrabasic rocks, as well as the effects of more calcium-rich solutions on normal ultrabasics, results in the formation of tremolite amphibole and of chlorite if sufficient aluminium is present. However, mineralogical studies have demonstrated that tremolite is not present with any carbonates (magnesite, dolomite, calcite) that are associated with steatites (Wiik 1953). If carbonitisation occurs, tremolite may be altered by the following equations of consistent volumes (Bowen & Tuttle 1949).

$$\underset{\text{tremolite}}{Ca_2Mg_5Si_8O_{22}} + CO_2 = 2\ \underset{\text{dolomite}}{CaMg(CO_3)_2} + \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + 4\ SiO_2$$

$$4\ \underset{\text{penninite}}{Mg_2Al_2SiO_5(OH)_4} + 6\ \underset{\text{serpentine}}{Mg_3Si_2O_5(OH)_4} + 13.2\ SiO_2 =$$

$$7.3\ \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + 4.1\ MgO + 4\ Al_2O_3 + 12.7\ H_2O$$

Talc is the first new mineral to form as a result of thermal metamorphism of siliceous dolomites. Tilley (1948) described the talc that occurs at the edge of chert nodules within dolomite in the Kilchrist-Broadford area of Skye. Its formation can be described by the following reaction between dolomite and silica.

$$\underset{\text{dolomite}}{3\,\mathrm{CaMg(CO_3)_2}} + 4\,\mathrm{SiO_2} + \mathrm{H_2O} = \underset{\text{talc}}{\mathrm{Mg_3Si_4O_{10}(OH)_2}} + \underset{\text{calcite}}{3\,\mathrm{CaCO_3}} + 3\,\mathrm{CO_2}$$

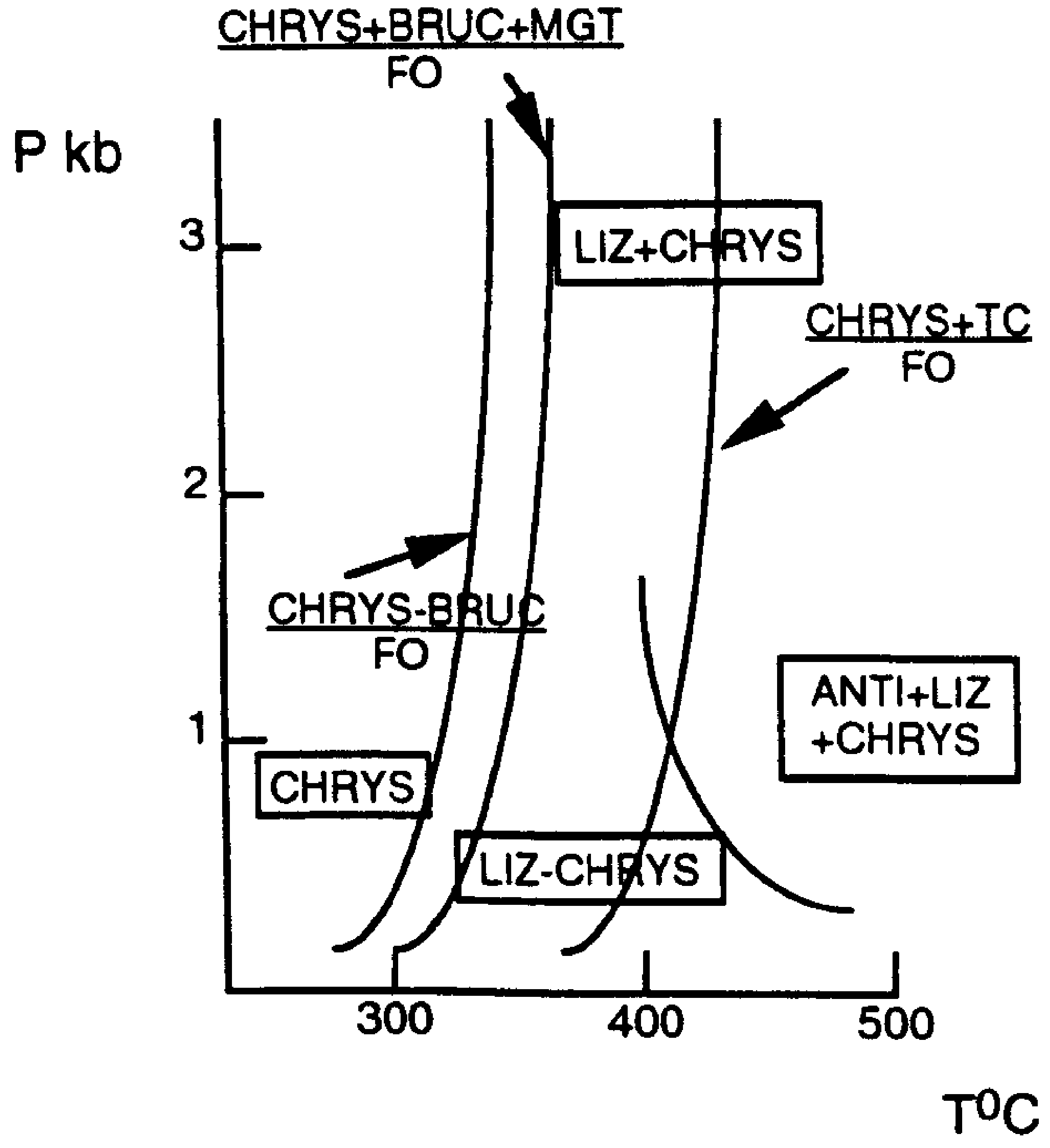
$$\underset{\text{dolomite}}{5\,\mathrm{MgCa(CO_3)}} + \mathrm{H_2O} + 8\,\mathrm{SiO_2} = \underset{\text{tremolite}}{\mathrm{Ca_2Mg_5Si_8O_{22}(OH)_2}} + 3\,\mathrm{CaCO_3} + 7\,\mathrm{CO_2}$$

Talc and tremolite are formed simultaneously as products of decarbonitisation and silicification of dolomite, leading to a talc-tremolite rock with a talc content of 56% by weight (Wiik 1953).

2.2.3 Pressure, temperature, CO_2 conditions of steatisation.

At many localities it has been shown that steatisation occurred subsequent to serpentinisation during periods of greenschist facies metamorphism (Hess 1933 a, b; Du Rietz 1935, Wiik 1953, Naldrett 1966, Nesbitt & Bricker 1978, Park 1983). Although Bowen & Tuttle (1949) and Bennington (1956) have shown that talc is stable at higher temperatures and pressures than serpentine, there is considerable overlap of the stability fields of the two minerals, and such factors as the greater ease of crystallisation of serpentine, and its greater ease of acceptance of replacement ions compared with talc are no doubt important factors that influence the crystallisation of these two minerals. The importance of brucite is that it may define a lower temperature of serpentinisation than by the presence of serpentine alone, figure 2.1

Figure 2.1 Serpentinite polyphase and phases relations in the system $MgO\text{-}SiO_2\text{-}H_2O$ (+FeO) after Chernosky (1973) and Moody (1976).



Chemosky (1973) observed the presence of brucite when antigorite is formed thus emphasising the fact that serpentinisation of ultrabasics and transformation of serpentine minerals is accompanied by CO_2-poor pore fluids. However the hydrous and anhydrous phases cannot co-exist together in equilibrium at low temperatures (Nesbitt & Bricker 1978). Two non-equilibrium models are proposed. Firstly, the dissolution of anhydrous minerals is rapid in comparison to the precipitation of hydrous phases, whereas in the second the converse pertains. On the basis of the available thermodynamic relations, non-equilibrium alteration processes will hold well up into greenschist metamorphic conditions (Nesbitt & Bricker 1978).

Factors other than pressure and temperature must be considered. Greenwood (1967) and Johannes (1969) demonstrated the importance of CO_2 solutions and particularly their effect on the temperature at which talc and anthophyllite form, figure 2.2. The upper limit of steatisation may be defined by the absence of periclase, or its pseudomorphs. A maximum temperature of 600°C may be imposed from the reactions:

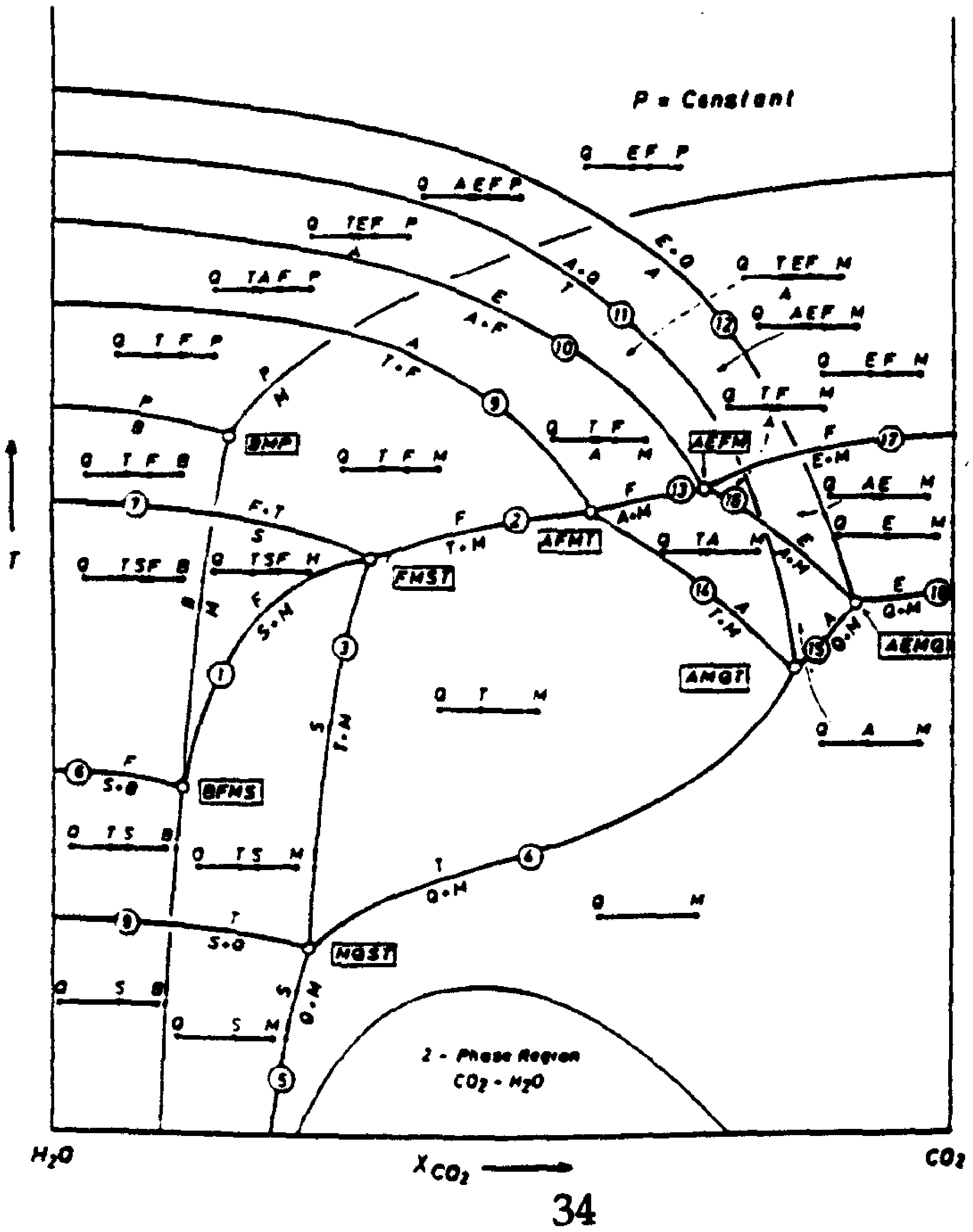
$$\underset{\text{brucite}}{Mg(OH)} = \underset{\text{periclase}}{MgO} + H_2O$$

and

$$\underset{\text{magnesite}}{MgCO_3} = \underset{\text{periclase}}{MgO} + CO_2$$

Johannes 1969, see fig 2.2)

Figure 2.2 A sketch of isobaric invariant points and isobaric univariant curves occurring in the system MgO-SiO_2-H_2O-CO_2 at elevated temperatures and pressures. The mineral phases that can appear in divariant fields are marked on the short horizontal lines with Q and M (or B or P instead of M) as endpoints. Abbreviations: A anthophyllite, B brucite, E enstatite, F forsterite, M magnesite, P periclase, Q quartz, S serpentine, T talc (after Johannes 1969).



The continued stability of talc implies temperatures below 550°C (cf. fig. 2.2). Below the univariant curves for brucite-periclase and magnesite-periclase reactions, the phase relations are dominated by the activity of CO_2 in the fluid phase. Reactions such as

$$\underset{\text{brucite}}{Mg(OH)_2} = 3\,CO_2 = \underset{\text{magnesite}}{MgCO_3} + H_2O$$

and

$$2\,\underset{\text{serpentine}}{Mg_3Si_2O_5(OH)_4} + 3\,CO_2 = \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_4} + 3\,\underset{\text{magnesite}}{MgCO_3} + 2\,H_2O$$

define univariant curves related to CO_2 activity rather than P and T. Furthermore, if carbonatisation of serpentine is considered, a lower maximum temperature must be invoked. This is constrained by the curves for reactions

$$2\,\underset{\text{serpentine}}{Mg_3Si_2O_5(OH)_4} = 2\,\underset{\text{forsterite}}{Mg_2SiO_4} + \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_4} + 5\,\underset{\text{brucite}}{Mg(OH)_2} + H_2O$$

and

$$\underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_4} + 5\,\underset{\text{magnesite}}{MgCO_3} = 4\,\underset{\text{forsterite}}{Mg_2SiO_4} + 5\,CO_2 + 4\,H_2O$$

as forsterite does not form part of most steatite assemblages. On this basis, the maximum temperature during steatisation must not exceed 500°C. A minimum temperature of *c.* 400°C is suggested by the absence of quartz from all steatite assemblages, and following the reaction

$$\underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_4} + 3\,CO_2 = 4\,\underset{\text{quartz}}{SiO_2} + 3\,\underset{\text{magnesite}}{MgCO_3} + 2\,H_2O$$

The higher CO_2 results in an increase in equilibrium temperature with an increase in total pressure and an increase of CO_2 content of the fluid phase. A schematic sketch of isobaric invariant points and isobaric univariant curves occurring in the system $MgO\text{-}SiO_2\text{-}H_2O\text{-}CO_2$ is shown in Figure 2.2.

2.2.4 The role of fluid in steatisation

The source of the hydrothermal fluids in many cases is at present unclear. However in others they are considered to have been derived from within the original precursor ultrabasic intrusion (Hess 1933b), but it seems unlikely that sufficient fluids are available from within most ultrabasic deposits. In other examples an external source seems more likely (Park 1983). Strontium isotope results given in chapter 5 suggest that there is a substantial crustal component to this fluid, even if the original parent ultrabasics have a low strontium concentration. A mantle source was suggested as a possibility by Park (1983), but this seems less likely in many of the British steatites as most are not associated with the large faults seen in Finland by Park.

Talc-quartz assemblages result in an acidic solution capable of producing extensive proton metasomatism in the wall rocks through which they pass. The more common forsterite-talc or forsterite-talc-brucite assemblages result in no or at best very mild degrees of proton metasomatism during cooling. This is not due to the small concentration of HCl in these solutions at higher temperatures, but to the presence of $Mg(OH)_2$ and/or other $Mg^{2+}OH$ complexes in sufficiently high concentrations to neutralise, during cooling, the HCl present in solution at higher temperatures. Ultramafic bodies can therefore be surrounded by zones of hydration, but should not show any signs of proton metasomatism.

Wenner & Taylor (1974) showed that the δD and $^{18}O/^{16}O$ compositions of talc-chlorite-biotite-actinolite from the metasomatic zones that surround antigorite bodies are not greatly different from the antigorite themselves. If this does not reflect uniformity in meteoric water, the isotopic data has been interpreted as agreeing with the geological observations suggesting the development of antigorites and metasomatic products during regional prograde or retrograde metamorphism.

Studies of δD and $^{18}O/^{16}O$ isotopic composition of the fluids produced from slightly altered ultramafic bodies in conjunction with chemical compositions of aqueous solutions issuing from dunites and peridotites (Wenner & Taylor 1969, 1971) suggest low temperature serpentinisation of anhydrous ultramafic bodies is relatively common. Wenner & Taylor (1974) showed that a mineralogically wide range of ultramafics displayed a variation in δD that correlated with geographical position and latitude indicating that meteoric waters were predominantly involved (Sheppard 1986). Overall evidence for the involvement of exchange of meteoric hydrothermal waters together with the evidence of low serpentinisation temperatures strongly supports the idea that the serpentinisation typically occurs at shallow depths, less than 4 kb and less than 200°C . In contrast pure antigorites have a δD similar to the chlorite. Estimates of the isotopic composition of the water involved in this type of serpentinisation are similar to those attained by metamorphic waters below peak metamorphism (Wenner & Taylor 1974).

2.3 Geological Provinces in which Steatite is found in Britain

Potential sources of steatite, within Britain and Scandinavia, occur in a number of distinct geological provinces based upon their lithostratigraphical and tectonic setting. In this study these regions will be referred to as *tectonic environments* although in all cases the groups are not strictly based on the geological tectonic environment of steatite formation, but their lithostratigraphical positions. The British sources are summarised in table 2.1. However in order to understand why these geological regions may result in steatite sources with differing characteristics one must first understand something of the nature of each geological region. The following section summarises current understanding about these regions. A detailed geological description of all British steatite sources is given in Appendix A, based upon sampling work done on these sources.

Table 2.1 Summary of the tectonic environments that contain British steatite sources.

Geological Province	**Steatite Source** **(National Grid References in brackets)**
Lewisian	Eilean Glas, Scalpay [NG 246 948] Scara Ruadh to Dun, Harris [NG 056 884] Loch na h'Oidhche, Sheildaig Forest [NG 895 628] Ardintoul, Glenelg [NG 843 244] Tigh Dhruideig, Glenelg [NG 877 244] Allt Mor, Glenelg [NG 845 168] Allt Dionach-caridh, Sutherland [NC 556 422]
Moine	Shinness, Sutherland [NC 552 139] Druim Klibreck, Altnaharra, Sutherland [NC 605 352] Mudale, Altnaharra, Sutherland [NC 554 358] Glen Urquhart [NH 763 354]
Dalradian	Gorsendi Geo area, Unst [HP 565 044] Clammel Knowes, Unst [HP 586 064] Houllans Ness, Unst [HP 567 054] Wick of Collaster, Unst [HP 596 077] Fiska Wick, Unst [HP 614 156] Cleber Geo, Hillswick Ness [HU 276 749] Orra Wick, Lunning [HU 505 670] Cunningsburgh, Dunrossness [HU 425 271] The Berg, Dunrossness [HU 426 228] Damshead, Portsoy [NJ 575 636] Corrycharmaig, Glen Lochy [NN 622 358] Bolfracks Hill, Aberfeldy [NN 836 477]
Shetland Basement	Fethaland, North Roe [HU 378 943] Pundy Geo, North Roe [HU 377 938] Head of Calster, North Roe [HU 377 878]
Highland Border Complex	Toward/Inellan, Cowal [NS 134 687]
Ophiolite hosted (Shetland) (Anglesey) (Lizard)	Cross Geo, Clibberswick, Unst [HP 652 122] Queyhouse, Unst [HP 614 123] Wick of Hagadale, Unst [HP 641 106] Uyeasound, Unst [HU 599 011] Belmont to Head of Mula, Unst [HU 566 996] Scolla Wick, Unst [HP 634 007] Clemmil Geo, Fetlar [HU 620 905] Dammins, Fetlar [HU 618 903] Leagarth, Fetlar [HU 627 905] Hesta Ness, Fetlar [HU 664 927] Porth-delise, Anglesey [SH 282 845] Gew-graze, Lizard, Cornwall [SW 675 144] Pentreath, Lizard, Cornwall [SW 685 135] Kyanace, Lizard, Cornwall [SW 674 174]

2.3.1 The Lewisian Complex

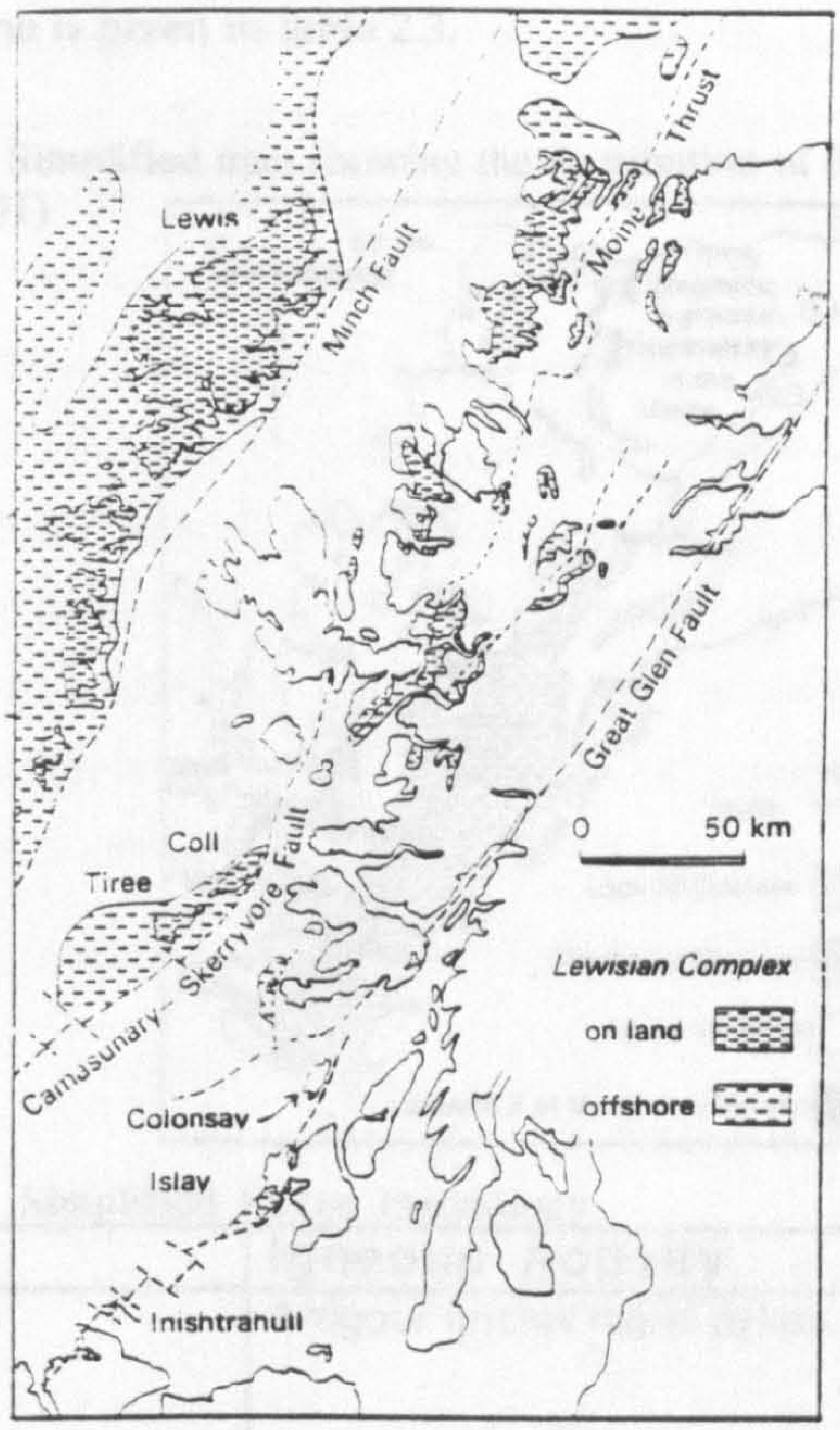
The north-western corner of Scotland has a crystalline basement, the Lewisian Complex, figure 2.3, overlain by undeformed or gently tilted sediments of various ages ranging from late Precambrian (Torridonian) to Mesozoic. This Lewisian basement is a comparatively small part of a very extensive region of Precambrian crust that includes the Laurentian shield of North America, Greenland and Scandinavia. Peach *et al* (1907) established a simple chronological sequence for these rocks, which was later "improved" by Sutton & Watson (1951). Thus a sequence of events was established from protolith formation Badcallian (Scourian) metamorphism, Inverian metamorphism, Scoure dykes and Laxfordian metamorphism. A summary may be found in Park (1991).

Giletti *et al* (1961) provided the first radiometric ages on a variety of Lewisian rocks. Rocks from the Scourian complex yielded Archaean ages whereas in areas of Laxfordian reworking granites, gneisses and the Scourie dykes gave Proterozoic ages ranging from 1 610 Ma to 1 160 Ma. Subsequent geochronological studies have refined this chronology into the following episodes 1) granulite facies (Badcallian) metamorphism in the central belt, amphibolite facies in the north and south, at ~2 700 Ma (Moorbath *et al* 1969, Pidgeon & Aftalion 1972, Hamilton *et al* 1979. 2) the periods of Scoure dyke intrusion at 2 400 and 2 000 Ma (Evans & Tarney 1964, Cohen *et al* 1988, Waters *et al* 1990), 3) Laxfordian granulite injection and amphibolite facies metamorphism at ~1 800 Ma (van Breemen *et al* 1973, Taylor *et al* 1984). A simplified chronology of the Lewisian is given in Table 2.2.

Table 2.2 Simplified Lewisian chronology (Park 1991)

Ga (approx.)	Events
2.9	Formation of early Scourian sediments and mafic/ultramafic igneous rocks (oceanic crust ?)
2.9-2.7	Emplacement of tonalite/granodiorite plutonic complex.
2.7	Badcallian high-grade metamorphism; granulite facies at deep levels, amphibolite facies at higher.
2.5	Post-Badcallian biotite-pegmatites; initiation of Inverian shear zone, associated with uplift and isolation of Archaean blocks.
2.4	Emplacement of early Scourian dykes; continuing Inverian metamorphism ? and shear zone movement.
2.0	Emplacement of later Scourian dykes; formation of Loch Maree Group supracrustal assemblage (crustal extension or transtension).
1.9	Early Laxfordian deformation and metamorphism
1.7	Main Laxfordian deformation and metamorphism, emplacement of Laxfordian granites and pegmatites, and formation of migmatites
1.5	Late Laxfordian retrogressive metamorphism and deformation
1.4-1.1	Late Laxfordian and/or Grenvillian brittle deformation and retrogressive metamorphism

Figure 2.3 Simplified map showing the distribution of the Lewisian Complex.



Lewisian basement is exposed in numerous inliers within the Caledonides of the Northern Highlands. Later modifications produced by Caledonian deformation have obscured many of the original Lewisian features within these inliers, but general petrological and geochemical characteristics of the original rocks can be recognised. An Rb-Sr age of c 2 700 Ma obtained from the Scadroy inlier (Moorbath & Taylor 1975) confirms the Scourian age of the basement. The typical Scourian grey gneisses in the Glenelg district are unconformably overlain by Moine metasediments. Metasediments cut by Scourian type amphibolites indicate that the Glenelg metasediments are part of the Scourian complex. High Na/K ratios and low levels of incompatible elements are among the geological features that characterise the Lewisian.

2.3.2 Moine Supergroup

The Moine Supergroup of the northern highlands of Scotland is usually considered to be predominately metasediments, which lie to the east or south-east of the Caledonian frontal thrust belt, figure 2.4. They unconformably overlie the Lewisian and are older than the Dalradian Supergroup. The Moine must be younger than 1010 Ma, the age of the Glenelg ecologites (Sanders et al 1984), but older than the Ardgour gneiss 876 Ma (Rogers & Paterson unpublished), or ~780 Ma oldest Morarian pegmatite age, see Rogers & Pankhurst (1989) for details. Isotopic ages suggest various orogenic events, a late Proterozoic Grenvillian, the

Morarian c 750 Ma, and later a Caledonian overprint. A summary of the main tectonic events in the Moine is given in table 2.3.

Figure 2.4 Simplified map showing the distribution of divisions of the Moine (adapted from Harris & Johnson 1991)

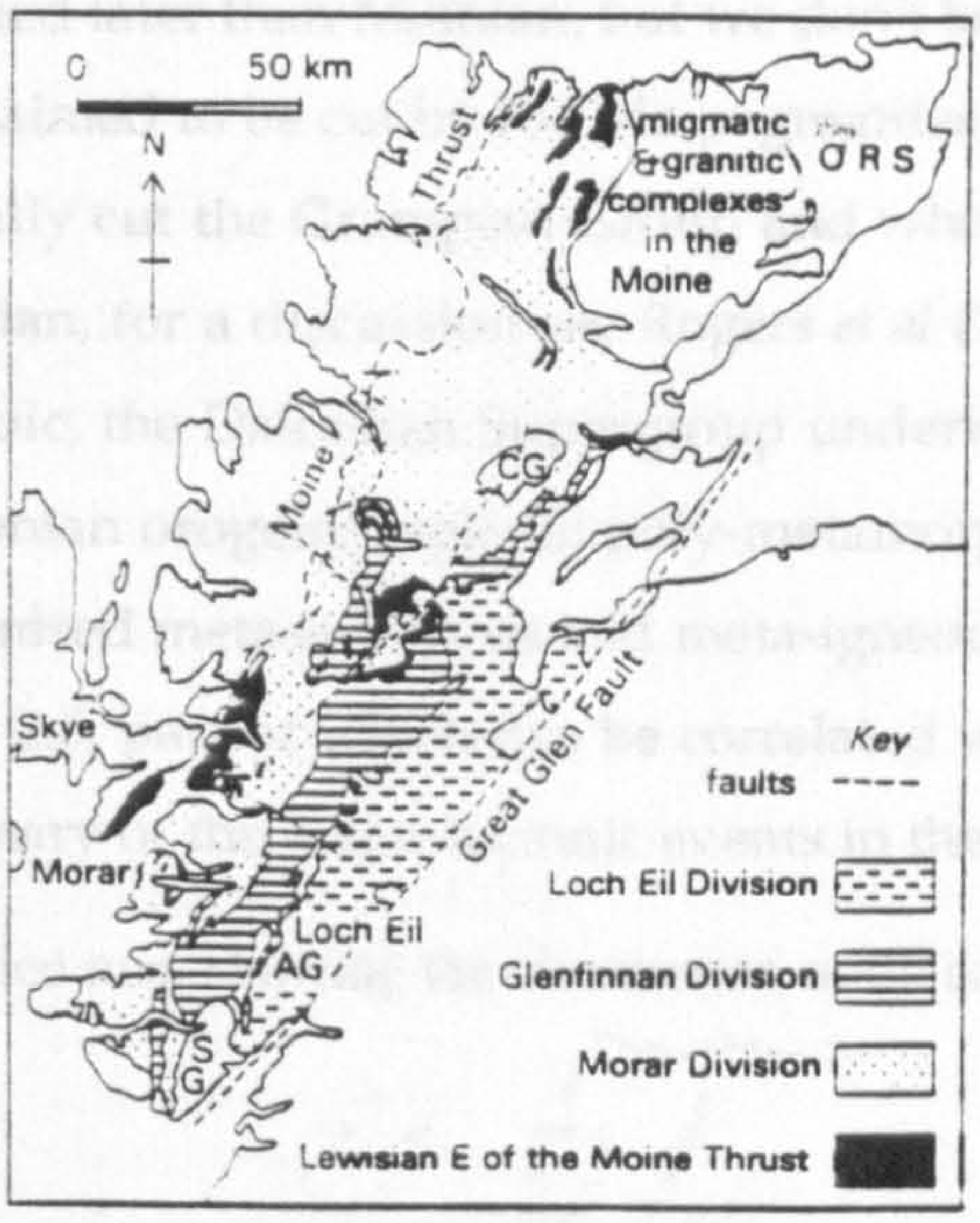


Table 2.3 Simplified Moine chronology

Event	Igneous Activity	Metamorphism
Grenvillian	Ardgour gneiss mafic dykes	Regional high grade metamorphism and migmatisation
Morarian	Local pegmatites (c 760 Ma)	Continued high grade metamorphism
	Strath Halladale (649 Ma), Carn Chuinneag granites [c. 560 Ma]	
Caledonian		High grade regional metamorphism in central N. Highlands, low grade in West.
	Granite and pegmatites (456-440 Ma)	
	Post-tectonic granites (425-400 Ma)	General retrogression

The Moine metasediments have been metamorphosed to lower or upper amphibolite facies, for a summary of dates see Rogers & Pankhurst (1993). These metasediments were emplaced onto the north-west foreland across the Moine thrust belt. All or part of the Moine have been correlated at various times with the Torridonian foreland. Several suites of igneous intrusions cut the Moine, early amphibolites, Caledonian and pre-Caledonian granites and various other minor intrusions.

2.3.3 Dalradian Supergroup

The Dalradian rocks are mostly metamorphosed marine sediments of late Precambrian age. They crop out on the Scottish mainland from the Banffshire coast through the central Highlands into the south-west Highlands, figure 2.5. They are also present in the Shetland

Isles, Islay and Jura. Dalradian evolution is viewed as a rifted margin. Rifting commenced in the late Proterozoic prior to the formation of the Iapetus ocean. Dalradian sedimentation ceased between ~595 and 590 Ma ago (Halliday *et al* 1989, Rogers *et al* 1989) so Dalradian deposition continued later than Moinian, but we don't know the maximun age of Dalradian deposition. It is claimed to be cut by 750 Ma pegmatites, but there is arguement as to whether the pegmatites really cut the Grampian Group and whether the Grampian Group is really part of the Dalradian, for a discussion see Rogers *et al* (1989). During the late Precambrian and early Palaeozoic, the Dalradian Supergroup underwent polyphase deformation and during the Caledonian orogeny regional poly-metamorphism. In east Shetland, Flinn *et al* (1967), have recognised metasediments and meta-igneous rocks, termed the East Mainland Succession, figure 2.6, part of which can be correlated with the Dalradian of mainland Scotland. A summary of the major tectonic events in the Dalradian can be found in Table 2.4.

Figure 2.5 Simplified map showing the distribution of divisions of the Dalradian Supergroup.

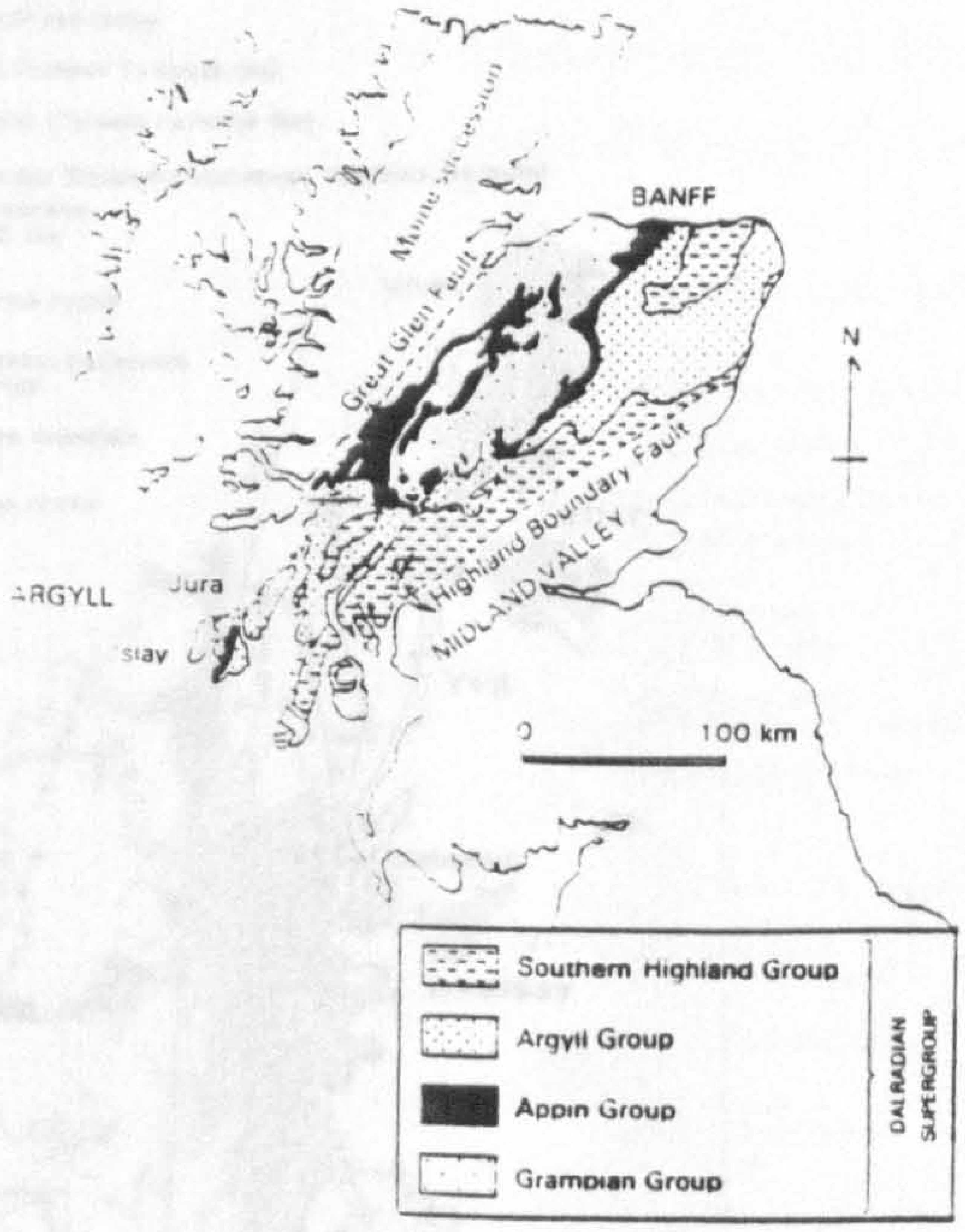


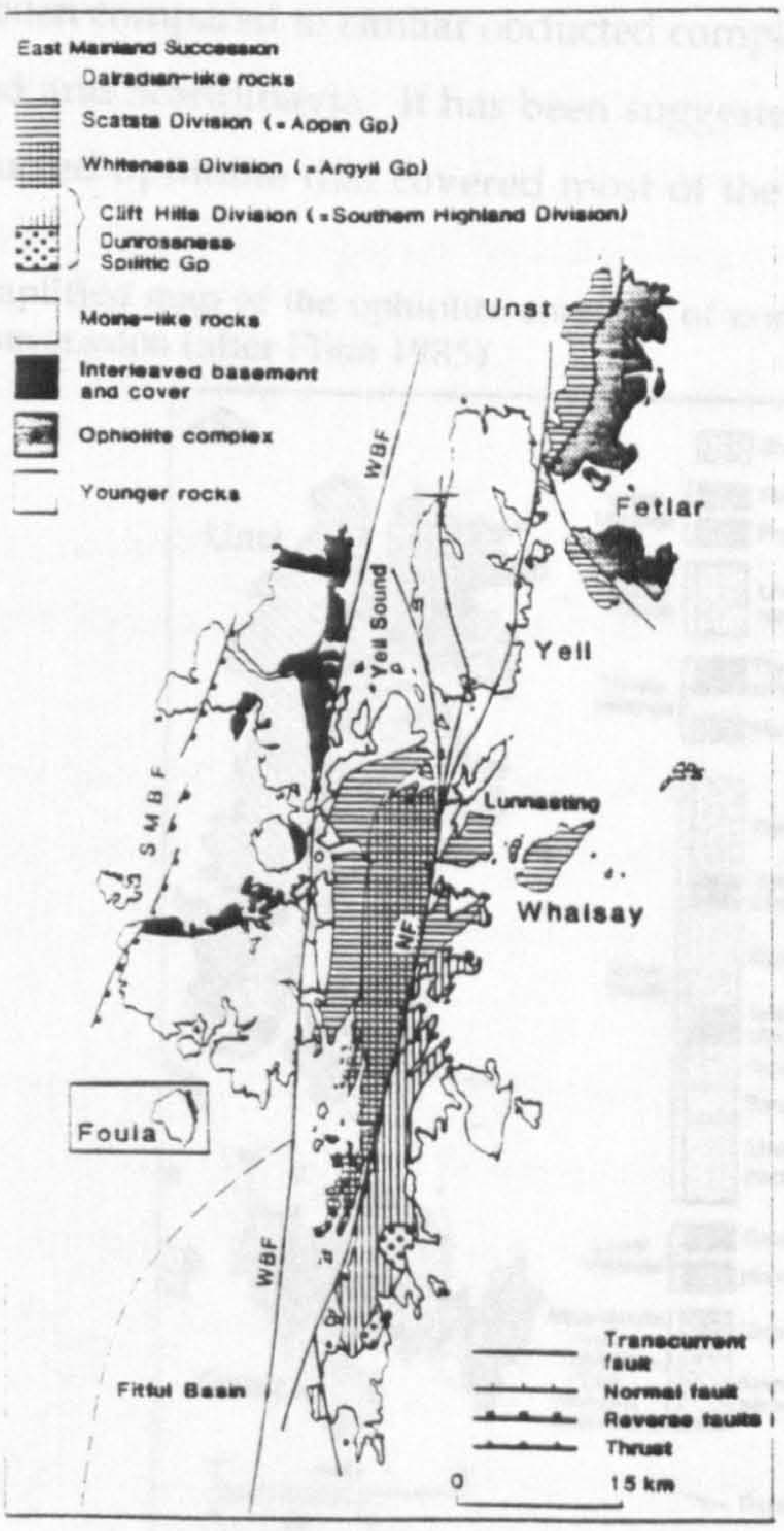
Table 2.4 Ages of metamorphic and related events in the Dalradian

Age (Ma)	Scottish Mainland Dalradian	Shetland Isles
>860		Metamorphism in Walls Metamorphic Series
595	Age of Tayvallich volcanics D_1 and D_2 nappe structures	
590	Ben Vuirich granite. metamorphism and Newer Gabbro intrusions	
ca 540	D3 folding between 590 - 490 Ma	Peak regional metamorphism and migmatisation
490	Peak pressure	Unst ophiolite crystalisation
440-460	K-Ar mica cooling ages and uplift with D_4 structures and Highland Border downbend formation	Ophiolite nappe emplacement
430 - 400	Late granites	
420 - 380		K-Ar cooling ages (420-380 Ma)

2.3.4 The West Shetland Basement

In the north-west of the Shetland mainland to the West of the Walls Boundary fault there are a series of slices of basement and cover rocks. The basement is composed of two types of gneiss: Firstly an acid banded orthogneiss with accessory hornblende. Secondly a banded schistosed hornblende gneiss. The rocks have given a wide range of K-Ar ages, 2313 to 1043 Ma (Flinn *et al* 1979) and their exact tectonic nature is unclear. Miller & Flinn (1966) have interpreted them as a segment of the Caledonide frontal thrust. These basement rocks have been overlain by a series comformable cover rocks, however Flinn (1985) has suggested that in some places the contact may be tectonic.

Figure 2.6 Simplified geolgical map of Shetland (after Flinn 1985).



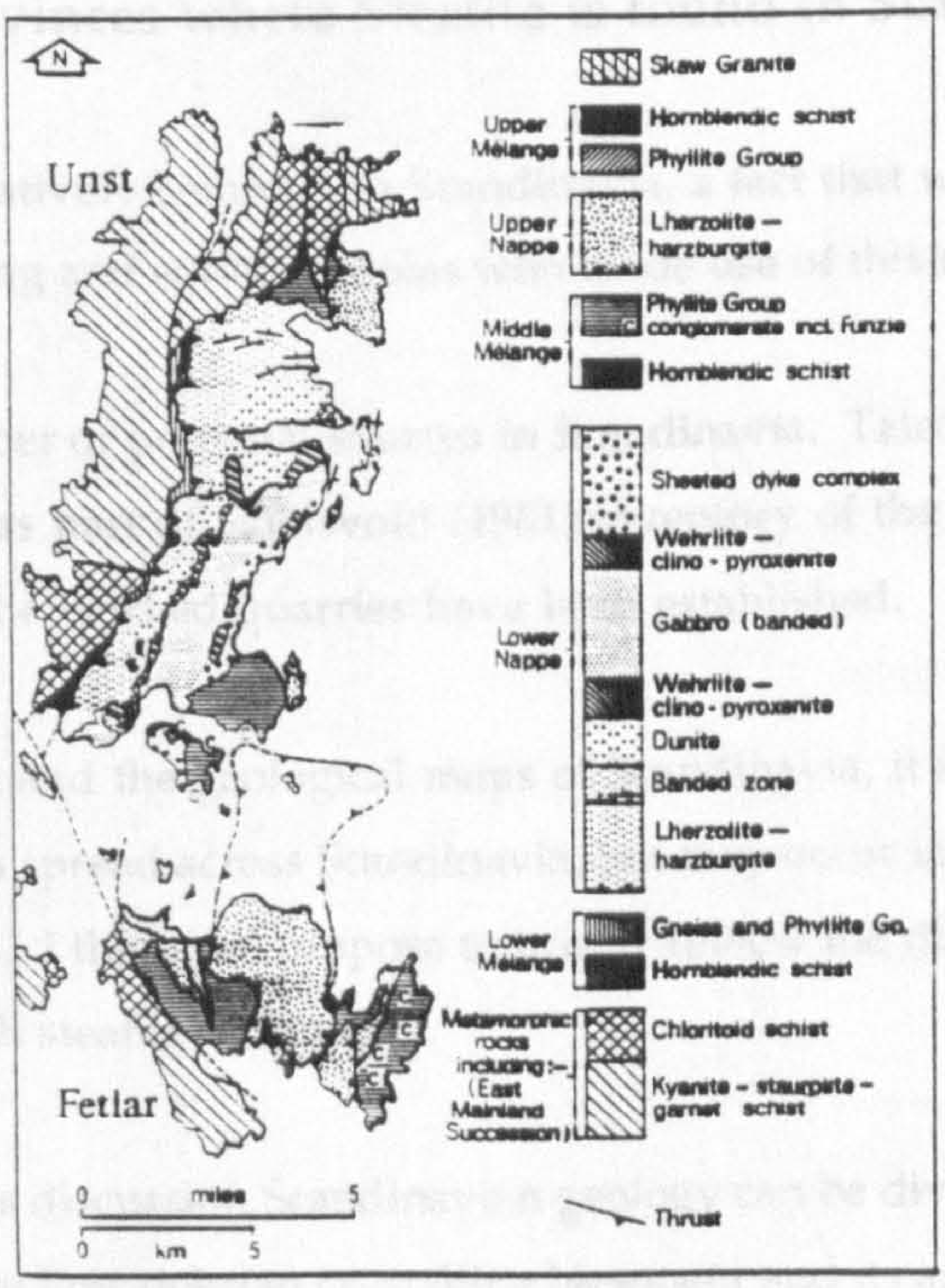
2.3.5 The Highland Border Complex

Along the southern boundary of the Highlands a distinctive suite of rocks is distinguishable from the main Dalradian succession. The rocks of the Highland Border Complex (HBC) are varied in lithology and are found in discontinuous fault-bounded wedges and lenses. Re-examination of structural features led Harte *et al* (1984) to conclude that the deformation history of the HBC was significantly different from that of the Dalradian Supergroup. The HBC faunas confirm the distinction between the two groups (Curry *et al* 1984, Ingham *et al* 1985). It is believed that the complex was floored by an ophiolite, now represented by serpentinites and pillow lavas. These are overlain by marine sediments. The HBC was strongly deformed post late Ordovician and at some stage overthrust by the Dalradian from the North.

2.3.6 Unst Ophiolite, Shetland

The main unit of the Unst ophiolite (an ophiolite complex is part of oceanic crust that has been thrust (obducted) onto the continental margin) is a slice of rock, 6 km wide and over 20 km long, composed of the standard ophiolite sequence; peridotite, dunite , pyroxenite, gabbro, sheeted dyke complex and capped by metamorphosed basic volcanics. This ophiolite complex has been compared to similar obducted complexes such as those found in Newfoundland and Scandinavia. It has been suggested that this formed part of a large 10-15 km thick obducted ophiolite that covered most of the Scottish Highlands, figure 2.7.

Figure 2.7 Simplified map of the ophiolite complex of north-east Shetland in thrust contact with the East Mainland succession (after Flinn 1985)



The ophiolite rocks are not deformed, but have suffered low-grade metamorphism, including serpentinisation, prior to thrusting (Flinn 1985). The emplacement of the lower nappe took place before that of the upper nappe and both nappes must have been transported several kilometres to reach their present position. A crystalisation age of 492 Ma has been suggested by Spray & Dunning (1991). Nappe transport occurred after the high grade metamorphism of the East Mainland Succession (see table 2.4).

2.3.7 The Mona Complex, Angelsey

This complex of rocks contains a volcanic and plutonic sequence of mostly splitic lavas. The trace element composition of the lavas and associated serpentinite mass suggest a Mid Ocean Ridge Basalt (MORB) signature (Thorpe 1972). It has been suggested that this forms part of Eocambrian ophiolite sequence. However, Maltman (1975) has suggested that the serpentinites are an altered magmatic intrusion and not part of the ophiolite.

2.3.8 The Lizard Complex, Cornwall

The complex was interpreted by Strong et al (1975) as a fragment of oceanic lithosphere obducted onto continental crust. The exact age of the Lizard Complex is uncertain. However, from radiometric ages, Sm-Nd 375±34,Ma. a Silurian age for the oceanic crust has been suggested (Davis 1984), which was obducted during the early Devonian.

2.4 Geological Provinces where Steatite is found in Scandinavia

Steatite sources are relatively common in Scandinavia, a fact that was undoubtedly of great importance to the Viking and earlier peoples who made use of this resource.

There are a large number of potential sources in Scandinavia. Talcose rocks that are listed by Holtedahl (1953) and as part of Skjølsvold (1961) inventory of the use of lithic materials, the localities of many of the worked quarries have been established.

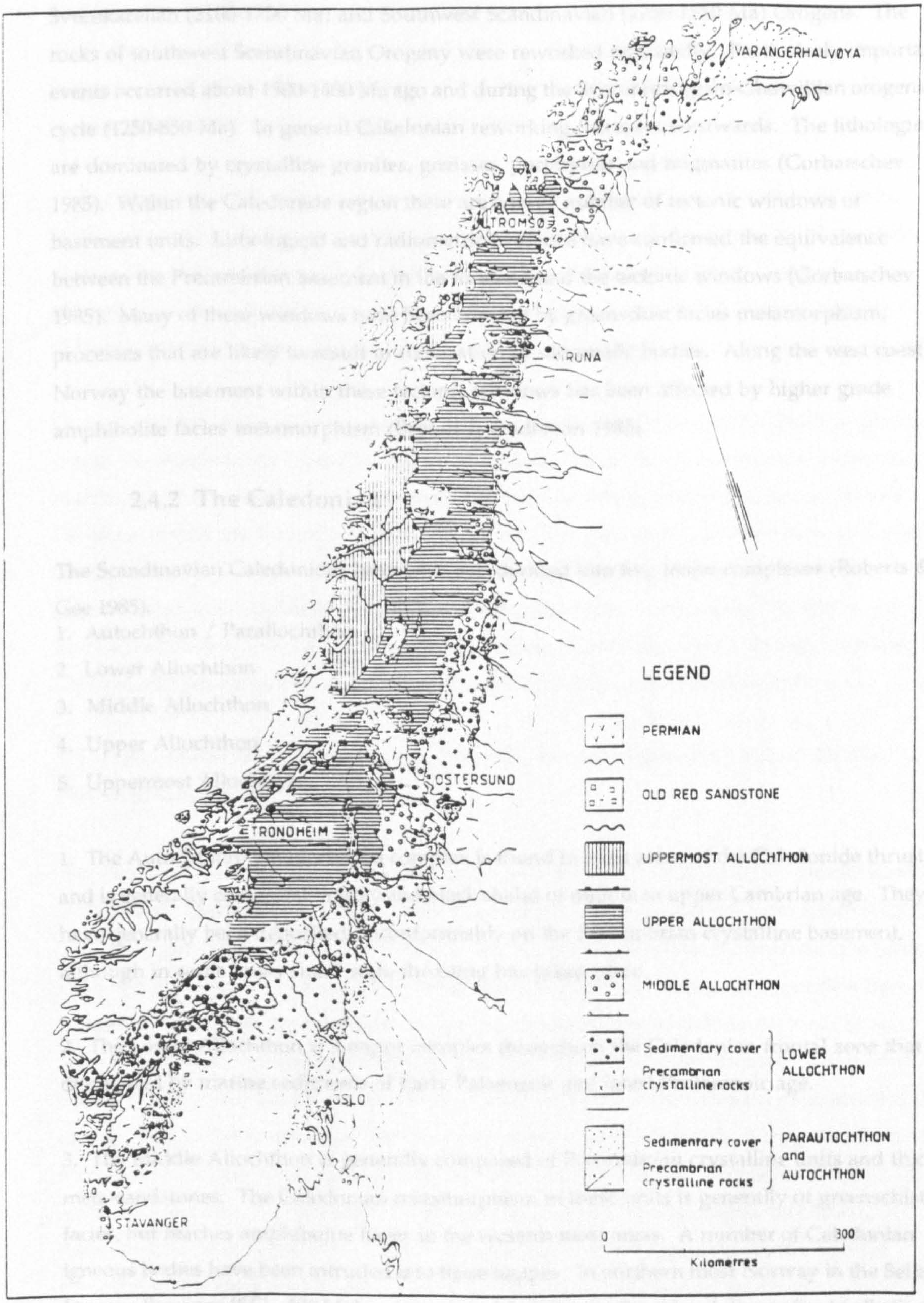
From this information and the geological maps of Scandinavia, it is apparent that not only are the steatite sources spread across Scandinavia, but they occur in a number of different tectonic environments. I therefore propose to briefly review the different tectonic environments in which steatite in found.

For the purpose of this discussion Scandinavian geology can be divided into two distinct regions:

1. The Precambrian crystalline basement and its associated tectonic windows.
2. The Caledonian Nappe Complexes

See figure 2.8 for a simplified tectonostratigraphic map

Figure 2.8 Tectonostratigraphic map of Norway.



2.4.1 The Precambrian basement and its associated tectonic windows.

The Precambrian crystalline basement belongs to the Archaean (3100-2700 Ma), Svecokarelian (2100-1750 Ma) and Southwest Scandinavian (1750-1550 Ma) Orogens. The rocks of southwest Scandinavian Orogeny were reworked repeatedly. Particularly important events occurred about 1500-1400 Ma ago and during the Sveconorwegian-Grenvillian orogenic cycle (1250-850 Ma). In general Caledonian reworking increases westwards. The lithologies are dominated by crystalline granites, gneisses, porphyries and migmatites (Gorbatschev 1985). Within the Caledonide region there are a large number of tectonic windows of basement units. Lithological and radiometric evidence have confirmed the equivalence between the Precambrian basement in the foreland and the tectonic windows (Gorbatschev 1985). Many of these windows have been affected by greenschist facies metamorphism, processes that are likely to result in steatisation of ultramafic bodies. Along the west coast of Norway the basement within these tectonic windows has been affected by higher grade amphibolite facies metamorphism (Bryhni & Anderson 1985).

2.4.2 The Caledonian

The Scandinavian Caledonides have been sub-divided into five major complexes (Roberts & Gee 1985).

1. Autochthon / Parallochthon
2. Lower Allochthon
3. Middle Allochthon
4. Upper Allochthon
5. Uppermost Allochthon

1. The Autochthon/Parallochthon complex is found in most areas of the Caledonide thrust and is generally composed of grey and black shales of middle to upper Cambrian age. They have generally been deposited unconformiably on the Precambrian crystalline basement, although in some areas small scale thrusting has taken place.

2. The Lower Allochthon is a nappe complex throughout the Caledonian frontal zone that is dominated by marine sediments of Early Palaeozoic and latest Proterozoic age.

3. The Middle Allochthon is generally composed of Precambrian crystalline units and thick meta-sandstones. The Caledonian metamorphism in these units is generally of greenschist facies, but reaches amphibolite facies in the western most areas. A number of Caledonian igneous bodies have been intruded into these nappes. In northern most Norway in the Seiland Igneous Province (540 - 500 Ma) an igneous suite ranges from gabbro/ultramafics to alkaline

rocks. These were later deformed during the Finnmarkian events, resulting in alteration products such as steatite.

4. The Upper Allochthon is the most heterogeneous and complexed tectonic unit. The lithologies are dominated by high grade gneisses, schists, amphibolite as well as the fragments of ophiolites and transported island arcs. The deformation history is complex and facies range from greenschist to granulite/ecolgite.

5. The Uppermost Allochthon of the northern part of central Norway is largely gneisses, partly migmatitic and schists psammites. However it also contains fragments of ophiolites, greenstones and serpentinites. These have reached amphibolite facies and many serpentinites show alteration to steatite. Rb-Sr dating of the gneiss has suggested a pre-Caledonian origin, possibly Sveconorweigen (c 1000 Ma) tectonic history (Roberts & Gee 1985).

Of these separate tectonic areas a number are important sources of steatite. Steatite occurs within the Precambrian crystalline basement and associated tectonic windows; within the Middle Allochthon associated with metamorphosed ultrabasics and the Seiland Igneous Province; within the Upper Allochthon associated with the ophiolite fragments; and within the Uppermost Allochthon allied with the ophiolites. Thus it can be recognised that steatite occurs in a number of distinct tectonic regions within Scandinavia. However, the exact age of steatisation is not known although there is probably a large time gap between the Precambrian basement steatites and the steatites within the Caledonian belt.

2.5 Discussion of Provenancing Techniques and how they relate to the Physical Characteristics of Steatite.

The use of petrological and geochemical techniques in characterising source material is now widespread. Geochemical methods have frequently used trace elements in an attempt to produce a geochemical "fingerprint" of the source material, and thus by comparing artifacts of unknown provenance to the source signature the unknown maybe assigned a specific origin. In the past steatite provenance studies have used relatively simple techniques, such as hand specimen comparison, optical mineralogy and XRD, to characterise different sources. As Buttler (1984) points out the comparison of hand specimens of steatite is very subjective and cannot be regarded as conclusive proof of provenance. Lithic materials, such as obsidian, are sometimes relatively homogeneous in character. This allows small samples to be taken from source site to reflect the character of the source as a whole. This homogeneity of source material is ideal for relatively simple techniques such as petrography. By the careful description of textures and mineral assemblages a source may be assigned certain characteristics. However, metamorphic rocks such as steatite and marble have undergone complex formation processes that often, as can be seen from the description of the various bodies, produce inhomogeneous bodies. In the case of steatite, the source bodies are often zoned, with a gradational change across the body. These inhomogeneities within the sources make characterisation using petrography virtually impossible. In order to be useful in characterisation of a source material the technique used must reveal differences between different source localities. In many cases the processes in the formation of steatite result in very similar bodies. Thus petrographic description may not reveal any differences between different sources.

Elemental studies may be more likely to give a unique signature for source materials. The inhomogeneous nature of the material will be problematic when major elements are considered. The major elements are contained within the different mineral phases and as these mineral phases vary across zoned bodies the corresponding elements will vary. Curtis & Brown (1969) showed how in a model system, Mg decreased towards the edge of the body whereas Si and Al increased markedly and Ca and K increased slightly. This may also lead to problems when sampling artifacts, as a small sample size may give an unrepresentative sample, due to a particular mineral phase being preferentially sampled. Obviously large samples in order to homogenise any inhomogenities are impractical when dealing with artifact material.

Trace elements may be of more use in steatite characterisation. Although some elements are phase dependant, such as Zr and Hf which are largely concentrated in zircon, others, such as the Rare Earth Elements (REE), are more evenly distributed between the phases present in most steatites (Williams 1977, Henderson 1982). These and other trace element groups such as the Platinum Group Elements (PGE) and other less phase dependent elements may be able to discriminate between different steatite sources. An advantage of using REE and PGE is that although absolute concentrations may vary across a body their chondrite normalised pattern may remain essentially unchanged as these are process derived, and the processes will remain constant across the relatively small extent of most steatite deposits. Hence the chondrite normalised pattern maybe a suitable provenancing parameter rather than the absolute concentration. Also it has previously been established that steatite is formed by the interaction of a metasomatic fluid and an ultrabasic deposit. It is proposed that groups of trace elements, due to their geochemical behaviour, may characterise this fluid and the precursor ultrabasic body. Trace elements that are readily soluble, under the conditions of steatisation, in a metasomatic fluid, such as Rb, Cs, Ba and Pb, may characterise the fluid, while those that are insoluble and immobile, such as REE, Zr, Hf and Th, may characterise the precursor ultrabasic body.

Other possible areas that might enable suitable steatite source characterisation are isotopic studies. Steatite deposits are located in several distinct geological provinces, both in Britain and Scandinavia. Isotope techniques such as $^{40}Ar/^{39}Ar$ and Sm-Nd are dependant on the geological age of the steatite deposit. The age these methods give, whether it is the age of steatisation or the age of the ultramafic precursor formation or magma partition from the mantle, is dependant on the characteristics of that particular isotope system. However, these ages will probably be relatively consistent within individual geological provinces and sources, yet significant differences exist between the ages of the geological provinces. Thus isotopic dating techniques have much to offer steatite provenance studies.

Other isotope techniques, such as $^{87}Sr/^{86}Sr$, Pb isotopes and stable oxygen and hydrogen are dependant on the interaction of the ultramafic precursor and the metasomatic fluid. These interactions between different parent bodies and different fluids will probably result in differences in these isotopic systems hence enabling precise characterisation of the source or source region.

Thus there are several possible techniques that might enable steatite source characterisation, from broad elemental characterisation of geological provinces by both trace element and isotope techniques, to more source specific characterisation by chondrite normalised REE and PGE, and other isotopic methods. This study after identifying all known British sources aims to investigate several of the possible methods that ultimately may enable artifacts to be compared to sources and thus allow archaeological interpretation of the results. Firstly, by the use of the multi-elemental capabilities of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and the use of a rigorous and structured statistical analysis of the data, the large number of trace elements that can be analysed will be assessed in order to identify if any of these elements is able to discriminate between steatite sources. Secondly, the low detection limits of the ICP-MS will allow the investigation of the ultra-trace REE concentration known from most steatites. Other techniques; Sr, Ar, Pb isotopes will also be considered as these may display differences between different sources.

CHAPTER 3: THE USE OF MULTI-ELEMENT ICP-MS ANALYSIS AND STATISTICAL METHODS TO ESTABLISH GEOCHEMICAL DIFFERENCES BETWEEN STEATITE SOURCES.

3.1 Introduction

Having established the archaeological relevance and potential geochemical approaches of discriminating between sources, this chapter presents a systematic investigation of the use of ICP-MS trace element analysis as a first step towards a solution of the problem.

These analyses are believed to be among the first to utilise ICP-MS for a systematic archaeological provenance study. Representative samples from all British sources were analysed in multi-element mode for 68 major and trace elements. Within this study the steatite provenance problem has been approached from two principal directions; the use of an informed geochemical approach in the selection of elements that are considered potentially useful in separating sources and the use of a rigorous statistical analysis of multi-element ICP-MS data. The aims of this statistical investigation of the source data were to establish the geochemical differences between steatite sources and groups of sources; the identification of elements with discriminating potential; the examination of the geochemical behaviour of the trace element systems; and the examination of ICP-MS performance. All these aims will further enable the identification of elements for further more precise analysis.

In order to fulfil these aims an analytical procedure had to be developed and validated. Steatite and similar materials have not previously been analysed using dissolution methods. Therefore sample dissolution techniques had to be developed that were compatible with the ICP-MS. The ICP-MS reproducibility was characterised over the period of the analyses.

In chemical characterisation studies using multi-elemental techniques such as ICP-MS substantial volumes of data may be generated with complex relationships between analytical variables. A systematic approach to data analysis is required to enable an objective interpretation to be made. It is notable that the ICP-MS with up to 68 elements produces considerably more trace element data for each sample than other analytical approaches, and that there is a more consistent error structure to such results. This lends itself well to multivariate statistical methods, whose underlying assumptions are possibly not violated in the manner that may occur with analytical data from methods with less predictable error structures. This study, through the multi-element ICP-MS data sought to rigorously examine the statistical techniques used in most provenance studies. This is considered to be an example of the structured use for statistical methods of analysis of large multi-element data sets. A structured approach utilising initial data screening, univariate, bivariate and a range of multivariate techniques will be discussed and the potential use of individual techniques in relation to provenance studies evaluated. The extent to which the different methods have been successful in relation to the steatite provenance problem will be further discussed.

The following sections include: samples used in the study, the operations of the ICP-MS, dissolution of these samples, the analytical precision over the period during the analysis, statistical techniques used and the applications of these methods to the steatite data set.

3.2 Samples

In the previous chapters all the steatite sources in Britain were identified. It can be demonstrated that these sources are from four separate tectonic regions. This study sought to demonstrate if any differences could be identified between sources from these tectonic regions. If differences could be identified, artifacts could be related to these geological regions.

A set of 132 samples including replicates was formed as follows; seventeen samples representing a cross section of British sources and an additional five samples from a single quarry, each sample was replicated six fold. These were to provide an exploratory collection with which to establish any major differences between the different geological tectonic groups. Samples were taken from each of the four major tectonic regions in Britain where steatite occurs. The number of samples from each region reflects the number of quarries within that tectonic region and are as follows; three Lewisian, six Dalradian, two Shetland basement and six ophiolite. A further five samples were taken from a single site in order to characterise the within site variability. Cunningsburgh is probably the largest steatite quarry in Britain and therefore was chosen for this intra site characterisation. Cunningsburgh was included to give an indication of the spread of the data within a single source quarry. Clearly this would not be possible for all sources due to cost, time and ICP-MS availability. If this intra-site variability was found to be relative small for a given variable then clearly if this variable also demonstrated differences between source greater than this internal variation then a more site specific provenance may be possible. These samples were further used to define the Dalradian source region. Control samples of Shap granite were included in each run.

The samples were cleaned of all weathered material with a diamond saw to obtain clean blocks of approximately 100g. These were then crushed and milled to 150 μm. 200 mg samples to be used in the analysis were further ground to 53 μm using an agate mortar and pestle.

3.3 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

The ICP-MS is described in Appendix B, including a full description and operating condition of sample introduction, the inductively coupled plasma, ion extraction, ion focussing/mass analysis/detection, plasma ion population and system response background and peak interferences, continuum background and background peaks, oxide and doubly charged species, polyatomic ion formation, isobaric overlap, non-spectroscopic interferences. The range and combination of elements that can be analysed by ICP-MS is very broad. Modern instruments provide the possibility for the simultaneous determination of most elements in the periodic table at major, trace and ultratrace levels. However, there are a number of limitations that restrict those elements that can be measured simultaneously in a single solution. For example some volatile trace elements may be lost during sample preparation, see section 3.4, and therefore may not be available for determination. The preferred isotopes for elemental determination and the ones used in this study are given in Table 3.1.

Table 3.1 Preferred isotopes for elemental analysis (adapted from Jarvis et al 1992).

Element	Preferred (m/z)	Abundance (%)	Comments and interferences
Li	7	92.2	Most abundant free isotope
Be	9	100	Mono-isotopic
B	11	80	Most abundant free isotope
Na	23	100	Mono-isotopic
Mg	24	79	Most abundant free isotope
Al	27	100	Mono-isotopic
Si	29	4.7	NH, dissolution problems
P	31	100	NO, NOH
S	33	0.75	O_2H, digestion is unclear
Cl	35	76	Poor sensitivity, dissolution problems
Ca	44	2.08	N_2O
Sc	45	100	CaH
Ti	47/49	7.3/5.5	SOH, CaH
V	51	99.7	ClO
Cr	52/53	83.8/9.5	ClOH
Mn	55	100	Mono-isotopic
Fe	56/57	91.7/2.2	ArO, ArOH
Co	59	100	Mono-isotopic
Ni	60	26.1	Most abundant free isotope
Cu	63/65	69.2/30.8	Average isotopes
Zn	66/68	27.9/18.8	S_2
Ga	71	39.9	^{139}Ba
Ge	72/73	27.4/7.8	FeO, FeOH, FeO
As	75	100	Mono-isotopic
Se	77	7.6	ArCl, digestion unclear
Br	79/81	50.7/49.3	Average
Rb	85	72.2	Most abundant free isotope
Sr	88	82.6	Most abundant free isotope
Y	89	100	Mono-isotopic
Zr	90	51.4	Average, dissolution may present problems
Nb	93	100	Mono-isotopic
Mo	95	15.9	Most abundant free isotope, digestion unclear
Ru	99/101	12.7/17	Average
Rh	103	100	Mono-isotopic
Pd	105	22.3	Most abundant free isotope
Ag	107/109	51.8/48.2	Average, dissolution may present problems
Cd	111	12.8	Most abundant free isotope
Sn	118	24.2	Most abundant free isotope

Table 3.1 cont. Preferred isotopes for elemental analysis (adapted from Jarvis et al 1992).

Sb	121	57.3	Most abundant free isotope
Te	125	7.1	Most abundant free isotope
I	127	100	Mono-isotopic, problems with dissolution
Cs	133	100	Mono-isotopic
Ba	137	11.2	Most abundant free isotope
La	139	99.9	Most abundant free isotope
Ce	140	88.5	Most abundant free isotope
Pr	141	100	Mono-isotopic
Nd	143	44.4	Most abundant free isotope
Sm	147	28.8	Most abundant free isotope
Eu	151/153	47.8/52.2	Average
Gd	157	15.7	Most abundant free isotope
Tb	159	100	Mono-isotopic
Dy	163	24.9	Most abundant free isotope
Ho	165	100	Mono-isotopic
Er	166/167	56.3	Average
Tm	169	100	Mono-isotopic
Yb	172/173	38.1	Average
Lu	175	97.4	Most abundant free isotope
Hf	178	27.9	Most abundant free isotope, possible dissolution problems
Ta	181	99.9	Most abundant free isotope
W	182	26	Most abundant free isotope
Re	185	37.4	Most abundant free isotope
Os	189	16.1	Most abundant free isotope
Ir	193	62.7	Most abundant free isotope
Pt	194/195	32.9/33.8	Average
Au	197	100	Mono-isotopic
Hg	202	29.8	Most abundant free isotope, problems with dissolution
Ti	205	70.5	Most abundant free isotope
Pb	208	98	Most abundant free isotope
Bi	209	100	Mono-isotopic
Th	232	100	Mono-isotopic
U	238	99.3	Most abundant free isotope

Table 3.2 gives the instrument operating conditions for multi-elemental semi-quantitative analysis.

Table 3.2 Instrumental operating conditions for multi-elemental determination

Forward power	1300 W
Reflected power	< 5 W
Nebuliser gas flow rate	0.751 min-1
Coolant gas flow rate	131 min-1
Auxiliary gas flow rate	0.5 l/min-1
Sample uptake rate	1 ml min-1
Nebuliser	De Galan / Meinhard concentric
Spray chamber	Scott double pass water cooled
Scan range	4 - 240 amu
Number scan sweeps	400
Dwell time	160 μs
Number of channels	1024
Points per peak	5
Sweeps results averaged from	3

3.4 Sample Dissolution

Despite considerable new research on sample introduction techniques, solution nebulisation remains the preferred method for routine ICP-MS analysis. Therefore dissolution of samples is a pre-requisite for routine analysis. The considerable importance of dissolution has been recognised by the inclusion of the successful techniques as procedures in Appendix F.

For semi-quantitative multi-element analysis the primary objective was to develop a consistent and reproducible method of sample dissolution. Since absolute standards were not used in the development of these techniques the criterion used for an acceptable digestion procedure was the elimination of visible insoluble residues. International standard reference materials used in the quantitative analysis support the conclusion that total digestion was achieved.

A sample weight of 200 milligrams from the 100 gram homogenates was considered to be a reasonable compromise between the requirements of trace element analysis and the amount of material that would be required from artifact samples. All samples were weighed out in the various digestion vessels used in this study.

Several separate techniques were examined in an attempt to produce a rapid method that resulted in total dissolution. In order to characterise the whole sample it was considered that total dissolution was required. However, the rapid methods of sample dissolution investigated initially left insoluble minor residues. Although these residues contributed only a small percentage of the total mass of the sample, they could have contained phases that formed significant proportions of individual elements. It is recognised that a case could be made for excluding these minor constituents, or analysing them separately since under these circumstances sub-sampling errors may lead to poor precision in total analysis. However, in the development of dissolution techniques reliable total dissolution was considered to be a prerequisite to the investigation of alternative approaches and therefore efforts were made to achieve total dissolution.

In all the approaches investigated hydrofluoric (HF) and nitric mixtures were used in the initial phase of dissolution. This resulted in a more stable solution than would have been obtained with HF alone, since fluorosilicic acid tends to hydrolyse and precipitate on standing or dilution. HF is not a suitable reagent alone as some of the salts (e.g. K and Ca) do not have high solubilities in this acid, therefore it is normally mixed with perchloric or in this case nitric acid. There is some discussion in the literature about optimal combinations of acid mixtures and the role of the second mineral acid. Langmyhr & Sveen (1965) have questioned the role of the second mineral acid and suggested that in some circumstances that HF alone was more effective. If anything, adding the second mineral acid to the sample first makes the initial mixing safer, allowing more reactive minerals to react before adding the HF. In some cases it has been suggested that a small quantity (<10% of the total dissolution) avoids the formation of insoluble fluorides within reaction vessels. Samples were volatilised under heat lamps allowing the removal of Si and F, so reducing the salt content and producing a far more stable solution. However, Potts (1987) suggests that other volatiles such as B, Hg, Se and Sb may also be lost.

Initially microwave dissolution was attempted as this would provide a very rapid means of dissolution. Standard methods used for rock dissolution were undertaken, 5 ml of 40% HF and 1 ml of 14M HNO_3 were added to the sample in a Savillex® microwave digestion bomb. The sample was then taken to dryness, 5 ml of 14M HNO_3 was then added before the sample was evaporated to dryness again. Several series of digestions were conducted using many combinations of HF HNO_3 and HCl in varying quantities and in a number of different microwave exposure cycles. However, none of these procedures was totally successful in eliminating insoluble residues. Examination of these residues by XRD demonstrated that the black residue was magnetite and a white residue was non-mineralic, magnesium and aluminium fluorite along with another unidentifiable substance. It was also noticed that some precipitation of salts occurred when samples were re-dissolved in weak (5%) HNO_3. Because of these problems and the desire to make the most productive use of the available ICP-MS time it was decided to investigate sealed digestion methods.

Sealed vessel dissolution methods have been used for many years although they have been regarded as time consuming and potentially dangerous. However, they have a number of advantages compared with open vessel digestion:

1. Higher temperatures are reached as the boiling point of the reagents is raised by the increased pressure within the vessel.
2. Volatile elements such as B, Cr, Hg, Sb, Se, Sn will remain within the vessel, allowing retention in solution.
3. Smaller reagent volumes are required, thus reducing the blank levels.

The first approach investigated dissolution using steel pressure bombs with an inner PTFE beaker and lid. Samples were weighed directly into the digestion vessel. The outer jacket had a screw top which, when tightened, formed a gas tight high pressure seal between the PTFE beaker and it's lid. These were filled with 5 ml of 40% HF and 1 ml of 14M HNO_3 (approximately 20% of the vessel's volume) then placed in an oven for five days at 220°C. After cooling, the sample was taken to dryness under heat lamps. The salts were then re-dissolved in 5 ml of 14M HNO_3, put back in the oven for 24 hours and taken to dryness again. Under these conditions pressures of 70-120 atmospheres may be achieved within the bombs (Potts 1987). Under these hostile conditions total dissolution was achieved and fluorides were not produced.

However, this method did take relatively long periods of time as the steel bombs must be cool before opening. Therefore it was decided to investigate the use of sealed vessels on a hotplate.

The final method attempted used PTA teflon screw-top beakers (Savillex). Samples were weighed directly into the digestion vessel. These 50 ml beakers were filled with 1 ml of 14M HNO_3 and approximately 8 ml of 40% HF, sealed and left to boil on a hot plate for 72 hours. They were then removed, cooled, and dried down under lamps. To minimise fluoride formation, a drop of HNO_3 was added to the HF/HNO_3 mixture when it had nearly reached dryness. The residue was then re-dissolved in 5 ml of 14M HNO_3 and replaced on the hot plate for a further 24 hours, then evaporated to dryness for a second time. Next the samples were taken up in 5 ml of 6M HCl and put on the hot plate for 12 hours, before removal and evaporation to dryness again. This method produced total dissolution for all samples with no problems of fluoride formation. Finally the samples were easily redissolved in 5% HNO_3 in a form compatible with ICP-MS introduction. Analysis of standard reference materials confirmed that total dissolution had been achieved.

3.5 Results

The ICP-MS multi-element semi-quantitative results for 68 elements from the 132 samples, blanks and controls, are given in Appendix C. Blank subtraction was performed on all samples. A data capture programme was written to translate the format of the VG Plasma-Quad semi-quantitative multi-elemental report files into a matrix form, suitable for manipulation by a PC and transfer to the University of Glasgow mainframe (VME) for statistical analysis.

The statistical analysis of the data is presented in the following sections. Firstly, precision evaluation of the ICP-MS during the period of this study will be discussed. Data screening was then undertaken in order to check for completeness and consistency. The bulk of the statistical analysis is divided into two sections; univariate/bivariate analysis, and multivariate analysis. In each of these sections the methods used will be presented followed by the data analysis. The sections are concluded by an evaluation of the techniques utilised. The implications of the results for the provenancing of steatite are discussed in a final section.

3.6 Control Samples and Precision Evaluation

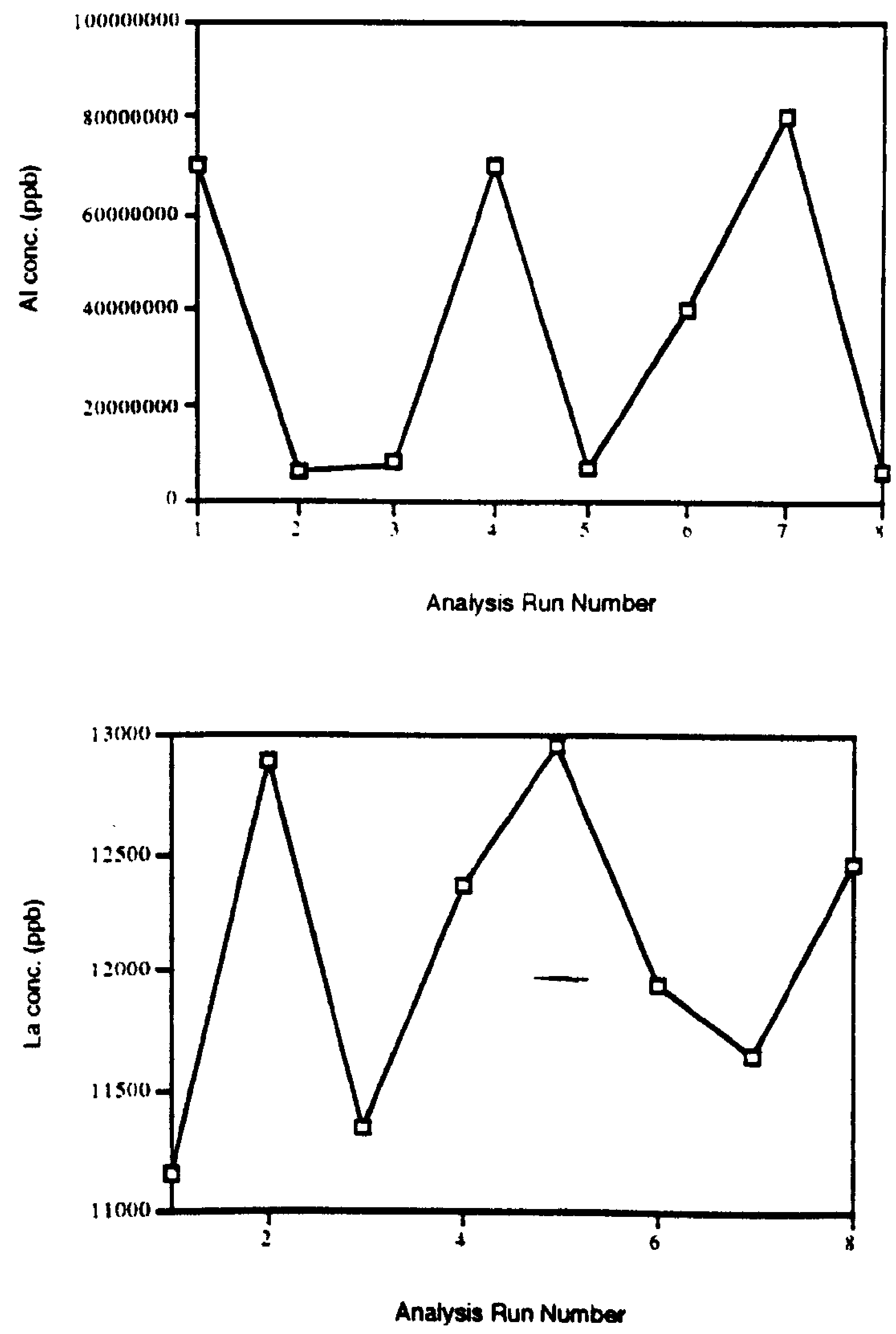
The bulk of the analysis in this study was carried out over a period between July 1991 and December 1992. During this period an internal control sample of Shap granite was included with each batch of samples being prepared and analysed with each multi-element ICP-MS run. This has allowed a long term assessment to be made of the precision of the complete analytical methods over the 18 month period of this suite of analyses. The control sample data can be found in Appendix C. The data were analysed to examine the run variability in a standard material. Table 3.3 shows the coefficient of variation of these control samples. A number of elements showed a greater standard deviation than the mean result. These elements demonstrate high analytical variability due to a number of factors discussed in section 3.2.1, and may obscure any meaningful results. In order to demonstrate that variations in measured values were not a product of machine changes through time, several elements, with high and low precision, were plotted over the time period of analysis, figures 3.1. These graphs demonstrate that variations in analysis concentration are not a product of an instrumental change through time. It was expected that elements with high concentrations, hundreds ppm and greater, would give poor precision due to ion counting saturation by such concentrations. In ICP-MS used for this study the response of signal versus concentration is typically linear over 6 orders of magnitude. New generation machines are equipped with dual counting mode, thus enabling a linear response over 8 orders of magnitude, hence a linear response calibration may be generated up to about 500 ppm (Jarvis et al 1992).

For this reason and because major elements were not expected to characterise different steatite sources most of the major elements have been largely excluded from any further analysis. Other elements, such as many of the platinum group elements, occur in very low abundances, making precise analysis difficult without pre-concentration. Elements further from the internal standard used, In, also display lower precision. However, a large number of elements were measured with reasonable precision; 20 with coefficients of variation of less than 10%, and 34 less than 20%. Multi-element semi-quantitative analysis is claimed by the manufacturer to have a precision of around 20 - 30% (Date & Gray 1989), however this and other studies (Taylor & Garbarino 1988) have shown that this figure varies considerably from element to element depending on the abundance of the specific isotope being monitored for the determination. This analysis has allowed the identification of elements that can be measured with a reasonable degree of precision by ICP-MS, thus allowing these elements to be used in the analysis of steatite sources.

Table 3.3 Summary of Control sample results

Element	mean (ppm)	Standard Dev.	Co. of variation
LI	157.366	45.312	28.79
Be	4.001	1.760	43.98
B	60.597	79.859	131.79
Na	28977.487	14786.113	51.03
Mg	1875.487	927.605	49.46
Al	44470.214	87965.875	197.81
Ca	6379.142	5136.933	80.53
Sc	3.249	2.334	71.85
Ti	147.001	25.894	17.61
V	32.860	3.846	11.70
Cr	130.954	52.735	40.27
Mn	164.044	141.306	86.14
Fe	6561.107	3789.547	57.76
Co	6.401	1.306	20.41
Ni	845.157	246.322	29.15
Cu	10.818	0.605	5.59
Zn	43.150	1.424	3.30
Ga	24.600	1.304	5.30
Ge	1.483	0.061	4.09
As	1.019	0.140	13.75
Se	1.214	0.369	30.39
Br	0.174	0.233	134.13
Rb	111.873	10.511	9.40
Sr	138.326	11.831	8.55
Y	1.876	0.314	16.77
Zr	80.288	18.930	23.58
Nb	9.209	0.400	4.35
Mo	1.321	0.341	25.79
Ru	0.005	0.002	31.30
Rh	0.002	0.001	65.49
Pd	1.166	0.422	36.20
Ag	0.339	0.149	44.04
Cd	0.253	0.113	44.43
Sn	5.023	0.554	11.03
Sb	0.095	0.008	8.86
I	0.330	0.448	135.60
Te	0.028	0.013	46.21
Cs	3.042	0.187	6.14
Ba	390.754	46.373	11.87
La	12.048	0.721	5.98
Ce	25.170	2.996	11.90
Pr	3.356	0.045	1.33
Nd	12.522	0.254	2.03
Sm	2.170	0.079	3.65
Eu	0.578	0.061	10.64
Gd	1.494	0.049	3.29
Tb	0.186	0.011	5.74
Dy	0.883	0.060	6.85
Ho	0.144	0.012	8.22
Er	0.450	0.054	11.98
Tm	0.060	0.002	2.74
Yb	0.390	0.031	8.05
Lu	0.057	0.003	5.58
Hf	4.924	1.184	24.05
Ta	1.719	0.191	11.09
W	2.840	0.284	10.02
Re	0.004	0.006	140.19
Os	0.002	0.004	184.58
Ir	0.009	0.009	96.14
Pt	0.038	0.026	69.04
Au	0.077	0.030	39.31
Hg	0.127	0.047	36.70
Tl	1.519	0.096	6.30
Pb	82.901	10.670	12.87
Bi	0.558	0.067	12.03
Th	8.329	1.891	22.70
U	8.424	1.739	20.65

Figure 3.1 Al and La concentrations in control samples during the period of analysis of this study.



3.7 Preliminary Data Screening and Transformation

The data was initially screened for: outliers, replicates examined, results below detection limits, and log transformation. Outlying observations examined were defined as any observations that lay beyond three standard deviations of the mean. Replicates for each outlying observation were checked to confirm their genuine nature. All were considered to be reflections of the underlying compositional distribution.

When analysing a large number of elements it is almost certain that concentrations below detection limits will occur. Rather than eliminate such data it is possible to substitute these values with values that will minimise their effect on later analysis. Hence much of the possible variability is retained within the data. However, elements with large numbers of values below detection limits were eliminated, and this led to the removal of the elements Sc, I and Hg from any further analysis. In all other cases, values below detection limits were replaced by a value of 50% of the minimum reported value for that element. This replacement did not seriously affect the mean, standard deviation and variance. It is recognised that other approaches exist in the replacement of such values.

Major elements must be treated separately as their sum totals are constrained to the whole sample, i.e. 100%; a constraint that does not affect trace elements. Statistical analysis of such data may be compromised by this closure of the data. This induces elemental correlations between major elements that may invalidate the use of techniques such as cluster analysis. Aitchison (1986) considered standardisation may alleviate these effects . These techniques have recently been applied to archaeological data by Baxter (1989, 1991), although recently Tangri & Wright (1993) have questioned the value of using the changes.

The following analysis, of mainly trace elements, was performed on a log transformation of the data. Ahrens (1954) demonstrated that all elements in geochemistry were log-normally distributed, but noted that if the mean is larger in comparison to the variance the difference between normal and log-normal distribution is insignificant. Various authors have treated data as log-normally distributed (Bieber et al 1976, Glascock 1992), while others have dealt with normal distributions (Picon et al 1975). At the outset it was established that the data was more log-normally distributed than normal, this is consistent with the nature of the data, which contains more trace elements than majors. This transformation gives a more nearly normal distribution for each element in a homogeneous group. This is important in later analysis as normality of data is often assumed when dealing with multivariate statistics (Chatfield & Collins 1980). Secondly, log transformation reduces the effect of elements that have greater abundances dominating the analysis simply because of the magnitude of the results. For example, if a Euclidean distance metric is used to construct the Similarity Matrix for cluster analysis, the results will be dominated by the elements that have the highest absolute abundances. Even after the removal of the major elements, there is a large variation in magnitude, from 1 ppb to 1000 ppm, that will produce scale dependent effects in some statistical procedures. However, in many cases it may be more appropriate that equal weight is given to each variable in creating natural taxa (Sneath & Sokal 1973). This maybe accomplished, as Harbottle (1976), states by log-transformation or standardisation of the data. With this exploratory data set it was felt that there was no obvious element to which to standardise the data and it was perhaps unnecessary if the data was log-transformed.

3.8 Univariate and Bivariate Analysis

Univariate and bivariate statistics were applied to the data to identify elements that displayed significant differences between the different tectonic regions and thus elements that had the greatest ability to discriminate between regions.

Inter-elemental correlation of geochemical data is well known and reflects fundamental underlying gechemical properties and processes. The extent of these correlations is important in certain techniques of multivariate statistics commonly used to simplify data sets. The effect of correlation is to spread out the "volume of space" occupied by groups and may fail to separate discrete groups as a direct result of the distorting effects of correlations. These correlations can be identified by correlation coefficients and bivariate scatterplots. These plots also enable sample groups to be identified and further identification of elements that discriminate between the separate groups.

The use of a number of "immobile" elements in geochemical classifications is a recognised method of establishing tectonic setting of basic volcanic rocks (Pearce & Cann 1971, 1973, Floyd & Winchester 1975). This approach may be of use in determining different provenances for steatite sources as they are found in a number of different geological provinces (see section 2.3). These methods were applied to the steatite source data in order to test whether the separate geological regions could be differentiated. However, it must be born in mind that steatite samples are considerably different from the volcanic rocks this method was originally intended for. Firstly, steatite is not fresh from alteration, it is an alteration product of metasomatism and therefore soluble elements will have been mobilised during hydrothermal alteration. Secondly, the method was originally intended for volcanic rock that had cooled rapidly, where composition may reflect the parent magma. Steatite is an alteration product of ultrabasic rocks, more slowly cooled plutonic rock, therefore processes during cooling may have affected the trace elements.

In order to further investigate the concentration of individual elements and the relationship between these and the variations between tectonic groups Analysis of Variance (ANOVA) and Bartlett's Test were performed on the data. This allowed judgement to be made as to whether the measurements vary from class to class due to sampling errors, resulting from a relatively small sample being taken from a source site that is considered to be representative, or could be attributed to some kind of relationship between the variable and the tectonic groups on each element individually.

3.8.1 Methods

Summary statistics were produced for the entire data set and selected parts using simple arithmetic mean ($\overline{X}$) and standard deviation (s) values (Williams 1984).

Correlation effects were investigated by the use of Pearson's product moment coefficients (r). A correlation coefficient is a numerical measure or index specifying the direction and degree of closeness of a linear relationship between two variables.

$$r = \frac{\Sigma[(X - \overline{X})(Y - \overline{Y})]}{\sqrt{\Sigma(X - \overline{X})^2}\sqrt{\Sigma(Y - \overline{Y})^2}} \qquad (3.1)$$

where the two variables are X and Y and their means are $\overline{X}$ and $\overline{Y}$.
Because of the way in which it is defined the product-moment coefficient cannot be less than -1 or greater than +1. A minus sign indicates an inverse or negative relationship between X and Y, a plus sign a direct or positive relationship. If there is no linear relationship the coefficient is zero. The more perfect the linear relationship the more the coefficient deviates from zero closer to one.

Bartlett's Test of homogeneity of variance was applied to the geological group variability. This test was developed by Bartlett (1937) and revised by Neyman & Pearson (1937) it should be conducted before ANOVA to ensure that the variance within the groups that the ANOVA is conducted upon is the same. This is an assumption made by ANOVA when it tests if the means differ between the groups.The test of homogeneity of variance concerns the question of whether several populations have the same variance. This test is frequently referred to as Bartlett's *M*-test, or the Neyman-Pearson-Bartlett test. Test statisic:

$$M = -v \ln L = v \ln\left(\sum_{j=1}^{k}\left(\frac{v_j}{v}\right)S_j^2\right) - \sum_{j=1}^{k} v_j \ln S \qquad (3.2)$$

where n_i denotes the sample size for the *j*th population, and $\{X_{ji}\}$, i=1,.....,nj,
Further, the sample $v_j = n_i - 1$

and $$S_j^2 = \left(\frac{1}{v_j}\right)\sum_{n=1}^{n_i}\left(X - \overline{X}_j\right)^2, \text{ where } \overline{X}_j = \left({}^{1}\!/_{n_j}\right)\sum_{i=1}^{n_j} X_{ji}. \qquad (3.3)$$

Single factor ANOVA tests the null hypothesis that the values of variable X are independent of the classes of the factor under study. In other words the mean values of the classes (samples or sub-samples) vary solely because of sampling error, and there is no underlying relationship between the group and the variable.

The ANOVA proceeds in the following manner:

1. A number, n, measurements are made of a continuous variable X. The measurements are grouped into classes according to some criterion (factor A). The number of classes is a and there are k_1 measurements in the first class, k_2 measurements in the second class, k_3 measurements in the third, etc (Williams 1986).

2. A null hypothesis is set up: the different populations share the same mean. Thus any differences between the sample means are due to chance sampling. In addition ANOVA also assumes a common variance within groups. Then the following are calculated:

3. Correction factor (C) calculated, $C = (\Sigma X)^2/n$ (3.4)

4. Total sum of squares, $SST = \Sigma X^2 - C$ SSt is equal to the total variance of the n measurements multiplied by (n - 1). (3.5)

5. Degrees of freedom associated with SST. These are df = n - 1 (3.6)

6. Sum of the Squares associated with factor A

$$SSA - [\frac{(class_1 total)^2}{k_1} + \frac{(class_2 total)^2}{k_2} + etc] - C \quad (3.7)$$

7. Degrees of freedom associated with SSA, df = a - 1 (3.8)

8. Error (or residual) sum of squares, SSE = SST - SSA (3.9)

9. Degrees of freedom associated with SSE, df - (n - 1) - (a - 1) = n - a (3.10)

10. Variance estimates for Factor A and from the error. The variance estimates are the respective sums of the squares divided by their degrees of freedom.

11. F ratio calculation, $F = \frac{\text{variance estimate for FactorA}}{\text{variance estimate for error}}$ (3.13)

12. If the value P is equal or less than the chosen level of significance the null hypothesis may be rejected. Thus it maybe concluded that the differences in means are not entirely due to chance sampling and that some kind of relationship exists between the classes of Factor A and the variable X. If the value of P is greater than the chosen level of significance, judgement must be reserved, i.e.. the null hypothesis is retained as possible, but not necessarily correct.

3.8.2 Summary Statistics

In order to investigate the properties of the data acquired, summary statistics were produced for all replicates and geological regions. Both the means and standard deviations for all the replicates and of the geological groups and the total data set are given in Appendix C. These helped to identify any differences between the groups in the element patterns and the identification of elements that had greatest variation and thus greatest discriminating power.

The major points noted were:

1. Elements that showed little or no difference in concentration between the different tectonic settings are:
Li, Be, B, Sc, Cr, Co, Ni, Cr, Zn, Se, Br, Rb, Zr, Mo, Ru, Rh, Pd, Ag, Cd, Sn, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Tb, Er, Yb, Lu, Ta, Re, Os, Ir, Pt, Au, Tl, Bi, Th.

2. Elements that showed differences between the tectonic groups are:
V, Ga, Ge, As, Sr, Y, Nb, Sb, Cs, Ba, Sm, W, Pb, U.

3. Elements that were measured with a precision of better than 20% and showed differences between tectonic groups:
V, Ga, Ge, As, Sr, Y, Nb, Sb, Cs, Ba, Sm, W, Pb, U.

4. Elements that were measured with a precision of less than 10% and showed differences between tectonic groups:
Ga, Ge, Sr, Y, Nb, Sb, Cs, Ba, Sm, Pb, U.

3.8.3 Correlation Effects

The existence in geochemical data of correlation between elements has been known for many years. It was important to understand any correlation between elements within this data set. Appendix C displays the calculated Pearson product moment coefficients for each of the elements. The values vary between -1, for perfect negative correlation, and +1, for a perfect positive correlation. If there is no linear correlation the coefficient is zero. Examination of the results shows elements that are well correlated and thus care must be taken when using these elements together in further analysis. If the data set is viewed as containing 22 samples with 6 fold replication then, at a level of significance of 0.01, values greater than 0.5368 are significant.

The following correlations are therefore significant within this data set. These are especially important in multivariate analysis when variance-covariance matrices are constructed for the data set.

Li - Y, Dy, Er, Tm, Yb, Lu, U
B - Te, Ir, Pt
Cr - Co, Zn, Ta
Cu - Ga, Zr, Sb, Hf
Rb - Cs, Ba, Th
Y - Nb, Ag, Cd, REE, Tl Pb, Bi, U
Nb - LREE, Eu, Gd, Tb, Dy, Ho, Er, Pb, Bi, Tl
Rh - Ag, Cd
Cd - Sm, Tb, Dy, Ho, Lu, Tl, Pb, Bi
Te - Tm, Lu, Ir
Ba - Th
Ce - LREE, Eu, Gd, Tb, Dy, Ho, Tl, Pb, Bi
Nd - LREE, Eu, Gd, Tb, Dy, Ho, Tl, Pb, Bi
Eu - Gd, Tb, Dy, Ho, Tl, Pb, Bi
Tb - Dy, Ho, Er, Tm, Yb, Lu, Tl, Pb, Bi
Ho - Er, Tm, Yb, Lu, Tl, Pb, Bi, Th, U
Tm - Yb, Lu, Tl, Pb, Bi, U
Lu - Ir, Th, U
Ir - Pt
Pb - Bi

Be - Cu, Zr, Nb, Sb, Hf
V - Cr, Ga
Co - Ge
Ga - Rb, Cs, Ba
Sr - Mo, Ru, Rh, Cd, LREE, Eu, Gd, Tb
Zr - Dy, Ho, Er, Yb, Hf
Ru - Rh, Ir, Pt
Ag - Te, REE, Tl, Pb, Th
Sn - Re
Cs - Ba, Th
La - LREE, Eu, Gd, Tb, Dy, Ho, Tl, Pb, Bi
Pr - LREE, Eu, Gd, Tb, Dy, Ho, Tl, Pb, Bi
Sm - LREE, Eu, Gd, Tb, Dy, Ho, Tl, Pb, Bi
Gd - Tb, Dy, Ho, Er, Yb, Tl, Pb, Bi
Dy - Ho, Er, Tm, Yb, Lu, Tl, Pb, Bi
Er - Tm, Yb, Lu, Tl, Pb, Bi, U
Yb - Lu, Pb, U
Ta - Au
Tl - Pb, Bi

The following elemental groups having been identifed as having a strong positive correlation with one another:

1. Li, Y, REE, U
2. Be, Cu, Zr, Sb, Hf, Sc
3. V, Cr, Ga, Co, Zn, Pd, Ni, Ge
4. Ga, Rb, Ba, Cs, Th
5. Sr, Mo, Ru, Rh, Pd, Bi
6. Y, Nb, Cd, Ag, REE, Pb, Tl, Bi, Th, U
7. Ru, Rh, Os, Ir, Au, Pt, Re

3.8.4 Bartlett's Test

Bartlett's Test of homogeneity of variance was applied to the geological group variability. The test of homogeneity of variance concerns the question of whether the populations have the same variance.

The test was significant in the cases of Li, Cu, Rb and Ba that gave M-values of 45.1, 61.2, 45.2, and 59.3 respectively for the Lewisian Group.

For the Dalradian samples Bartlett's test was significant for elements Cs, Cu, Cd. These gave M-values of 47.3, 83.9 and 51.2 respectively.

There were no elements that gave significant M-values for the Shetland basement group.

The tests were significant in the cases of B, Zr, Hf and Sb that gave M-values of 38.5,51.3,62.8 and 41.0 respectively for the Ophiolite group.

The test was significant in the cases of Sr, Ba and Pb. These gave M-values of 39.8, 54.1 and 44.2 respectively for the variance within all the geological groups.

These results indicate that the variances are not the same within both individual geological groups and the different tectonic group for the elements that gave significant M-values and thus may influence the analysis of variance that assumes the variance is the same within groups.

3.8.5 Analysis of Variance (ANOVA)

Single factor ANOVA tests the null hypothesis that the values of X are independent of the classes of the factor under study. In other words the means of the classes (samples or sub-samples) vary solely because of sampling error, and there is no relationship between the groups and the variable. Table 3.4 gives the p and F values for the ANOVA of the separate geological groups. F values greater than 3.16 are significant at 0.05 confidence level. Only the values for Mo, Cd, Ba are greater than this F value. However values for V, Ga, Rb and Cs are close to the level of significance. These elements show some differences, in the data collected, between the geological groups in these elements. It must be stressed that ANOVA was used as an exploratory tool and even if values are below confidence levels, it still indicates elements that may display values worthy of further investigation.

Table 3.4 F and p values calculated from an Analysis of Variance of the separate geological groups

Element	F	P
Li	0.68	0.557
Be	0.82	0.501
B	0.89	0.463
Sc	0.80	0.508
V	2.89	0.064
Cr	1.91	0.164
Co	1.86	0.172
Ni	1.12	0.369
Cu	0.87	0.473
Zn	1.48	0.254
Ga	2.81	0.069
Ge	1.75	0.192
As	1.40	0.274
Se	0.68	0.575
Br	0.18	0.911
Rb	2.54	0.089
Sr	1.59	0.227
Y	0.52	0.671
Zr	1.46	0.258
Nb	0.60	0.626
Mo	5.42	0.008
Ru	0.36	0.782
Rh	1.10	0.374
Pd	0.89	0.466
Ag	0.36	0.782
Cd	4.88	0.012
Sn	1.89	0.167
Sb	1.27	0.315
Te	1.63	0.218
Cs	2.25	0.117
Ba	5.03	0.011
La	0.39	0.761
Ce	0.39	0.764
Pr	0.34	0.795
Nd	0.32	0.811
Sm	0.20	0.893
Eu	0.36	0.782
Gd	0.18	0.906
Tb	0.07	0.978
Dy	0.30	0.826
Ho	0.29	0.835
Er	0.65	0.595
Tm	1.33	0.295
Yt	0.75	0.534
Lu	0.78	0.521
Hf	0.07	0.975
Ta	0.12	0.885
W	1.28	0.312
Re	1.84	0.175
Os	1.01	0.409
Ir	1.66	0.210
Pt	0.52	0.671
Au	0.47	0.709
Tl	0.27	0.845
Pb	0.79	0.514
Bi	0.89	0.466
Th	1.93	0.161
U	0.47	0.705

3.8.6 Graphical Plotting of Data

Univariate results were plotted for every element against the four distinct geological regions. The aims of this were to allow the comparison of the elemental concentrations in the separate geological groups, thus allowing the identification of elements able to separate these groups. These plots indicated that no element was able to separate all the geological regions. However, a number of elements were able to segregate one or more of the regions. These elements were Ga, As, Sr, Nb, Ba and Sm. A number of other elements were also identified that were unable to separate the group individually, but which showed promising distributions suggesting that together they might distinguish the grouping using multivariate methods. These elements were; Sb V Cu Zn Cs Pr W.

Bivariate plots, of which the following are examples, are a frequently employed to search for groups in compositional data. The elements that displayed differences between the geological regions in univariate analysis were plotted against each other. The best of these plots are shown in figures 3.2 - 3.5. Cunningsburgh was included to give an indication of the spread of the data within a single source quarry. Clearly this would not be possible for all sources due to cost, time and ICP-MS availability. If this intra-site variability was found to be relative small for a given variable then clearly if this variable also demonstrated differences between source greater than this internal variation then a more site specific provenance may be possible. Several features of the data were noted at this stage of the analysis. Firstly, the steatite from Lewisian sources may be separated from all other steatite with a number of different variables. The Lewisian steatite is characterised by a lower than average concentration of Sr and As and a higher than average concentration of Nb. The samples from Loch na h'Oidhche (Lewisian) have a particularly high concentration of Nb. The Lewisian samples from Glenelg and Loch na h'Oidhche have high concentration of Ba. This contrasts with the ophiolite sources that have low Ba concentration. However, Ba alone is not able to separate the ophiolitic sources from the rest of the data. Cs is also characteristically high in concentration in samples from Glenelg. Clearly the elements used in these plots are worth further more precise investigation.

Figure 3.2 Bivariate plot of Sr vs. Nb for all the steatite samples, including single Cunnigsburgh source, showing the separation of the Lewisian sources, low concentrations of Sr and high concentrations of Nb.

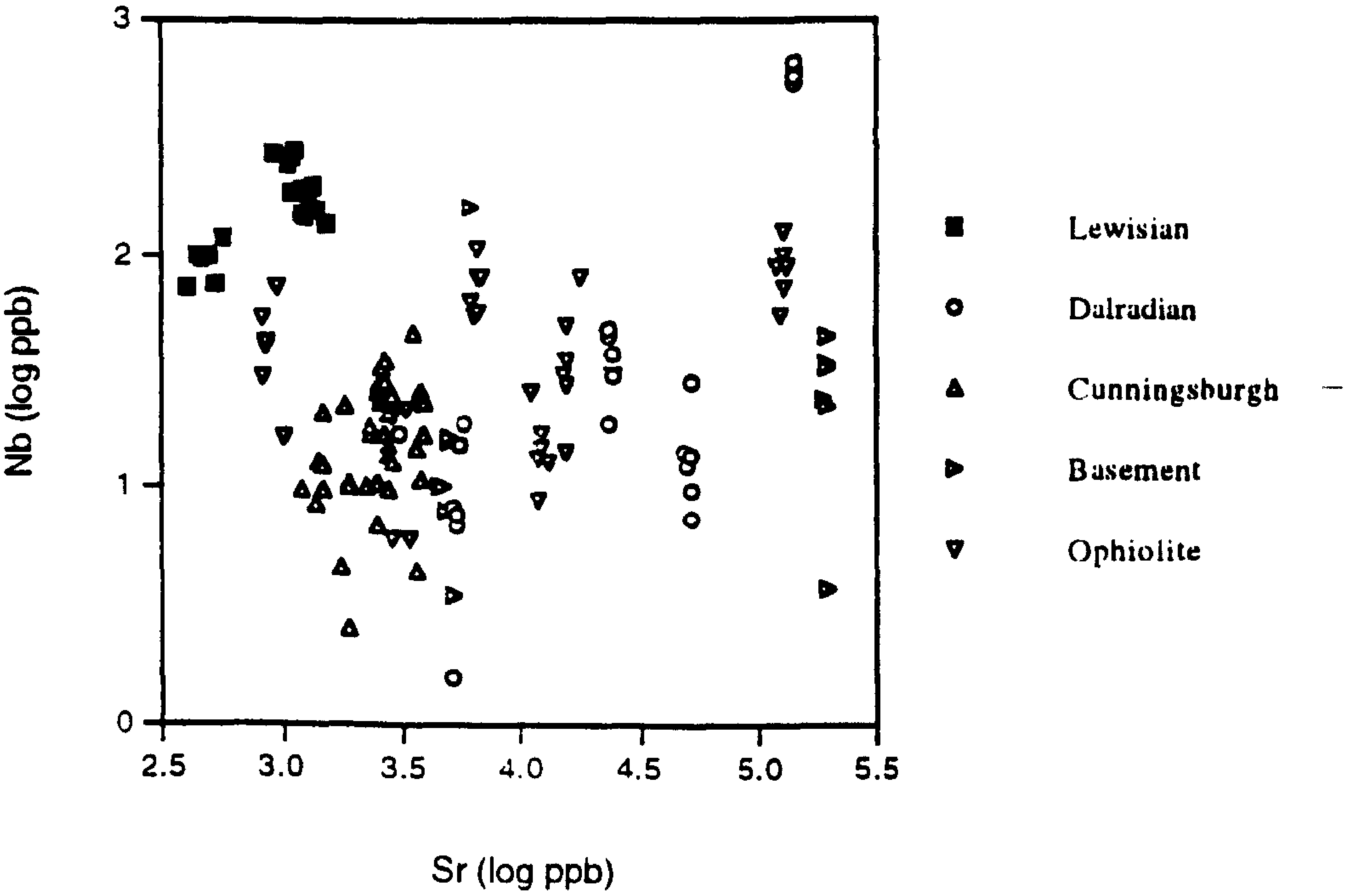


Figure 3.3 Bivariate plot of As vs. Sr for all the steatite samples, including single Cunnigsburgh source.

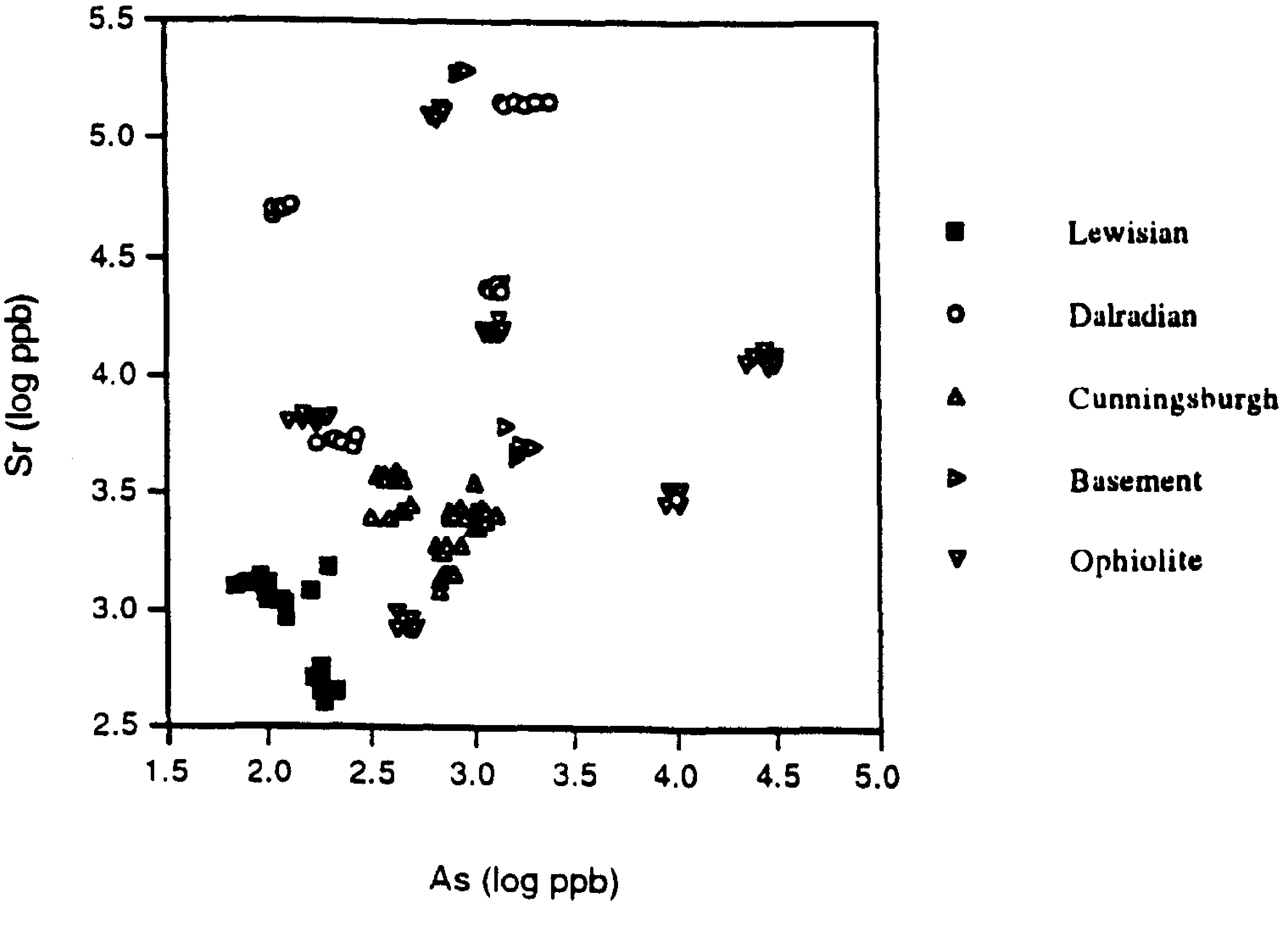


Figure 3.4 Bivariate plot of As vs. Nb for all the steatite samples, including single Cunnigsburgh source.

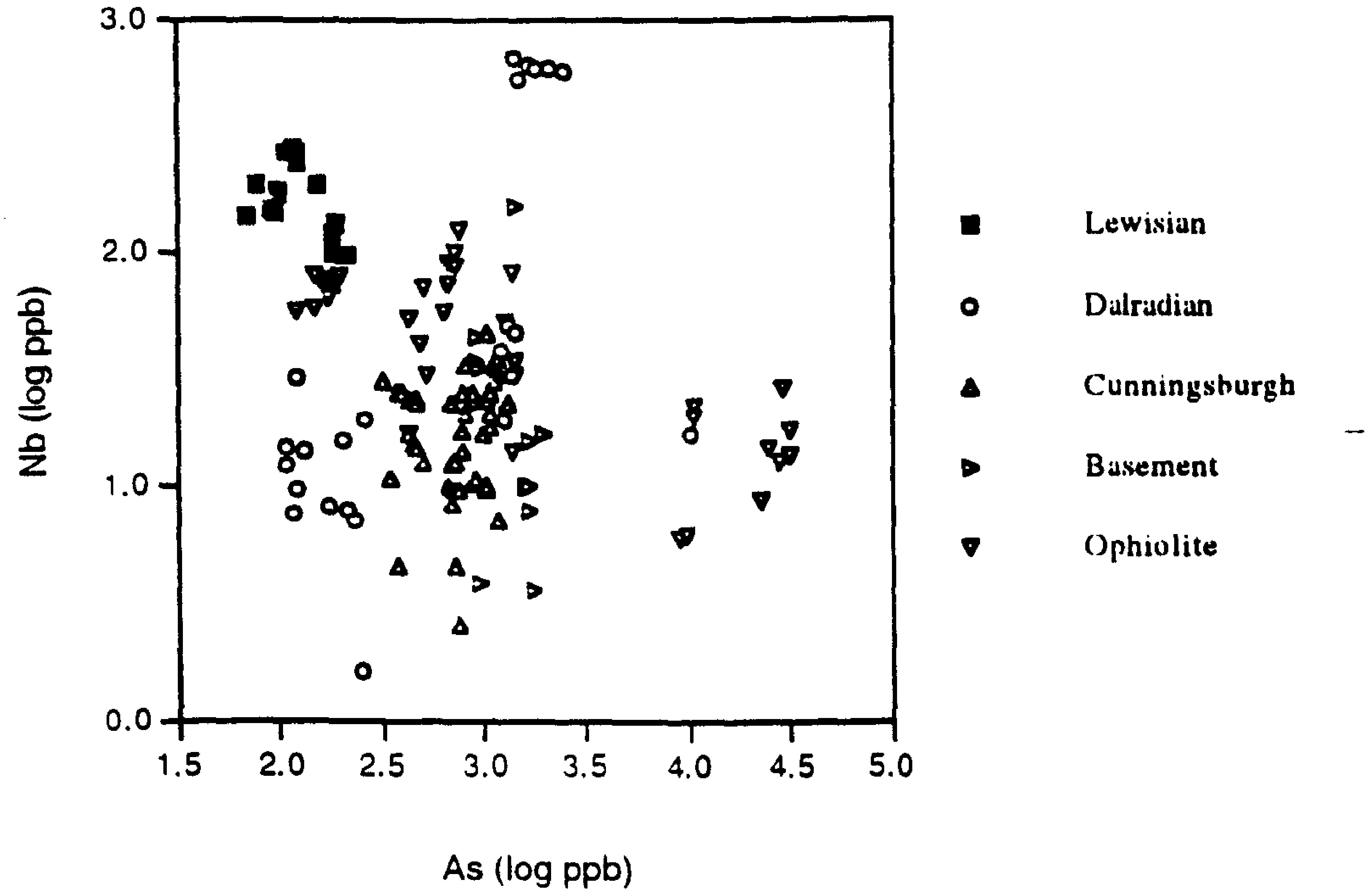
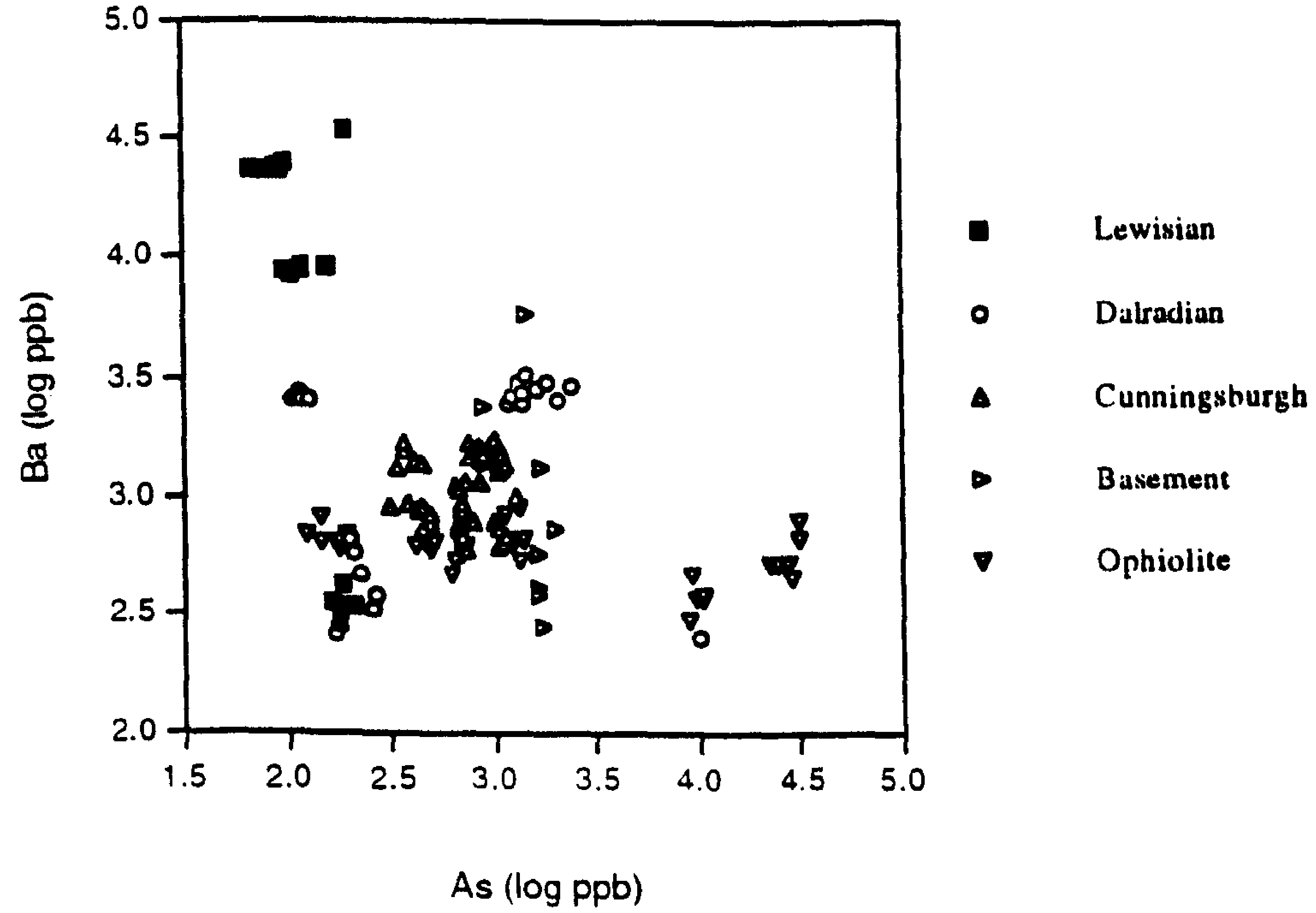


Figure 3.5 Bivariate plot of As vs. Ba for all the steatite samples, including single Cunnigsburgh source.



3.8.7 Pearce and Cann Discrimination Diagrams

Tectonic setting can be established for a range of basic volcanic rocks by the use of *immobile elements* (Pearce & Cann 1971, 1973, Floyd & Winchester 1975). This technique may be of use in determining different provenances for steatite sources as they are found in a number of different tectonic settings. There are however considerable differences between steatite and the basic volcanic of the original study, see section 2.8.1. Bearing in mind these differences, it was considered that steatite sources might fall into a number of areas. It is proposed to use the "less mobile elements" ; Ti, Zr, Y, as well as Sr. Pearce & Cann (1973) stress that care is needed when Sr is used as it is easily susceptible to the affects of metamorphism. The results are plotted in Figures 3.6-3.7.

Figure 3.6 Discrimination diagram using Ti, Zr and Y. Field as described by Pearce & Cann (1973); refer to basalts. WPB - D, OFB - B, LKT - A & B, CAB - C & B.

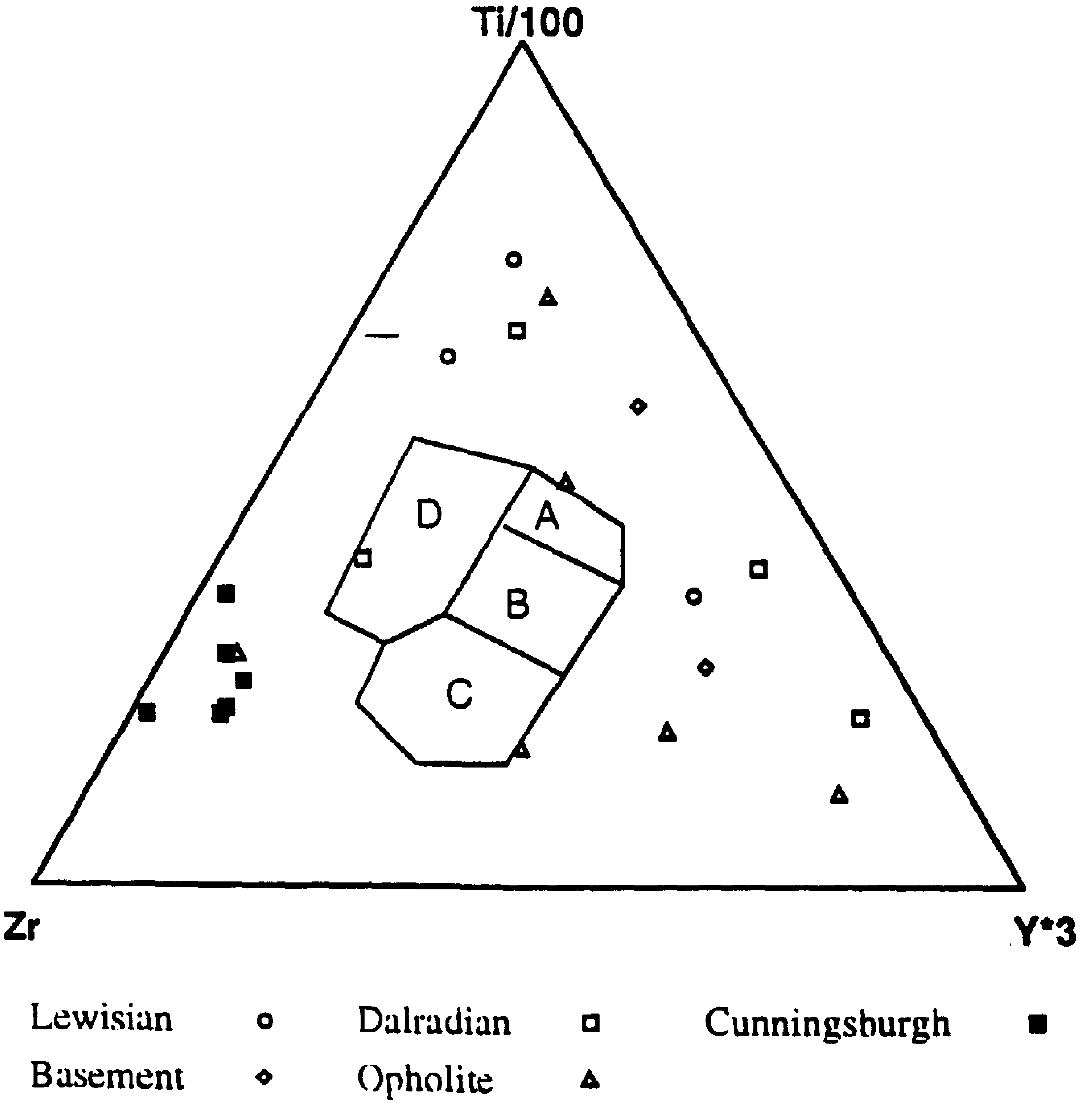
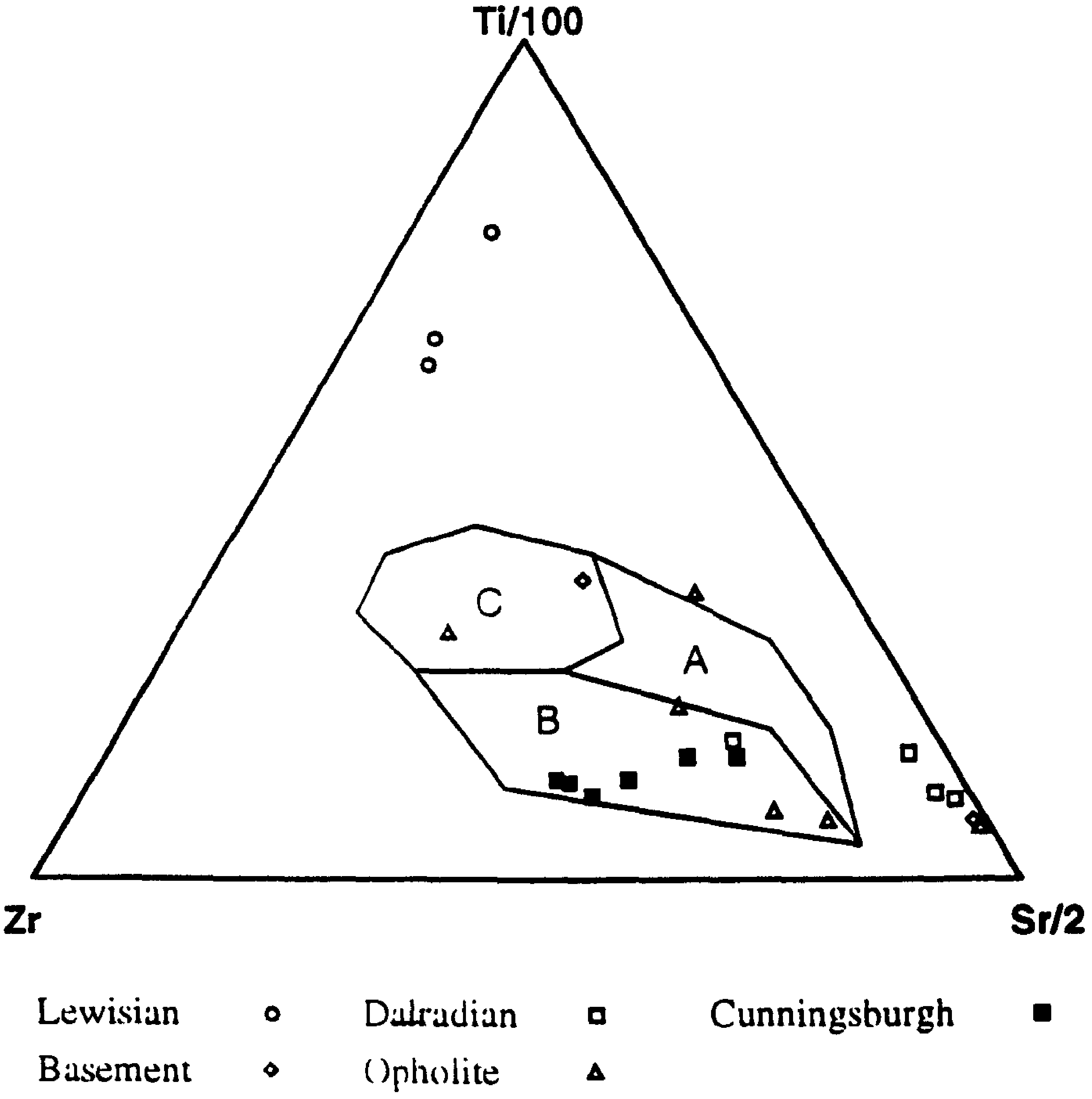


Figure 3.7 Discrimination diagram using Ti, Zr and Sr. Field as described by Pearce & Cann (1973); refer to basalts, OFB - C, LKT - A, CAB - B.



These results indicate that steatites from different tectonic settings cannot be discriminated on the basis of Pearce and Cann diagrams. Although the data displays structured nature by the formation of several groupings, especially of samples from the quarry at Cunningsburgh. Figure 3.6 & 3.7 show that the scatter of points is much larger than that seen in volcanic rocks, largely defined by the plotted fields. Also samples from a single tectonic environment do not form a distinct group that allows group separation. However, Figure 3.7 shows the relatively low Sr concentration of the Lewisian samples.

There are a number of possible explanations for these results. Firstly, the separate tectonic environments may not have had original trace element concentrations that form a distinct group based on environment. The separate environments may not have had distinct trace element characteristics before alteration to steatite. The plutonic nature of the parent ultrabasic rocks may account for lack of discrimination. Tectonic setting studies have generally concentrated on volcanic rocks. Also, the large differences between some of the environments in certain complexed geological areas such as the Lewisian may contain more than one tectonic setting. This would further confuse the plotted distribution. The second major factor that may account for these results is the metamorphism and metasomatic alteration. The large spread of the data is probably a result of differences in condition between sources resulting in differences in trace element mobility. The conditions during metasomatism probably resulted in trace element mobility and therefore the present composition is a function of the alteration and not the tectonic setting. Thus it must be concluded that Pearce and Cann discrimination diagrams are not as yet of use in discriminating between steatite sources.

3.8.8 Evaluation of preliminary, univariate and bivariate data analysis techniques.

This study sought to investigate the geochemical differences between steatite sources. By the use of a systematic approach to data analysis an objective interpretation of the data acquired from multi-elemental ICP-MS analysis was made. This approach allowed the evaluations of both the techniques as applied to large data sets with complex relationships between analytical variables, and the geochemical differences between steatite sources based upon tectonic groups.

In any chemical characterisation study that uses large data sets a preliminary analysis of the data is very important. By the use of a few simple techniques data can be checked for consistency and completeness. This is of particular importance when data is being transferred between packages. Any inconsistencies can be identified at this early stage preventing time consuming mistakes being detected during later data analysis. In this study examination of outlying data, any observation that lay beyond 3 standard deviations of the mean, revealed that in all cases the data were a genuine realisation from the underlying distribution.

Within large multi-element data sets incorporating trace elements there is a reasonable certainty that values below detection limits will exist. Preliminary data analysis allows for their identification and replacement thus allowing the optimum use of the data set. A factor particularly relevant to later multivariate analysis can be identified at this early stage, the normality of the data. Thus various log-transformation or standardisation procedures can be applied to the data. In this study most of the data displayed a log-normal distribution so normality was achieved by log transformation.

The univariate and bivariate analysis served a number of useful functions.

1. These techniques allowed the identification of elements that displayed discrimination potential, i.e. significant differences between the tectonic groups.
2. Allowed the assessment of inter-elemental correlations within the data set. This is particularly important with respect to multivariate analysis.
3. Bivariate scatterplots represent a good means for the visual display of data. These enable comparison and assessment to be made of the elemental concentrations between and within the different tectonic groups. Thus any differences or similarities between the groups can be

identified. However problems arise with bivariate plotting techniques when large numbers of variables have been analysed as there are a large number of potential plots and the additional information gained from each is limited. In this study the following elements contributed little additional information in discriminating between the source regions; Li, Be, B, Sc, Cr, Co, Ni, Cr, Zn, Se, Br, Rb, Zr, Mo, Ru, Rh, Pd, Ag, Cd, Sn, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Tb, Er, Yb, Lu, Ta, Re, Os, Ir, Pt, Au, Tl, Bi, Th. Therefore these plots have only been used when previous analysis suggests a visual inspection of the data may be beneficial. Another problem with bivariate scatterplots is that they are limited to two dimensions. Thus with large multi-element data sets in which complex relationships exist between variables the use of bi-plots may tend to over simplify the data.

Pearce and Cann discrimination diagrams have proved to be of limited use in differentiating between the tectonic regions. However, this technique may prove useful for other materials that are more closely related to the material that this technique was originally designed to discriminate than steatite.

Analysis of Variance and Bartlett's test have proved useful in a number of respects. These techniques have enabled elements that show some differences in means between the different tectonic groups to be identified, thus allowing these elements to be investigated further. However, only a few elements showed significant difference between the tectonic groups at the confidence level chosen. These elements were; Mo, Cd, Ba, Ga, Rb, and Cs. A number of possibilities may explain this observation. The complex multi-element relationships may obscure any differences and/or no genuine differences existing between the tectonic groups in a single dimension.

Thus it has been demonstrated that rigorous preliminary, univariate and bivariate data analyses are important in studies of large data sets such as are produced by ICP-MS. Even if complex relationships are suspected between samples and variables much useful information can be acquired from this analysis thus allowing further analysis, if required to be targeted in order to optimise the variables analysed.

3.9 Multivariate analysis

Having shown that there are some promising individual elements and correlations existing, multivariate approaches will be considered. The univariate and bivariate analysis of the data in the previous stage of analysis were useful, but the information from the data set is difficult to interpret when four or more dimensions are used together. Using a multitude of graphs to display the data trends makes interpretation more difficult, and there is no single plot which summarises the overall pattern. Interpretation of such univariate data is often rather subjective in the selection of elements used and in the interpretation of the resultant plots. Multivariate analysis is less subjective than univariate techniques in the description and assignment of groups and it utilises all the available information in the data set. It is also worth bearing in mind a fundamental principle of numerical taxonomy as stated by Sneath & Sokal (1973) "... the more characters on which it is based the better the given classification will be" and "a priori, every character is of equal weight in creating natural taxa". Therefore it is best to include as many variables as possible. It is unnecessary to exclude elements having large variances as the variance will be included when the variance-covariance matrix is constructed, thus reducing the effect of these elements.

One advantage of the log transformed trace element data is that it does not compromise multivariate methods in the manner of major elements with respect to closure problems. Another is the general compatibility of the analysis within particular groups of elements in comparison to other techniques such as NAA.

With this firmly in mind the logical step was to employ techniques of multivariate statistical analysis to suggest possible simplification of the data set. These comprise statistical techniques that make use of the entire or selected parts of the data set in the establishment of classifications. The theory was to use a number of techniques to yield a set of results from which agreement could be sought enabling a high degree of confidence to be assigned to the interpretation.

In the following sections the methodology of the multivariate techniques used in this study will be discussed briefly along with references for more detailed methodological discussion. Then the results of each analysis will be presented with a discussion of these results. Each technique will be evaluated as to its usefulness to provenance studies and the section will be concluded by a discussion of these results in relation to the provenancing of steatite.

3.9.1 Methods

Principal Components Analysis

The main aim of principal component analysis (PCA) is to reduce the dimensionality of the problem and to find new variables that enable easier interpretation of the variance of the data set. PCA may also be used to eliminate those variables that contribute relatively little extra information to the problem (Jolliffe 1973). Principal components (PC) are the eigenvectors of a variance-covariance or correlation matrix, which makes PCA an extremely powerful tool when compositional data are highly correlated. PCA is sensitive to the magnitude of measurements. Therefore it is important that the same units are used for each variable and data is standardised to mean scores, or log-transformed. Standardisation tends to inflate variables whose variance is small and conversely reduces the influence of variables with large variances. In many provenance studies relative magnitudes may be of some use. Therefore log-transformation may be better than standardisations, although in other cases relative values may be of more use. In PCA a transformation of the data is based upon eigenvector methods that determine the direction and magnitude of maximum variance in the data in multidimensional space (Davis 1986). The PCs are a linear combination of the original variables so that the first PC is oriented in the direction of maximum variance. The second PC is oriented to optimise the greatest variance that is accounted for after the first PC has been eliminated, subject to the constraint that it must be orthogonal to the first. The third is orthogonal to the first two PCs, again representing the maximum variance, and so on until the number of PCs is equal to the original number of dimensions. After the eigenvalues and PCs of the covariance matrix are calculated the first few PCs will hopefully account for a large proportion of the total variance. A more detailed discussion and the mathematical derivation of PCs is given in Chatfield and Collins (1980) and Davis (1986).

Aitchison (1986) has argued that conventional multivariate analysis of mineral compositional data are radically flawed due to inherent problems in the data matrices. These problems are especially pertinent to archaeological studies of composition of artifacts (Baxter 1989). Aitchison has developed a statistical modification to standard PCA. This entails log transformation of the data matrix and its centring by row vector, before analysis by PCA of the covariance matrix calculated from non-standard column vectors. Standard PCA uses the covariance matrix calculated from standard column vectors, otherwise known as the correlation matrix. Aitchison's aim was to negate the problem of *closure restraint* that may lead to false correlations when the correlations are calculated on the ratios. Baxter (1989, Baxter *et al* 1990) has tested Aitchison's methods on scattergrams of glass objects and claims that this method appears better to respect the qualities of compositional data. In a later paper Baxter (1991) concluded that theoretical objections to standard PCA may be limited, and more recently Tangri & Wright (1993) have correctly asserted that the log linear transformation introduced spurious structure into the data matrix.

PCA has been often used widely in the search for some related sub-groups in compositional data (Baxter 1992, 1993, Bishop & Neff 1989, Glascock 1992, Lease *et al* 1989, Pollard 1985). This method is not precisely a group-formation technique, however PCA facilitates recognition of compositional groups by identification of the orientation of maximum variance within the data set. These directions of maximum elongation often coincide with axes along which separation between groups is more easily visible.

Beyond recognition of groups another goal of PCA is to understand the basis of group separation. In R-mode analysis the loadings of the original variables on each principal component may be inspected to obtain the desired information, whereas in Q-mode analysis the factor scores for the original variables may be viewed. Recently Neff (1994) has performed a more direct approach with simultaneous R-Q mode analysis which permits display of the data points and the variable on the same diagrams.

This study was principally concerned with minor and trace elements and therefore does not suffer in the same manner as major elements as suggested by Aitchison. Clearly the induction of spurious results to a preliminary study was dangerous and therefore standard PCA was performed on the data. The data was log transformed before the covariance matrix was calculated from standard column vectors. PCA and Discriminant analysis were performed in Minitab (PC version) and the cluster analysis was done in BMDP.

An advantage of PCA over other multivariate techniques is that it enables interpretation of the principal components in terms of the underlying combinations of correlated variables that contribute to any principal component. In order to attach meaning to principal components the usual procedure consists of examining the corresponding eigenvector and choosing the variables for which the coefficient in the eigenvector is relatively large, either positive or negative. Thus by utilising such techniques the variables that contribute most to the variance in the data set can be identified and further investigated if required. The loadings only reflect the relative importance of a variable within a PC, not the importance of the component itself. Chatfield & Collins (1980) suggest that eigenvalues of less than one may be disregarded in such interpretation. Sometimes the first few principal components are rotated in order to find a new set of components and variables that can be more easily interpreted. Some authors (Davis 1986) debate the extent to which meaning can be placed on the interpretation of principal component loadings and suggest that any interpretation must be treated with an element of caution. In this study the eigenvector coeffecients were interpreted in the manner suggested above, the results being treated with a degree of caution.

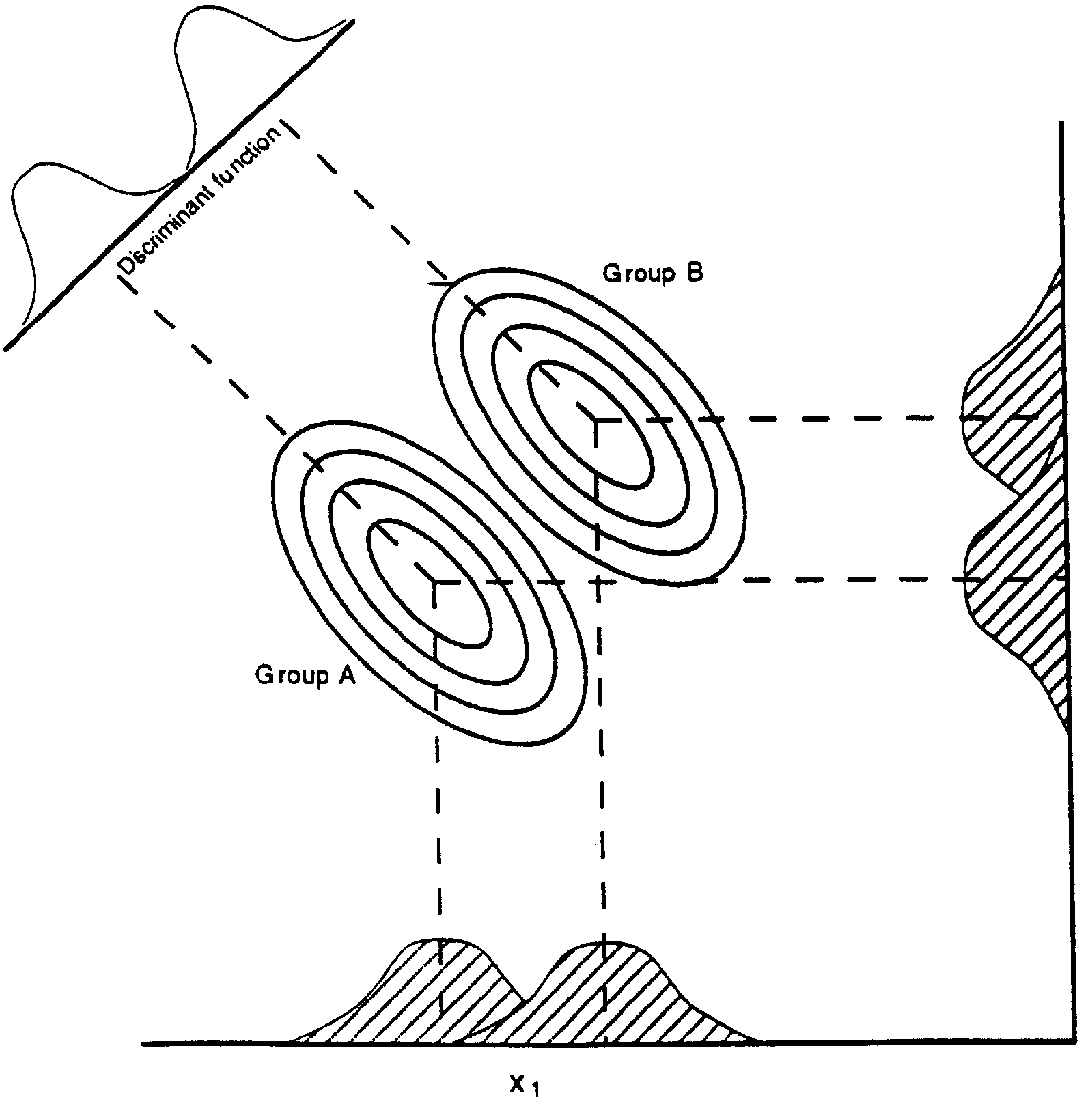
The plotting of the principal component scores against one another is generally regarded as the optimum method of viewing the data. In geometrical terms this is merely the same as looking at the data in a direction perpendicular to the plane defined by the two PCs. This enables principal components to be evaluated as to their potential in classifying the data. Thus further interpretation can be made of the variables, identification of variables that result in resolution of potential groups within the data set and those that contribute little to this classification.

To further reduce the dimensionality, variables may be removed from subsequent analysis. In order to do this it is necessary to decide what eigenvalues are "large" and what are "small" so that components corresponding to the latter may be removed from subsequent analysis. Various authors have suggested that eigenvalues of less than one may be disregarded. This is an arbitrary policy and is generally used as a rule of thumb as it has little theoretical justification therefore it has not been used in this study. Chatfield & Collins (1980) suggest that it may be better to look at the eigenvalues and see if there is a natural breakpoint. A more pragmatic approach was suggested by Jolliffe (1972, 1973) who discussed a number of methods for discarding variables in principal component analysis.

Canonical Discriminant Analysis

Canonical Discriminant Analysis is a useful technique when it is necessary to distinguish statistically between two or more groupings. It is intended to find a rule that allows a distinction to be made between groups. The mathematical objective of the technique is to weigh and combine linearly discriminating variables, in this case elemental concentrations, in some way to force the chosen groups as far apart spatially as possible. Discriminant analysis differs from PCA in that it extracts a new set of variables that maximise the differences between two or

Figure 3.8 Plot of two bivariate distributions, showing overlap between groups A and B along both variables x_1 and x_2. Groups can be distinguished by projecting members of the two groups onto the discriminant function line (after Davis 1986).



more groups rather than maximise the variance in the data set. Discriminant analysis is based on the assumption that the pooled variance-covariance matrix is an accurate representation of the total variance and covariance (Davis 1986). If we regard two groups as consisting of two clusters of points in multivariate space, the method searches for the function orientation along which the two clusters have the greatest separation, while simultaneously each cluster has the least inflation. This can be graphically shown in a two dimensional case, as in Fig 3.8.

The assumption is made that all analyses in a data set belong to one of the known groups. The discriminant analysis operation produces a series of discriminant functions, one less than the number of groups. For each sample the series of functions are calculated for every group. These discriminant functions can be regarded as axes of geometric space and are used to look spatially for relationships between the identified groups.

A simple linear discriminant function transforms an original set of measurements on a sample into a single discriminant score. That score, or transformed variable, represents the sample's position along a line defined by the linear discriminant function. Therefore we can think of the discriminant function as a way of collapsing a multivariate problem down into a problem which one variable may resolve.

A major factor that should be observed when utilising discriminant analysis is that the method requires a "training data set" of known groups on which the discriminant functions are based. In many archaeological provenance studies little is known about the group structure before the data is analysed. In these cases discriminant analysis is of little use in the establishment of group membership for unknown samples. This study has sought to define differences between the different groups that have already been established on firm geological grounds. PCA has been used to discover the variables that are of use in resolving structure within the data and confirming the underlying group nature. Thus discriminant analysis may be used to confirm the criteria that separate underlying groups that are known from the PCA.

One problem that arises with discriminant analysis is concerned with the distribution of the data set. The method assumes that within groups the data follow multivariate normal-distribution. Where this condition is not met the technique can be disrupted. However, the method is not a waste of time as analysis may provide very good discrimination on non-normal populations. Problems arise when the significance of the results is questioned as this may be complex to establish (Manly 1988). Discriminant analysis has been applied to non-normal distribution in complex archaeological characterisation studies by Spoery 1988.

Cluster Analysis

Cluster analysis is the name given to an assortment of techniques designed to perform classification by assigning observations to groups so each group is more or less homogeneous and distinct from other groups. There are a number of alternative classification procedures (Sneath & Sokal 1973). Most may be grouped into four general types.

1. Partitioning methods operate on the multivariate observations themselves, or on projections of these observations onto planes of lower dimensions.
2. Arbitrary origin methods operate on similarities between the observations and a set of arbitrary starting points.
3. Mutual similarity procedures group together observations that have a common similarity to other observations.
4. Hierarchical clustering joins the most similar observations, then successively connects the next most similar observation to these.

If we have n objects and measure m characteristics, the data form an n X m matrix. Again a measurement of similarity must be computed between every pair of objects. Several coefficients of resemblance have been used, including the correlation coefficient and a standardised m -space Euclidean distance, d_{ij}, the most frequently used distance measure.

$$d_{ij} = \sqrt{\frac{\sum_{k=1}^{m} (X_{ik} - X_{jk})^2}{m}} \qquad (3.15)$$

where X_{ik} denotes the k th variable measured on an object i and X_{jk} is the k th variable measured on object j. In all, m variables are measured on each object and d_{ij} is the distance between object i and j.

The exact method of establishing the relative *closeness* of an object in multidimensional space depends entirely upon the specific clustering algorithm chosen. There are two main types of algorithm available, Hierarchic where the starting point is taken with every object representing a single group which are then merged by a process of agglomeration to eventually form a single large grouping, and Diversive where as the name suggests the exact opposite is true, with a single large group comprising the starting point. The diversive techniques are by their very nature best suited for very large data sets therefore the decision was made to used hierarchical techniques. The general consense is that no one clustering procedure is most suitable for all cases (Pollard 1982, Gillings 1989). The following algorithms are the most commonly used in archaeology:

1. Nearest Neighbour - The nearest neighbour or single linkage method defines the similarities between clusters as the highest similarity coefficient between two individuals, one from each cluster. In practical terms the method finds straggling clusters but in general fails to partition large populations due to a tendency towards cluster chaining, ie. where the clusters run together to form a single large grouping.

2. Furthest Neighbour - The furthest neighbour or complete linkage method uses the smallest single similarity coefficient between two individuals originating from different clusters and is useful for finding spherical shaped clusters. The main problem associated with this method is its tendency to produce rather irregular results as the similarity coefficient is only calculated for two individuals and no measure is made of the group structure.

3. Group Average - The group average or average linkage method uses the average of all the similarity coefficients for pairs of individuals, one from each cluster. As a practical method it tends to find spherical clusters, is regarded as well behaved (Gillings 1989) and represents one of the first attempts to cope with group structure.

4. Centroid - This method obtains the coefficient value through the centroid or mean vector for the clusters and produces results which suffer from chaining syndrome although to a lesser degree than in the single linkage example.

5. McQuitty - This method utilises a transformation proposed by McQuitty (see Wishart 1978) to establish the similarity coefficient and is once again a method prone to chaining when faced with a large sample population.

6. Median - The median or weighted pair group centroid method defines the distance between any cluster X and the cluster resulting from the fusion of cluster Y and Z as the distance from the centroid of X to the mid-point of the line joining the centroids of Y and Z. Once again a method prone to chaining when faced with a large population.

7. Wards - This method is regarded as possibly the best (Wishart 1978) of the hierarchical methods and is frequently used in archaeological studies, however it is not necessary optimal for partitioning. The error sum of squares is taken to assess the similarity where this is taken as the sum of the distances from each individual to the centroid of its parent cluster, combining clusters whose fusion results in the smallest increase in the error sum of squares.

For completeness cluster analysis was included in this study. However, this analysis revealed little information about the structure of the data. The analysis and a discussion of the results, and problems associated with this technique may be found in Appendix C.

3.9.2 Principal Component Analysis

Principal component analysis was performed on the entire data set. Table 3.5 shows the eigenvalues, proportion and cumulative proportion of the total variance explained by the first six principal components. Table 3.6 shows the eigenvector coefficients for the first six principal components. It is apparent that this analysis was only able to explain a relatively small amount of the cumulative total for the variance from the initial PCs. This is probably a result of the large number of variables in comparison to the number of cases. The small amount of variance explained by the initial PCs make interpretation very difficult as the coefficients are very similar. If the eigenvector coefficients are examined the following interpretation can be made of the variance of the total data set. The variables that contribute most to the first three principal components, which account for the greatest proportion of the variance within the data:

PC 1	REE, Y, Pb all negative.
PC 2	V, Cr, Co, Ni, Zn, Ga, Ge, Rb negative. Br positive.
PC 3	Cr, Zn, As, Sb negative. B, Rh, Te, Re, Pt, Th positive.

It can therefore be seen that within this large data set the elemental groups above are correlated with one another. Furthermore the REE and Y (which behaves in a similar manner to the REE) are the group of elements that describe the greatest proportion of the variance in the data. Similarly, a group of mainly transition elements and another of platinum group and transition elements contribute highly to the variance. As these different elemental groups of all the 57 trace elements analysed describe much of the variance their further investigation may prove beneficial in discovering differences between sources.

It is generally regarded that the optimum method of viewing the data is by plotting the first few PCs against each other. In geometrical terms this is merely the same as viewing the data in a. direction perpendicular to the plane defined by the two PCs. The first three PC scores, calculated on all the data, are plotted against one another Figure 3.9 - 3.11. These plots graphically represent the new variables that explain a large proportion of the total variance. They demonstrate that there is considerable structure within the data. However these new variables are unable to resolve entirely group structure, but they do go some way towards it.

Table 3.5 Eigenvalues and proportion of the variance explained by each vector calculated on all the data

	Eigenvector					
	1	2	3	4	5	6
Eigenvalue	13.608	5.253	4.842	3.367	3.041	2.518
Proportion	23.9	9.2	8.5	5.9	5.3	4.4
Cumulative	23.9	33.1	41.6	47.5	52.8	57.2

Table 3.6 Eigenvector coefficients for the first six principal components calculated on all the data

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
Li	-0.171	0.049	-0.157	-0.192	-0.045	0.167
Be	-0.004	0.007	-0.196	-0.158	-0.096	-0.054
B	-0.074	-0.056	0.240	-0.063	0.202	0.117
Sc	-0.007	-0.048	-0.051	-0.072	0.146	0.203
V	0.024	-0.258	-0.191	-0.165	0.256	-0.040
Cr	0.109	-0.301	-0.205	0.049	0.131	-0.016
Co	0.070	-0.316	0.149	-0.042	0.022	-0.231
Ni	0.041	-0.338	0.074	0.050	-0.063	0.009
Cu	-0.081	0.013	-0.058	-0.202	0.079	0.118
Zn	0.054	-0.291	-0.232	-0.008	0.091	-0.053
Ga	-0.133	-0.245	-0.162	-0.201	0.071	-0.109
Ge	0.074	-0.272	0.135	0.016	-0.164	-0.137
As	0.076	-0.116	-0.205	0.262	0.129	-0.120
Br	-.0.081	0.212	-0.016	-0.144	0.008	-0.241
Rb	-0.090	-0.206	0.021	-0.322	-0.138	0.125
Sr	-0.154	-0.075	-0.122	0.270	0.130	0.127
Y	-0.241	0.025	-0.050	-0.052	0.043	-0.124
Zr	-0.129	-0.067	0.013	-0.075	-0.030	0.015
Nb	-0.052	-0.152	0.030	-0.131	0.126	-0.188
Mo	-0.046	-0.069	-0.067	0.142	-0.073	0.242
Ru	-0.046	-0.055	0.173	0.256	0.052	-0.049
Rh	-0.077	-0.142	0.208	0.149	0.138	0.070
Pd	0.017	-0.149	-0.037	0.052	0.223	0.239
Ag	-0.103	-0.127	0.167	-0.003	0.148	-0.042
Cd	-0.174	0.015	0.053	0.042	0.007	-0.320
Sn	0.005	-0.029	0.147	0.030	0.014	0.145
Sb	0.101	-0.017	-0.271	0.103	0.255	0.070
Te	-0.064	0.013	0.271	-0.145	0.142	0.181
Cs	-0.116	-0.163	0.055	-0.247	0.107	0.085
Ba	-0.124	-0.135	0.054	-0.146	-0.318	0.105
La	-0.194	-0.043	0.105	0.198	0.076	0.170
Ce	-0.223	-0.021	-0.037	0.191	-0.002	0.093
Pr	-0.215	0.017	-0.032	0.178	-0.032	0.007
Nd	-0.201	0.077	-0.080	0.091	0.017	-0.009
Sm	-0.246	0.002	-0.002	0.030	0.063	-0.071
Eu	-0.170	-0.001	-0.070	-0.012	0.004	0.183
Gd	-0.203	0.018	-0.134	0.033	0.045	-0.064
Tb	-0.215	-0.018	0.063	0.005	0.097	0.076
Dy	-0.191	0.018	-0.088	-0.017	-0.031	-0.032
Ho	-0.150	-0.045	-0.109	-0.029	-0.095	0.185
Er	-0.217	0.097	-0.064	-0.048	0.047	-0.190
Tm	-0.128	0.094	0.047	-0.117	0.094	-0.047
Yt	-0.160	0.046	-0.184	-0.031	-0.142	-0.032
Lu	-0.212	0.007	0.109	-0.034	0.036	-0.172
Hf	-0.023	-0.088	-0.018	-0.068	-0.068	0.194
Ta	0.020	-0.183	0.061	-0.085	-0.097	-0.195
W	0.178	0.099	0.007	-0.090	0.198	0.040
Re	0.068	0.144	0.211	-0.067	0.029	-0.063
Os	0.041	0.128	-0.044	-0.199	0.141	0.030
Ir	-0.085	0.030	0.059	-0.001	0.288	-0.244
Pt	-0.008	0.034	0.201	-0.078	0.070	-0.030
Au	0.011	-0.017	-0.113	-0.109	-0.096	0.037
Tl	-0.069	-0.111	-0.108	0.025	-0.350	0.029
Pb	-0.210	-0.084	-0.111	0.127	-0.051	-0.076
Bi	-0.086	-0.099	-0.091	0.224	-0.145	-0.083
Th	-0.120	-0.080	0.209	-0.036	-0.158	-0.017
U	-0.189	0.071	-0.079	-0.06	0.179	0.066

The following points can be made from these plots:

PC 1 / PC 2 Cunningsburgh - Basement samples may be separated
Cunningsburgh - Lewisian samples may be separated

PC 1 / PC 3 shows four distinct groups;

a. Cunningsburgh + some ophiolite
b. Basement + some Lewisian + some Dalradian
c. Some Lewisian + some ophiolite + some Dalradian
d. Some Lewisian + some ophiolite

PC 2 / PC 3 shows three groups;

a. Basement + some + Cunningsburgh + some Dalradian + some Lewisian
b. Lewisian + some ophiolite + some Dalradian
c. Some Cunningsburgh + some ophiolite + some Dalradian

These plots demonstrate that even if only the first three principal components are used, utilising 40 % of the total variance, the large numbers of trace elements reveal the highly structured nature of the data. The separation of several groups that do not reflect the groups known from the geological background of the sources, particularly using PC 1/PC 3 and PC 2/ PC 3, may indicate that the variables that contribute most to these components describe an underlying structure that is different from the preconceived idea of the group structure. This is not easy to interpret and may be a combination of a several factors such as low concentration or poor precision of certain elements. Therefore further PCA focussed on better analysed and geochemically significant groups of elements.

Figure 3.9 Principal component score plot of steatite sources from PCA using all variables.

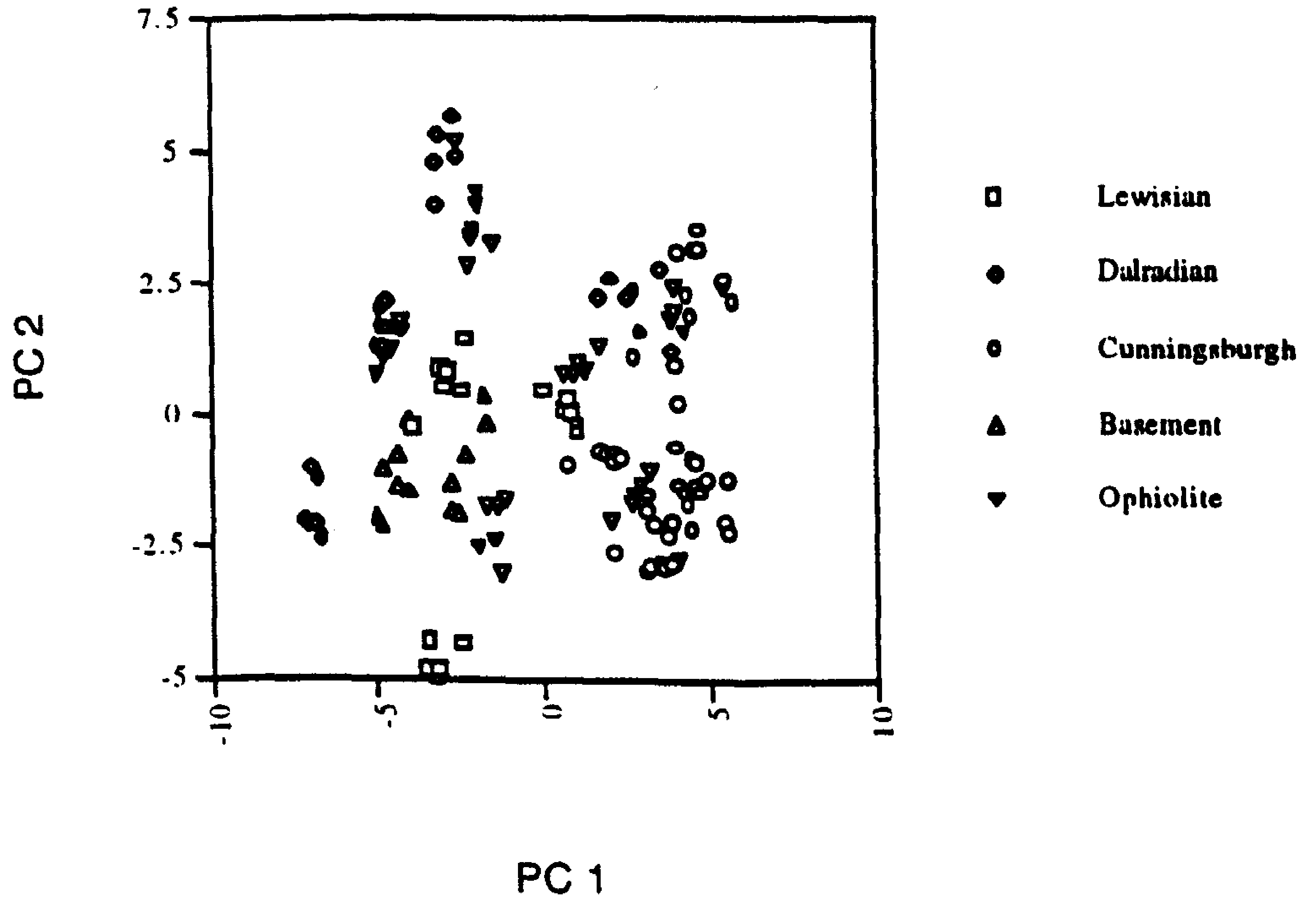


Figure 3.10 Principal component score plot of steatite sources from PCA using all variables.

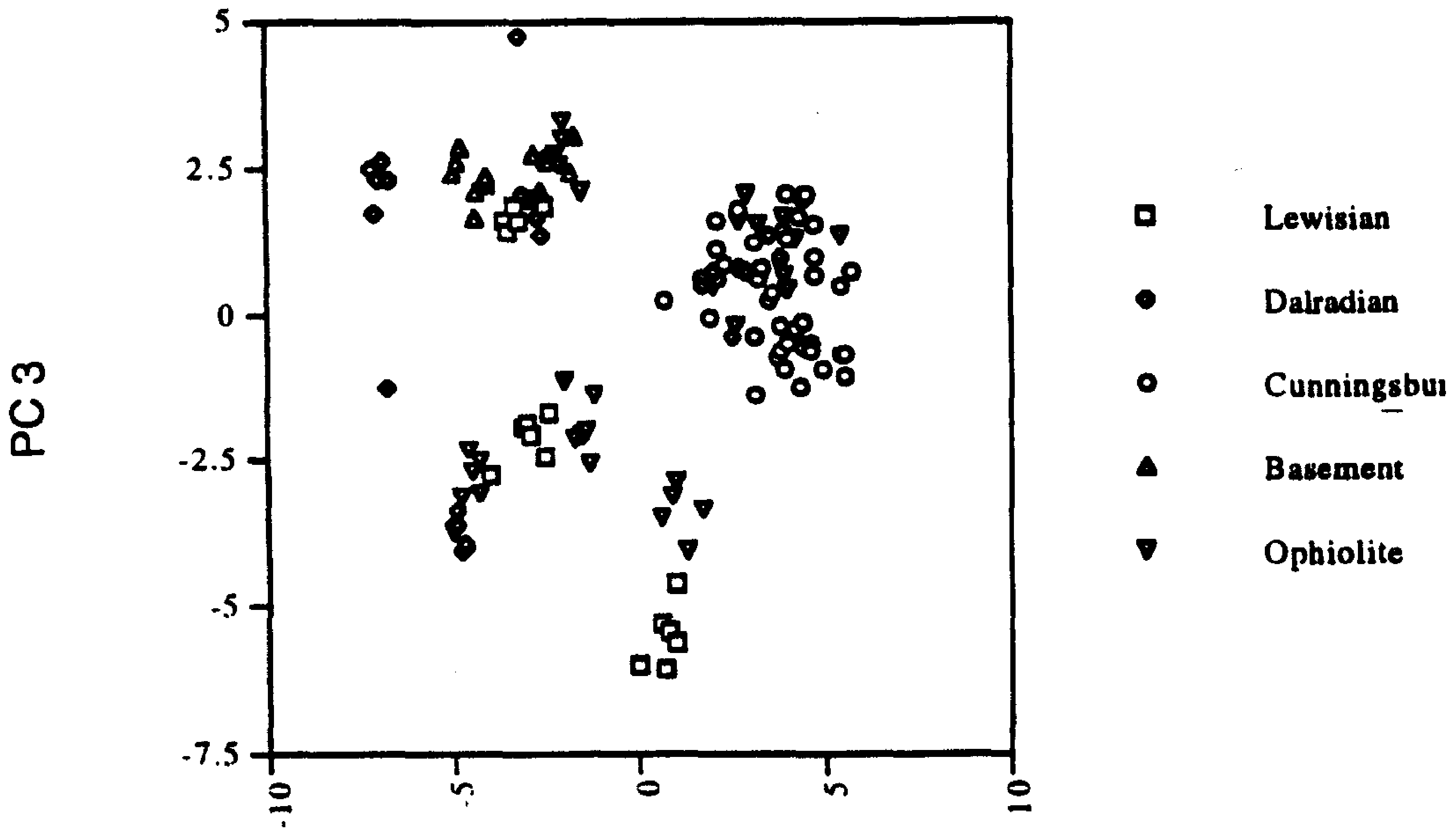
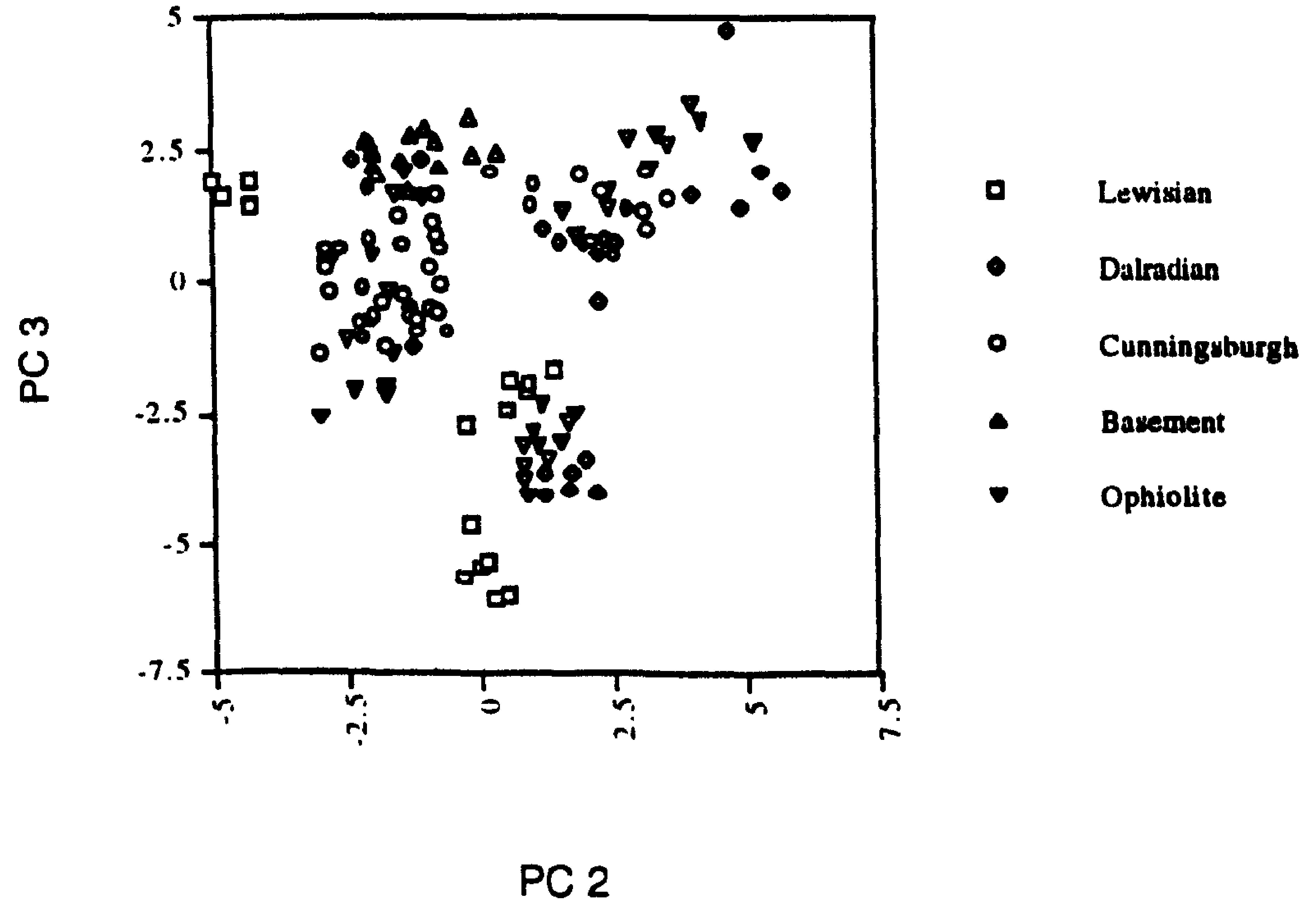


Figure 3.11 Principal component score plot of steatite sources from PCA using all variables.



In order to reduce the number of variables in line with the number of cases being analysed various groups of elements were used in further analysis. These sub-groups of elements were not chosen at random, but by geochemical affinities and on statistical grounds. These sub-groups consisted of:

1. Several elements were arrived at by a process of discarding variables. The method used follows techniques described by Jolliffe (1972, 1973). Variables are rejected which are associated with the last PCs. The number of variables rejected is equal to the number of eigenvalues, smaller than 0.7, associated with the components. The variable contributing most to this component, i.e. the one with largest coefficient, was eliminated. Further analysis based on the remaining elements was completed, the results of which are given in Table 3.7.

2. The elements considered to be well analysed. These were the elements measured with the greatest precision, and this was largely dependant on the elemental concentration. Further analysis was carried out on elements that were considered to be well analysed. These were defined as elements that were measured with greater variability in replicates than in the control samples and contained less than 10% zeros in the data (Group B). A sub-group (Group C) (see Table 3.7) was created by rejection of variables by the method discussed above.

3. A number of elements were identified during the univariate analysis that could separate one or more of the groups and were well analysed. The elements that appeared most suited in discriminating the groups are shown in Table 3.7. These were separated into three sub-groups based on the apparent discriminating power.

4. & 5. As discussed in chapter 2 the formation of steatite is dependent on the interaction of an original ultrabasic parent body with a metasomatic fluid. It was hoped that elements that readily form soluble cations and soluble complex anions may characterise this metasomatic fluid whereas the more immobile hydrolysates may characterise the original parent material. The geological distinct regions may have had similar formation histories within them resulting in similar trace element patterns characterising the parent body and the fluid. Both of these groups were separated into a number of sub-groups. In the soluble ions the original data (Group G) was reduced by the rejection of a number of variables, as discussed in method 1, the remaining elements form Group H, and by separating the most soluble (Group I). The hydrolysates were reduced first by the removal of poorly analysed results (Group K), again by rejection of variables as discussed in method 1 (Group L), and by separating the most insoluble and incompatible elements in a basaltic melt (Group M).

It is notable that these elemental groups are similar to those identified from the analysis of the coefficients of the eigenvectors calculated on the total data set.

Table 3.7 Groups and sub-groups of elements used in the multivariate analysis

Groups on which selection was based	Code	Elements
Elements remain after initial rejection based on preliminary analysis	A	B, V, Cr, Cu, Ni, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Sn, Sb, Cs, Ba, REE, Ta, W, Tl, Pb, Th, U
Elements considered well analysed	B	B V Cr Cu Ni Zn Ga Ge As Rb Sr Y Zr Nb Mo Sn Sb Ba La Ce Nd Ta Pb
Elements considered well analysed	C	Cu, Zn, Ga, Ge, Rb, Sr, ,Zr, Nb, Sb, Cs, La, Nd, Pb
Elements showing discriminating potential from univariate analysis	D	Sr Sm Nb Ba As Sb Ga V Cu Zn Cs Pr W
Elements showing discriminating potential from univariate analysis	E	Sr Sm Nb Ba As Sb Ga V Cu Zn
Elements showing discriminating potential from univariate analysis	F	Sr Sm Nb Ba As Sb Ga –
Soluble Cations	G	Rb Cs Ba Pb Ag Sr Li Cu Cd B Se Cd Zn
Soluble Cations	H	Ba Sr Cu Se Cd Zn
Soluble Cations	I	Rb Cs Ba Pb Sr B
Immobile hydrolysates	J	Be Bi Y Tl Au Cr Ga Th Hf Zr Sn Nd Re Ge Sb Ta As U Mo W & REE
Immobile hydrolysates	K	Be Y Cr Ga Th Hf Zr Sn Nb Ge Ta U Mo W & REE
Immobile hydrolysates	L	Be Gd Ho Tm Yb Cr Ga Hf Ge
Immobile hydrolysates	M	Zr Nb Hf Ga Ta La Ce

Principal component analysis was then performed on these different groups and sub-groups of elements. The eigenvalues, proportion and cumulative proportion of the total variance explained by the first three principal components for these analyses are given in Tables 3.8- 3.11.

Table 3.8 Eigenvalues and proportion of the variance explained by each vector calculated on Groups B and C of well analysed elements

Group		Eigenvector		
		1	2	3
B	Eigenvalue	5.315	4.359	2.939
	Proportion	21.3	17.4	11.9
	Cumulative	21.3	38.7	50.4
C	Eigenvalue	1.504	1.250	1.028
	Proportion	25.1	20.8	17.1
	Cumulative	25.1	45.9	63.0

The first three PC scores were then plotted against one another for the results that could explain the high proportion of the variance by the third PC. These plots, figures 3.12 - 3.23, demonstrate that the PC scores show some differences between the geological groups. The Lewisian samples form a group in all the plots. However, in the cases of the soluble elements (PC 1/PC 2 and PC 2/PC 3), insoluble (PC 1/PC 2 and PC 2/PC 3) and well-analysed elements (PC 1/PC 2 and PC 1/PC 3), the Lewisian samples overlap with the other samples. The Lewisian samples can be resolved from the other samples when the scores from the analysis using elements that showed discrimination potential are used.

Table 3.9 Eigenvalues and proportion of the variance explained by each vector calculated on Groups D, E and F of elements that showed discriminating potential from the univariate analysis

Group			Eigenvector	
		1	2	3
D	Eigenvalue	3.680	2.898	1.810
	Proportion	28.3	22.3	13.6
	Cumulative	28.3	50.6	64.6
E	Eigenvalue	2.871	2.440	1.421
	Proportion	28.7	24.4	14.2
	Cumulative	28.7	53.1	67.3
F	Eigenvalue	2.309	1.838	1.172
	Proportion	33.0	26.3	16.7
	Cumulative	33.0	59.2	76.0

Table 3.10 Eigenvalues and proportion of the variance explained by each vector calculated on Groups G, H and I of soluble cation and complex anions

Group			Eigenvector	
		1	2	3
G	Eigenvalue	3.274	1.624	1.524
	Proportion	27.3	13.5	12.7
	Cumulative	27.3	40.8	63.5
H	Eigenvalue	1.688	1.133	1.006
	Proportion	28.1	18.9	16.8
	Cumulative	28.1	47.0	63.8
I	Eigenvalue	2.315	1.346	1.112
	Proportion	38.6	22.4	18.5
	Cumulative	38.6	61.0	79.5

Table 3.11 Eigenvalues and proportion of the variance explained by each vector calculated on Groups J, K, L and M of immobile hydrolysates

Group			Eigenvector	
		1	2	3
J	Eigenvalue	10.431	3.343	2.551
	Proportion	29.0	9.3	7.1
	Cumulative	28.0	38.3	45.3
K	Eigenvalue	10.024	2.290	2.020
	Proportion	37.1	8.5	7.5
	Cumulative	37.1	45.6	53.1
L	Eigenvalue	9.978	2.295	1.794
	Proportion	37.0	8.5	6.6
	Cumulative	37.0	45.5	52.1
M	Eigenvalue	2.400	1.360	1.149
	Proportion	34.3	19.4	16.4
	Cumulative	34.3	53.7	70.1

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Figure 3.16 Principal component score plot using PC 1 and PC 3 from PCA of "elements that show discriminating potential".

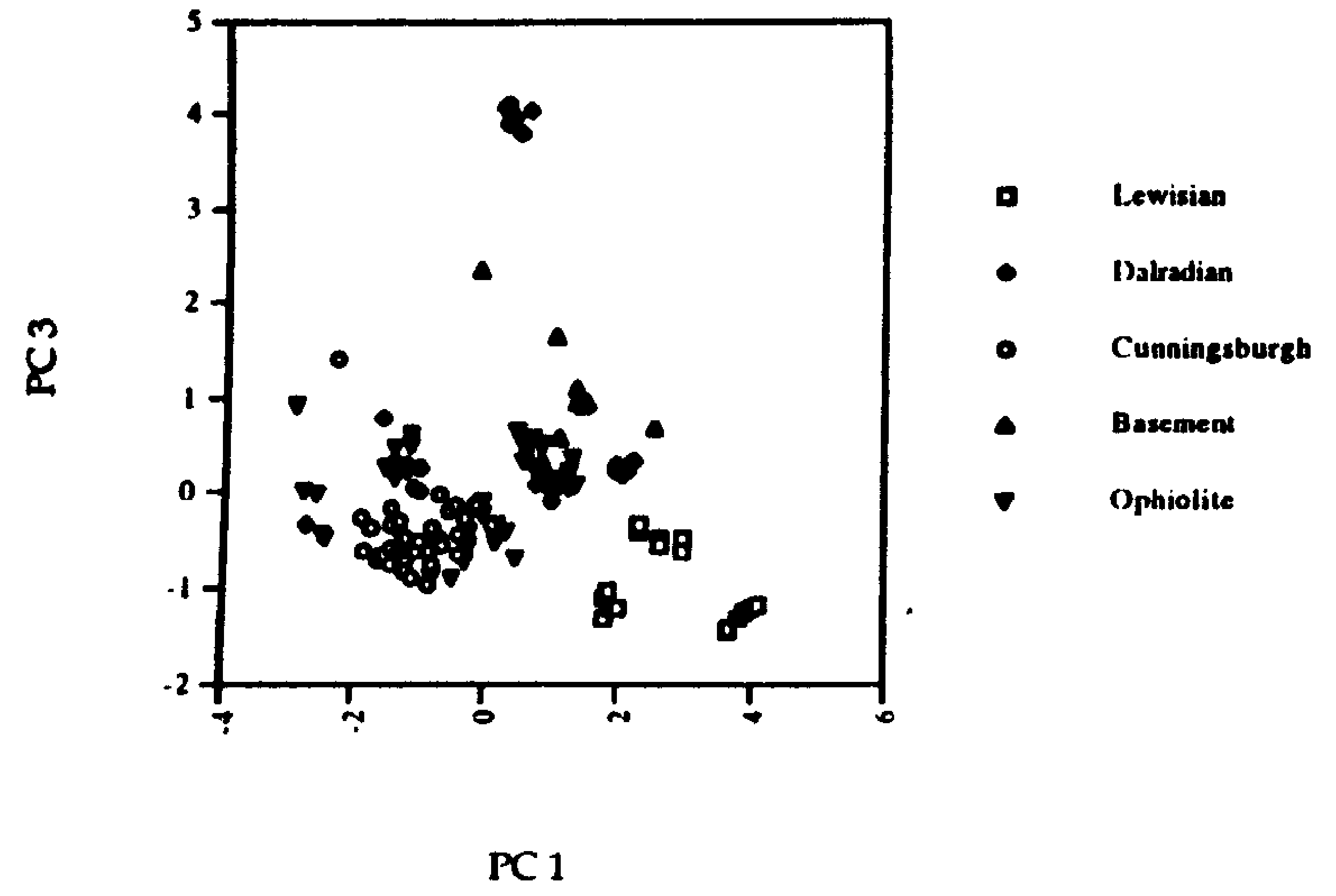


Figure 3.17 Principal component score plot using PC 2 and PC 3 from PCA of "elements that show discriminating potential".

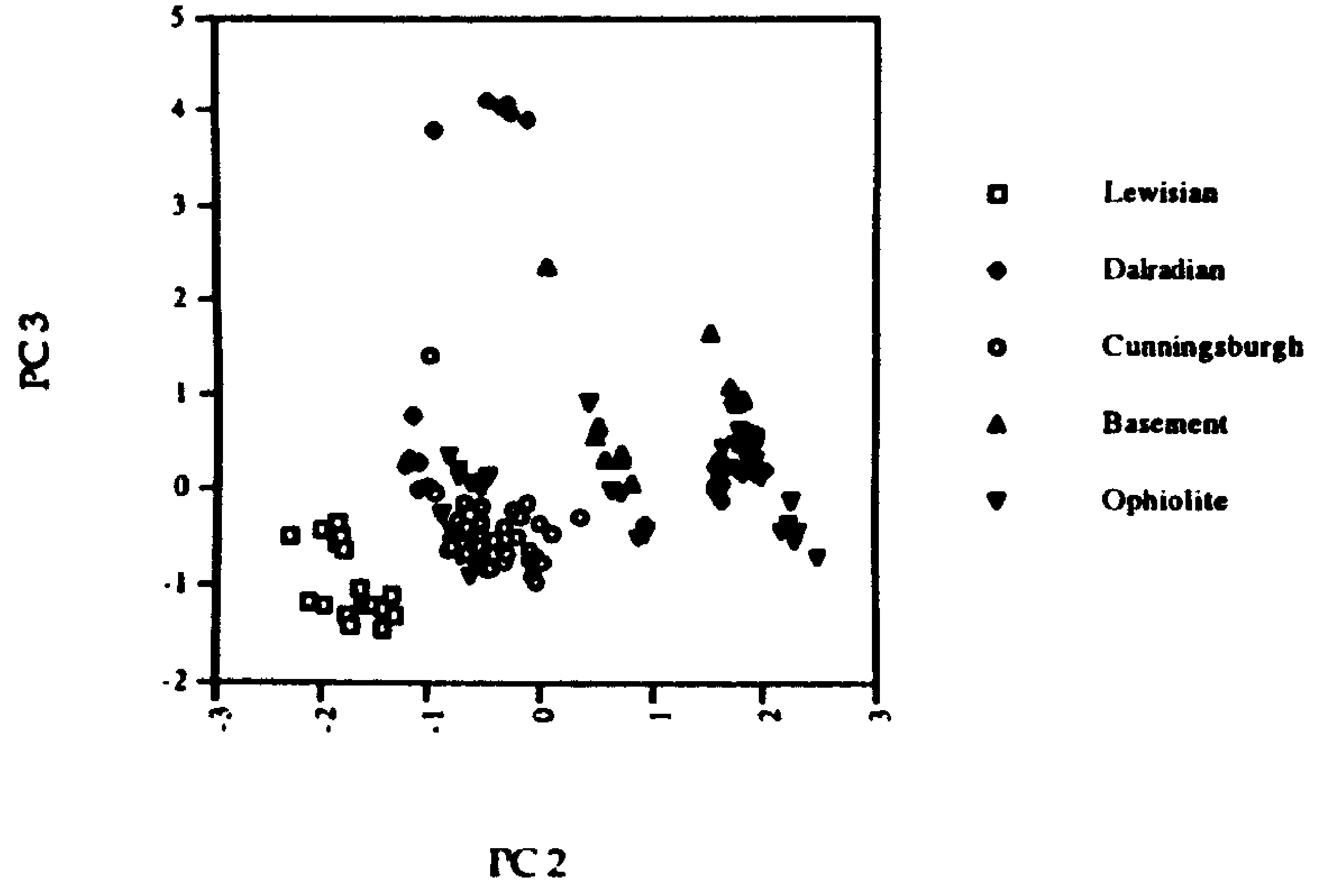


Figure 3.18 Principal component score plot using PC 1 and PC 2 from PCA of "soluble elements".

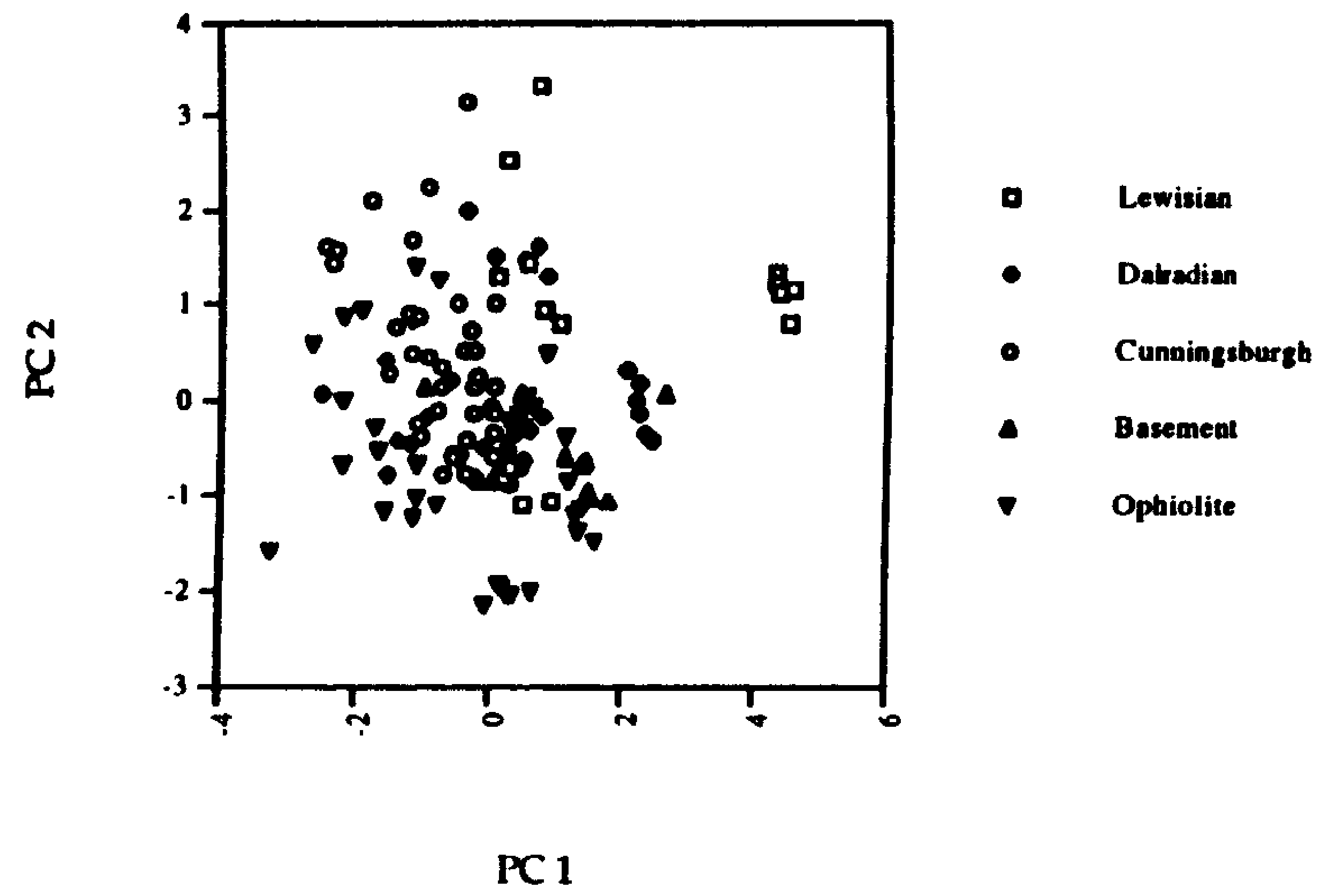


Figure 3.19 Principal component score plot using PC 1 and PC 3 from PCA of "soluble elements".

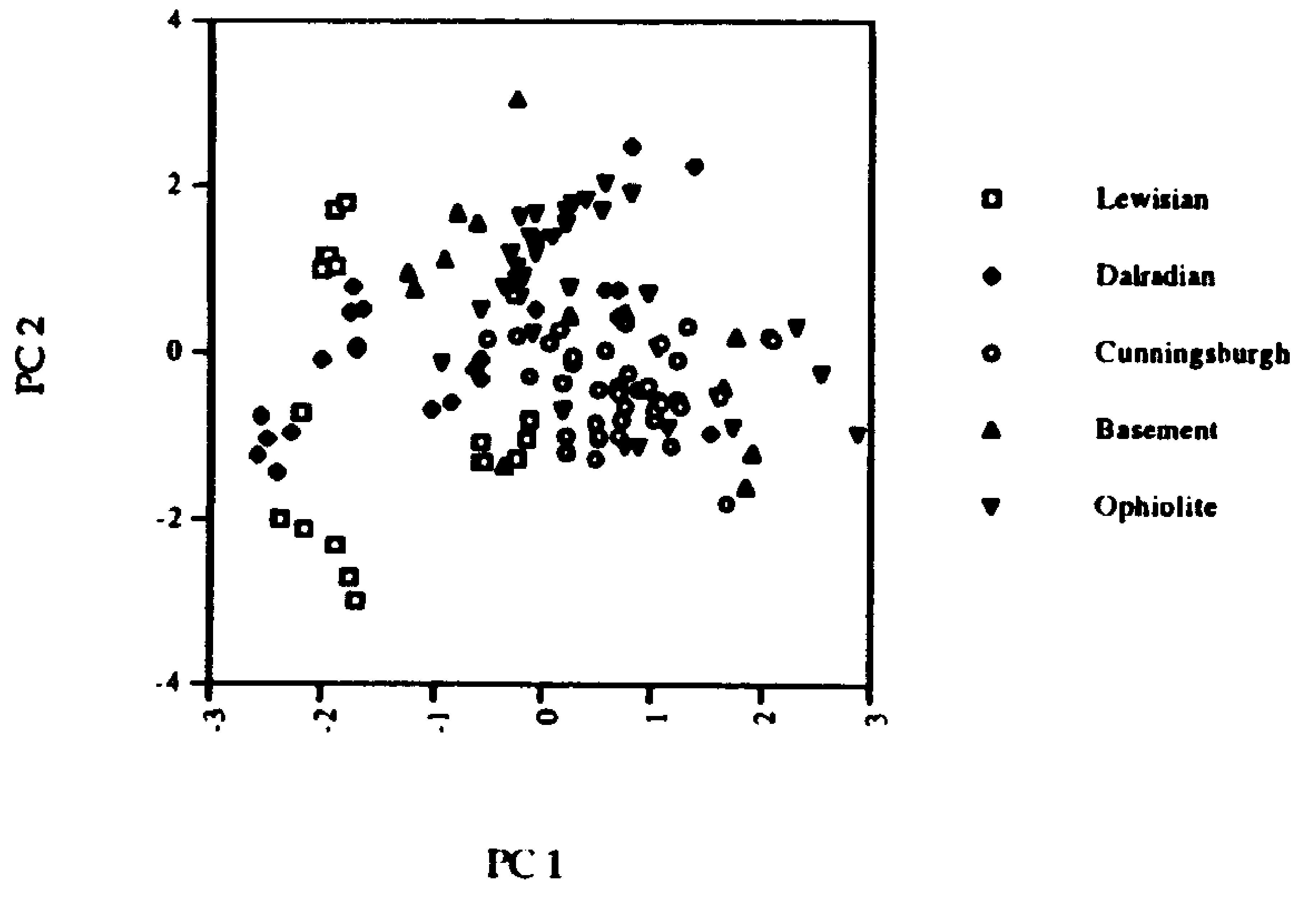


Figure 3.20 Principal component score plot using PC 2 and PC 3 from PCA of "soluble elements".

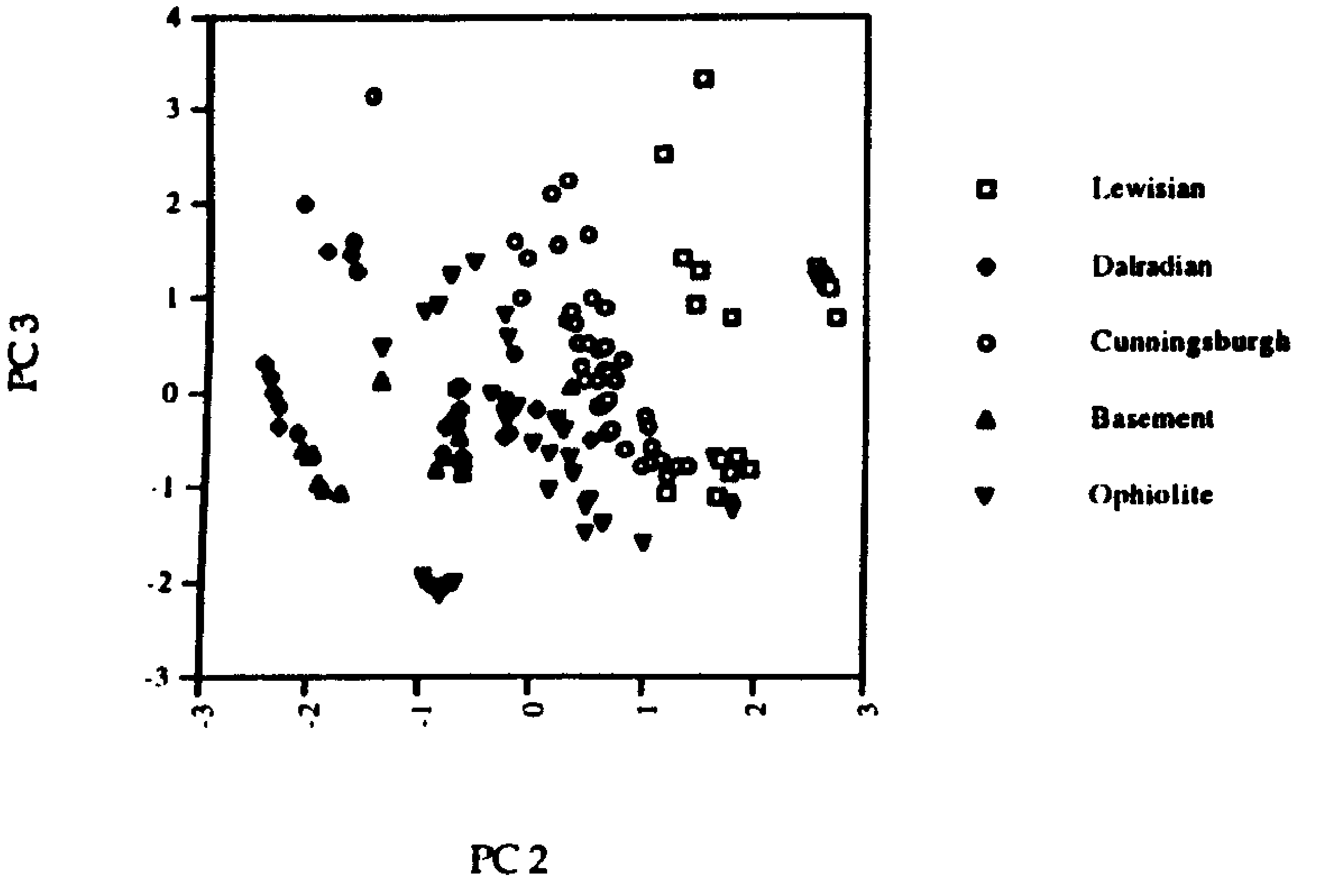


Figure 3.21 Principal component score plot using PC 1 and PC 2 from PCA of "insoluble elements".

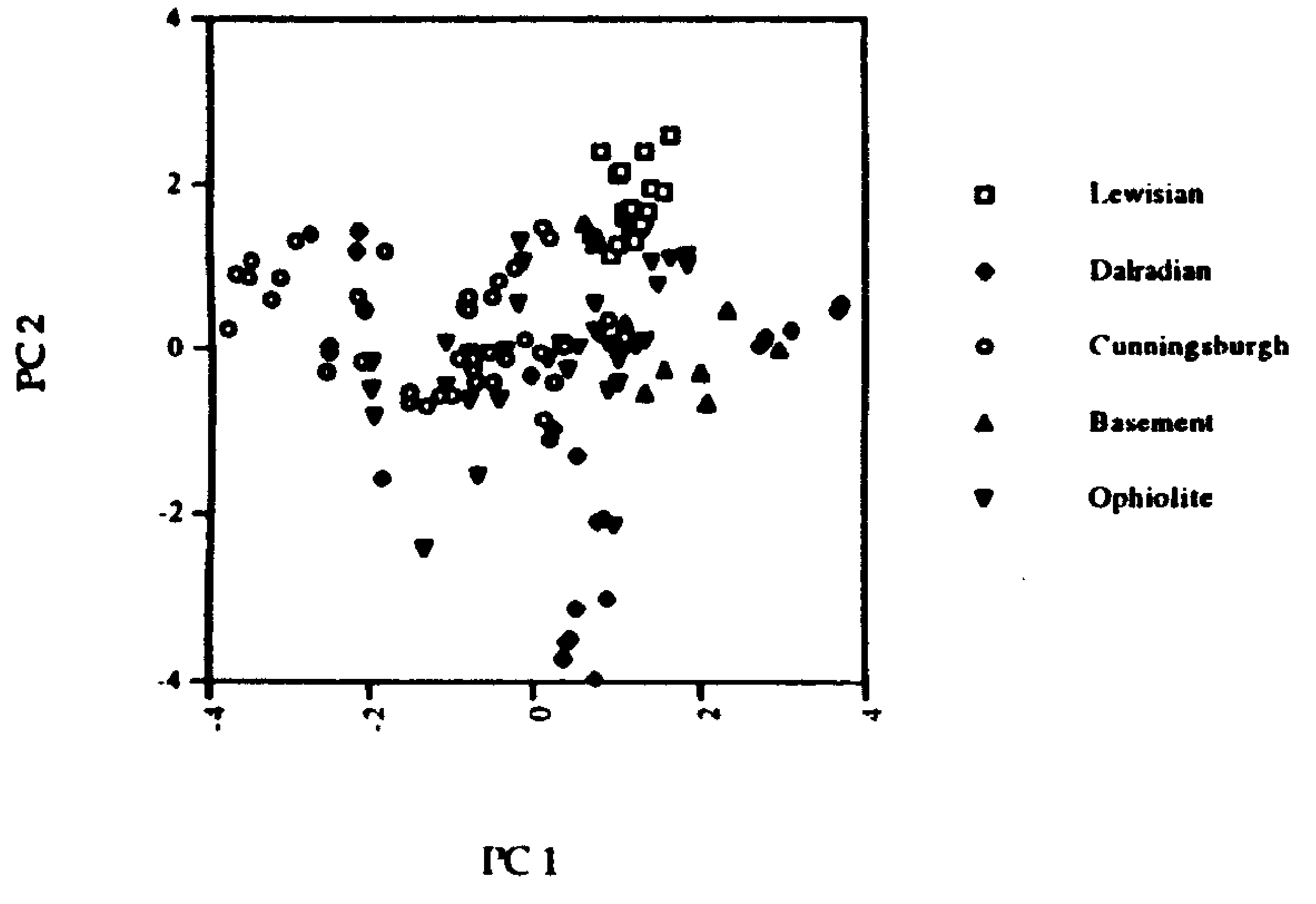


Figure 3.22 Principal component score plot using PC 1 and PC 3 from PCA of "insoluble elements".

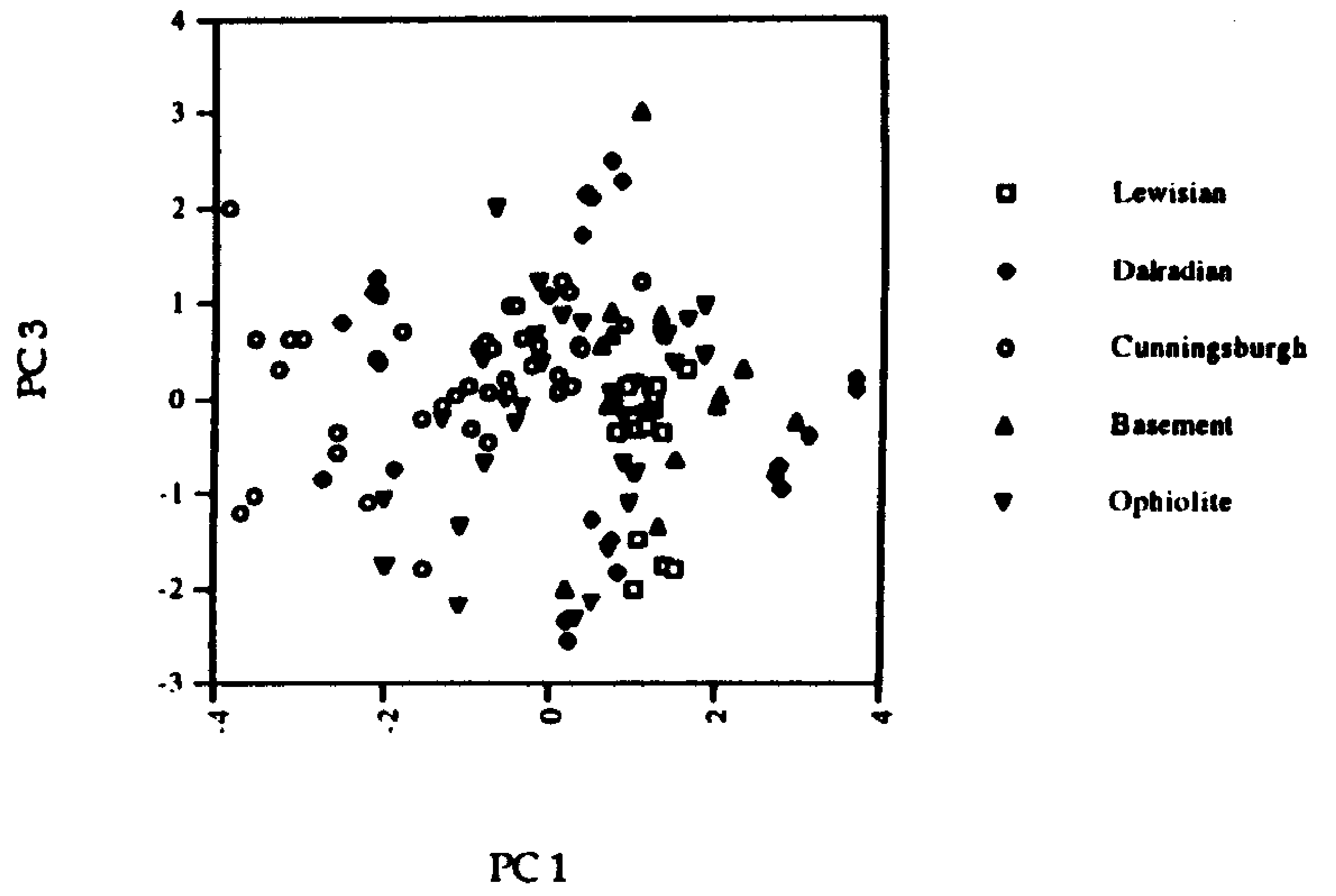
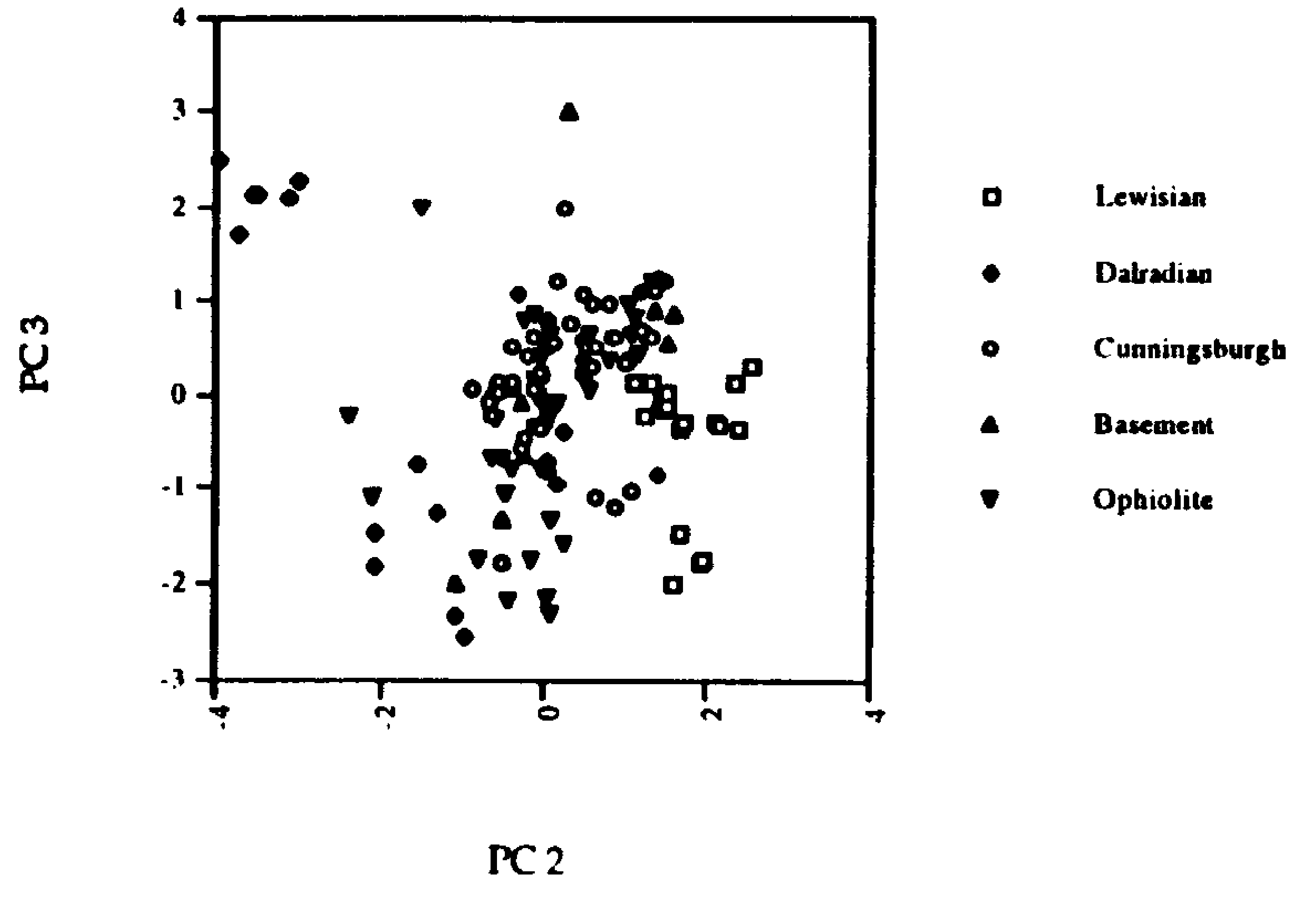


Figure 3.23 Principal component score plot using PC 2 and PC 3 from PCA of "insoluble elements".



The main points to note from the eigenvalues and the plots of the PC scores are as follows:

1. The geological groups cannot be totally separated from one another. However these geological groups form structural groupings within the data.
2. No group or sub-group is able to explain more than 80% of the cumulative proportion of the total variance after the third PC.
3. Using the groups and sub-groups of elements improves the variance explained in the data.
4. The soluble cations and soluble complex anions explain the highest percentage of the variance and PC 2 / PC 3 almost separates the groups.
5. The Lewisian sources can be separated from all other sources when the elements that were identified as possible discriminants from the univariate analysis were used.
6. The elements that showed discrimination potential from the univariate analysis were best able to separate groups when PC scores were plotted, along with the soluble cations and complex anions.

The eigenvector coefficient's were examined in order to identify the variables that contributed most to the initial PCs. The most significant factors upon each PC are given in Table 3.12

Table 3.12 Elements that contribute most to initial PCs after analysis using different variables.

Group	Elements that contribute most to Principal Components		
	PC 1	PC 2	PC 3
A	Rb Ba	Zn	Sr
B	Y Ce La	Ga Zn	Sb
C	Ba Nd	Cu	Sn
D	Sm	Zn	Sr As
E	Zn V Ga	Sm Be	Sr
F	Sm	As	Nb
G	Li Pb	B Zn	Sr
H	Cd Sr	Zn	Ba Se
I	Rb Cs Ba	Pb Sr	B
J	Y	Cr Ga V	Ge
K	Y	Ge	Be Th
L		Ge	Mo
M	La Ce	Ta	Nb Hf

It is apparent from Table 3.11 that the elements that were identified as having discriminatory potential from the univariate analysis also contribute highly in other groups in explaining the variance in the data. Also noteworthy is that certain elements, Y, Zn, Sr, Ba, As contribute highly to a number of elemental group PCs, and may warrant further investigation.

The eigenvalue coefficients from the plots that demonstrated that the new variables were able to resolve much of the group structure were further investigated in order to identify the elements that contributed most to these new variables.

The plots of the scores from the analysis using soluble elements are nearly able to resolve all the groups. If the coefficients of the PCs are examined the following contributions are considered significant:

PC 1	Rb, Cs, Ba, Pb, Li	all positive
PC 2	Rb, Ba, Zn - positive	Ag, B, Cd - negative
PC 3	Rb, Cs, B - positive	Pb, Sr, Cd - negative

The plots of the scores from the analysis using insoluble elements also come close to resolving the groups. From examination of the PC coefficients the following variables can be considered significant:

PC 1	REE, Y, Ga - all negative	
PC 2	Nb, Ta, Ge, Ga - all positive	
PC 3	Zr, Hf, Cr, Mo - positive	Nb, W - negative

This analysis again demonstrates that much of the variance of the total data set may be explained by a number of variables some of which have been identified from the univariate and the PCA of all variables. It is clear that the REE and Y form a group of variables that are highly correlated and analysis suggests that they may be able to resolve the source groups. A similar interpretation can be made for a group of transition elements, As, Nb, Cr, Ni, Ga, Ge, Zn, Ta. A third group of variables comprising first and second group elements is also consistently seen to explain a large proportion of the variance. Both these elements and the REE, Y group belong to groups of either the so called *incompatible* elements, elements that have very low crystal/basaltic magma partition coeffecients or the *large ion lithophiles* (LIL elements). These elements due to their large ionic radii and/or their oxidation states generally preclude their mobility after incorporation into mineral phases. Thus these elements will probably reflect the original ultrabasic precursors relative composition.

3.9.3 Discriminant Analysis

The same groups and sub-groups of elements that were used in the PCA were utilised in the discriminant analysis. These were viewed as a training set of analyses to assess the possibility of placing the samples into the correct groups, tables 3.13 - 3.20.

Table 3.13 Summary of Linear Discrimination Analysis for region based on entire data set (Group A)

Put into Group	True Group			
	1	2	3	4
1	10	9	0	0
2	8	40	2	12
3	0	4	7	1
4	0	12	4	23
n Total	18	65	13	36
n Correct	10	40	7	23
Proportion	55.6	61.5	53.8	63.3

N = 132 N correct = 80 Prop. correct = 60.6

	Square Distance Between Groups			
	1	2	3	4
1	0	6.063	21.021	11.854
2	6.063	0	7.754	2.028
3	21.021	7.754	0	5.587
4	11.854	2.028	5.587	0

Table 3.14 Summary of Linear Discrimination Analysis for region based on elements that were considered well analysed (Group C)

Put into Group	True Group			
	1	2	3	4
1	12	7	0	0
2	6	46	0	7
3	0	4	9	1
4	0	8	4	28
n Total	18	65	13	36
n Correct	12	46	9	28
Proportion	66.7	70.8	69.2	77.8

N = 132 N correct = 95 Prop. correct = 72.0

	Square Distance Between Groups			
	1	2	3	4
1	0	5.505	18.035	13.763
2	5.505	0	6.340	2.834
3	18.035	6.340	0	6.560
4	13.763	2.834	6.560	0

Table 3.15 Summary of Linear Discrimination Analysis for region based on elements that showed discriminating potential from univariate analysis (Group D)

Put into Group	True Group			
	1	2	3	4
1	18	0	0	0
2	0	64	0	2
3	0	0	13	0
4	0	1	0	34
n Total	18	65	13	36
n Correct	18	64	13	34
Proportion	100	98.5	100	94.4

N = 132 N correct = 129 Prop. correct = 97.7

	Square Distance Between Groups			
	1	2	3	4
1	0	44.701	68.631	55.007
2	44.701	0	32.912	18.304
3	98.631	32.912	0	22.161
4	55.007	18.304	22.161	0

Table 3.16 Summary of Linear Discrimination Analysis for region based on elements that showed discriminating potential from univariate analysis (Group F)

Put into Group	True Group			
	1	2	3	4
1	18	0	0	0
2	0	54	0	1
3	0	0	10	0
4	0	11	3	35
n Total	18	65	13	36
n Correct	18	54	10	36
Proportion	100	83.1	76.9	97.2

N = 132 N correct = 117 Prop. correct = 88.6

	Square Distance Between Groups			
	1	2	3	4
1	0	16.375	38.560	24.417
2	16.375	0	17.230	5.750
3	38.560	17.230	0	5.612
4	24.417	5.750	5.612	0

Table 3.17 Summary of Linear Discrimination Analysis for region based on soluble cations (Group G)

Put into Group	True Group			
	1	2	3	4
1	18	0	1	0
2	0	48	0	7
3	0	11	10	2
4	0	6	2	27
n Total	18	65	13	36
n Correct	18	48	10	27
Proportion	100	73.8	76.9	75.0
N = 132	N correct = 103		Prop. correct = 78.0	
		Square Distance Between Groups		
	1	2	3	4
1	0	19.229	28.338	29.092
2	19.229	0	7.418	4.525
3	28.338	7.418	0	7.647
4	29.092	4.525	7.647	0

Table 3.18 Summary of Linear Discrimination Analysis for region based on soluble cations (Group I)

Put into Group	True Group			
	1	2	3	4
1	13	0	1	1
2	0	48	0	8
3	5	7	12	4
4	0	10	0	23
n Total	18	65	13	36
n Correct	13	48	12	23
Proportion	72.2	73.8	92.3	63.9
N = 132	N correct = 96		Prop. correct = 72.7	
		Square Distance Between Groups		
	1	2	3	4
1	0	9.618	13.664	17.445
2	9.618	0	5.470	1.988
3	13.664	5.470	0	6.838
4	17.445	1.988	6.838	0

Table 3.19 Summary of Linear Discrimination Analysis for region based on insoluble elements (Group J)

Put into Group	True Group			
	1	2	3	4
1	16	0	0	0
2	1	59	0	4
3	0	0	13	1
4	1	6	0	31
n Total	18	65	13	36
n Correct	16	59	13	31
Proportion	88.9	90.8	100	86.1
N = 132	N correct = 119		Prop. correct = 90.2	
	Square Distance Between Groups			
	1	2	3	4
1	0	20.165	24.228	17.937
2	20.165	0	21.453	9.767
3	24.228	21.453	0	26.949
4	17.937	9.767	26.949	0

Table 3.20 Summary of Linear Discrimination Analysis for region based on immobile elements (Group M)

Put into Group	True Group			
	1	2	3	4
1	7	9	0	5
2	4	46	0	6
3	6	2	11	2
4	1	8	2	23
n Total	18	65	13	36
n Correct	7	46	11	23
Proportion	38.9	70.8	84.6	63.9
N = 132	N correct = 87		Prop. correct = 65.9	
	Square Distance Between Groups			
	1	2	3	4
1	0	2.539	7.072	1.626
2	2.539	0	7.254	2.025
3	7.072	7.254	0	4.703
4	1.626	2.025	4.703	0

Examination of these results allows the establishment of the following points:

1. The proportion of samples placed correctly by group/sub-group of elements is relatively high.
2. Elements that show possible discrimination from univariate analysis (Group D) are most successful at placing samples correctly.
3. The insoluble elements are able to place samples correctly more often than the soluble elements.

4. The Lewisian samples are the most easily separated from the other sources, reflected by the large square distance between the Lewisian group and the other groups. Element groups using insoluble elements and elements that show discrimination from the univariate analysis are able to place the Lewisian samples correctly in each sample case. These results suggest that the Lewisian sources have a substantially different character from the other sources, primarily based on their parent region.

5. The square distance measure suggests that the Dalradian and ophiolites sources are similar in trace element composition, making any separation difficult. It is noteworthy that although the Dalradian and ophiolite groups display the lowest square distance measure, when soluble elements are used, this value is greater than in the other analysis. A similar ability to separate these groups was noted from the PCA, especially the PC 2 / PC 3 plot.

3.9.4 Evaluation of multivariate techniques

Compositional analysis commonly results in many variables (elemental concentrations) determined for large numbers of observations. When large data sets are analysed interpretation is often difficult if four or more dimensions are considered simultaneously. Multivariate techniques allow for the analysis of large multi-dimension data sets with relative ease thus enabling complex relationships to be examined hence results that enable archaeological interpretation of the samples to be made.

Multivariate analysis also has an advantage over simpler univariate or bivariate methods as large numbers of variables can be used in a classification. Therefore in accordance with one of the fundamental principals of numerical taxonomy a better classification will be produced as the more characters on which a classification is based the better it is. Also the methods of multivariate analysis do not violate an underlying assumption of numerical taxonomy that every character must be given equal weight. Multivariate techniques also reduce the effects of certain elements with large variances biasing the results as these effects are accounted for in the calculation of the variance-covariance matrix. Therefore it can be concluded that in order to optimise the classification it is best to include as many elements that display variation as possible. A problem with some multivariate techniques is the existence of inter-elemental correlation. These correlations result in the spreading out of the "volume of space" occupied by groups within the data set. Thus possible separations between groups may be obscured.

Principal component analysis is an extremely powerful technique that enables a reduction in the dimensionality of the data set while sacrificing minimal information. The method is based on the premise that observed correlations are a result of some underlying structure in the data. The technique requires no assumptions to be made regarding the structure of the variables. When exploring a compositional data set the type of questions posed will determine the techniques used. PCA is particularly useful where no structure is imposed on the data set. Therefore the technique can reveal any underlying structure without subjective interpretation and thus archaeological interpretation can be made of this structure. This has proved a useful technique in many ceramic studies where the group structure is obtained from a representative set of artifact samples as many problems exist with precise sourcing of pottery. In many other provenancing studies a high percentage of the total variance in the sample population can be described by the first three PCs (Bishop & Neff 1989, Glasscock 1992). Samples of "unknown" affiliation can be analysed with a known group structure and similarities assessed by means of PC score plots. Unless the separation of the groups is distinct this assessment can be rather subjective.

Discriminant Analysis is another multivariate technique that examines the underlying structure of the data. Discriminant Analysis differs from PCA in that it extracts a new set of variables which maximise the differences between two or more groups rather than maximising the total variance. Therefore the structure of the data set must be known prior to analysis and all samples must be placed into two or more groupings. Discriminant Analysis attempts through a series of discriminant functions to maximise the variance between these groups and ideally separates the groups. Discriminant Analysis is most useful when it is necessary to distinguish between two or more groupings. Thus initial analysis maybe used to establish the discriminant functions that reflect the group structure. New samples of "unknown" group affiliation may be assigned to one of the original groups by the use of these discriminant functions. Thus a definite "answer" is provided that does not require subjective judgement. A potential for misinterpretation exists if the original data set does not represent all potential groups as "unknown" will be forced into one of the original groups.

Cluster Analysis has been a popular method of multivariate analysis of compositional data for provenance studies for many years. Cluster analysis is based on a dissimilarity matrix in which the distance between all pairs of samples is calculated using one of several possible distance measures. Cluster analysis may be viewed as an exploratory tool for helping to solve classification problems and it is best used when little or nothing is known about the structure of the data set. However, a number of problems exist. Firstly there are eight algorithms available for hierarchical cluster analysis but no explicit rules as to which method is most applicable in a given situation. There have been few attempts in order to establish a consistent methodology for cluster analysis (Prag et al 1974, Wilson 1978) and little in establishing an objective criterion for the evaluation of clustering methods (Rand 1971, Blashfield 1976, Cunningham & Ogilvie 1972). Further the different algorithms do not necessarily produce similar results on a given data set. Secondly, although the clusters obtained are formed by explicit and objective procedures there is a large subjective component in the actual choice of the number of clusters. Thirdly, the primary output and source of interpretation, the dendrogram, has been criticised

(Christie et al 1979) for its oversimplification of a hugely complexed multidimensional problem. Traditionally a set of data with known structure is analysed and thus the relevant algorithms selected. This type of approach can only work on data sets where cases are clearly distinct. If any overlap is present the algorithms may never produce the desired solution and a subjective decision must be made.

3.9.5 Summary of Multivariate Analysis

The use of three multivariate techniques has allowed these techniques to be compared as well as enabling the results from each method to be compared. Areas of agreement and disagreement have been recognised thus increasing the reliability of the interpretation and enabling elements to be identified for further more precise analysis. Cluster analysis revealed little information about the data set for a number of reasons discussed in Appendix C. This discussion is therefore largely based on the PCA and Discriminant Analysis.

In all techniques the use of all the variables reduces the useful information gain from the analysis. This implies that a number of the elements used in the analysis do not contribute to any group structure within the entire data set. Clearly a number of these elements were analysed with less than desired precision. Thus any group structure contained within these elements may be obscured.

PCA of the entire data set, of 57 trace elements, was able to explain 40 % of the total variance in the first three principal components. This is particularly good if the number of variables (57) is taken into account. Plotting the principal component scores, although unable to resolve the groups entirely, demonstrates that the data are highly structured. Thus the eigenvector coefficients have been examined to enable variables that contribute highly to these principal components to be identified. This analysis revealed that several elemental groups are responsible for much of the variance in the data. The REE contribute largely to PC 1, selected transition elements to PC 2 and the platinum group and other transition elements to PC 3. Clearly these elements warrant further investigation.

Although this analysis demonstrated that structure existed in the data, the resolution of the groups was insufficient to allow useful provenance information to be obtained. In order to enable a greater proportion of the total variance of the data to be explained by the initial principal components 3 elemental sub-groups were selected. These sub-groups were based on geochemical elemental grouping and statistical grounds. It is notable that the elements selected using the geochemical and statistical criteria were also highlighted by the analysis of the total data set eigenvector coefficients. This agreement by independent methods suggests that the elements selected display the greatest variance and thus may be the best at resolving the groups.

PCA and Discriminant analysis both indicate that variables which were selected from univariate and bivariate analysis, although unable to entirely resolve the group structure within the data set are "best" at explaining the structure. Both methods are able to distinguish between the Lewisian and all other British sources. This suggests that differences exist between these steatite sources in the elements; Sr, Sm, Nb, Ba, As, Sb, Ga.

The use of selected elements that were considered to be representative of the fluid, i.e. highly soluble elements, were almost able to resolve all the groups after PCA. The discriminant analysis demonstrated that these same elements were also relatively successful in placing samples into the true group. Analysis of the eigenvector coefficients revealed that the variables that contributed most to this resolution of the groups were; Pb, Sr, Rb, Cs, Ba, Cd, B, Zn and Se.

Variables were also selected that were considered to be representative of the ultrabasic precursor, i.e. elements that would be unaffected by the metasomatic process. PCA demonstrated that the data were highly structured. Although the principal component score plots are unable to totally resolve the groups, the Lewisian may be separated from all other groups and other groups form bunches that are almost resolved from one another. Discriminant analysis is able to place a large proportion of the samples into the true group using these same elements, 90 % correctly placed. This reflects the near separation obtained from PCA. Analysis of the eigenvector coefficients enabled the following elements to be identified as contributing most to the principal components that explained the greatest percentage of the variance, REE, Y, Cr, Ga, Ge, W, Th, Mo, Nb, Ta, Zr, Hf. Again many of these elements were identified from the analysis of the total data set as contributing highly to the total variance.

Elements were also selected by a process described by Jolliffe (1972, 1973) of eliminating variables that contributed little to the overall variance in the data. The agreement between elements selected in this manner and the other sub-groups of variables (soluble, insoluble and elements showing potential from univariate analysis) again emphasise that these elements are potentially the most likely to resolve the group structure totally. Of all the sub-groups of elements used these are the least successful following PCA in resolving the group structure, although structure remains apparent in the results. This poorer resolution of the groups is reflected in a lower percentage of correct placement of samples by discriminant analysis.

The use of different variables in separate analyses has allowed an assessment of the potential usefulness of variables. In separate analyses a number of different groups of elements have repeatedly explained much of the variance of the data; REE and Y, LIL, and a number of transition elements. These elements, due to their similar geochemical behaviour, are selected as groups after multivariate analysis. Clearly, these are the variables that are most likely to demonstrate differences between sources. Thus their identification is a step towards the potential resolution of steatite sources.

These analyses go a long way to resolving the group structure within the data, although no analysis was able to fully resolve all the source regions. However, the Lewisian may be separated from all other groups by the use of a number of different elements, both insoluble and elements that show potential from univariate analysis sub-groups. All the other source regions overlap with one another. However in several cases these groups are nearly resolved. The failure of these techniques to resolve the data may be a function of the complex multivariate relationships explored in this analysis. Alternatively no relationship may exist between these groups and the elements analysed.

Although the multivariate techniques have been unable to resolve all the source groups, by the use a of number of different elemental groups the Lewisian may be separated from all other sources. Therefore these techniques can answer the question as to whether a steatite sample is of a Lewisian source origin or not. This may have important implications for the study of steatite utilisation in Scotland, especially in areas where Shetland or Scandinavian sources appear unlikely.

3.10 Discussion of Geochemistry in Relation to Tectonic Province

The trace element concentrations in steatite are dependent on a number of factors, including composition in the parent material, concentration in the metasomatic fluid and partition coefficients between the mineral phases and the fluid. The partition coefficient is in turn dependant on variations in temperature, pressure and composition. These factors result in different concentrations in different mineral phases and the overall concentration in the steatite as a whole. These differences have important implications for steatite provenancing using trace elements.

The major elements have already been discussed in relation to mineral phases. With the changes in mineral phases within a steatite deposit there are changes in the major element concentration. Many steatite bodies have a zonal arrangement even in the "worked" area, see Curtis & Brown (1969), thus making provenancing using major elements very difficult.

Other factors that may account for any clear distinction between the separate sources are the potential lack of any regional characteristic to the parent ultrabasic and/or metasomatic fluids.

The similarities of the parental ultrabasics are discussed further in chapter 2 with particular reference to the Rare Earth Elements, however there is a remote possibility that all the ultrabasics are a result of similar formation process and environments, thus resulting in a similar trace element pattern. Also the ultrabasics within a single tectonic region may not represent a single "type" of ultrabasic as different processes in different environments may have resulted in their formation, thus further confusing the characterisation of the tectonic regions. The fact that the metasomatic fluid has a regional signature is an assumption made here. However, these fluids may have no overall regional character as their properties may be controlled by the immediate local environment. However, if this is the case, it may be expected that geological environments such as the ophiolites had a significantly different metasomatic fluid characteristic, as discussed in relation to the Sr isotopic ratio (see chapter 5).

Trace elements are distributed amongst the various phases of the system and are rarely significant constituents of any mineral phases. When a solution is sufficiently dilute with respect to a particular solute component, the behaviour will follow Henry's law. However, when trace elements are at extremely low concentrations deviation from Henry's law is possible (Watson 1985) because of the likely existence of defect sites, such as those caused by structural dislocations or intergrowths. However, defect sites are relatively few in number and soon become saturated with trace elements (Navrotsky 1978). This may account for differences in ultra-trace element concentrations even over small areas.

A number of trace elements show similar features to major components and demonstrate a strong correlation with mineral phases in ultramafic deposits. For example Sc, Cr, Ni, Ga, Ge, Co are largely dependant on the mineral phase. Others, as a result of processes and similar partition co-efficient for the different phases, do not show this phase dependency, Mn, Y and the REE. Elemental concentrations that are largely controlled by mineral phases will probably be less useful in any provenancing study as their concentration will vary across the often zoned steatite deposits, resulting in a high internal variation. These high internal variations will probably obscure any differences between sites. From both the univariate and bivariate analysis it was noted that a number of elements showed discriminating potential between the source regions, these elements are dominated by those that show little phase dependence in the system.

The trace element results demonstrate that the differences between the geological region groups are not evident as a unique and distinct trace element concentration character for the steatite found within the separate regions. However the Lewisian sources of steatite appear to be significantly different from the other sources in a number of different respects. These differences in the Lewisian sources may be explained by differences in the geochemical evolution of the Lewisian. The parent ultrabasics may represent a different type of Alpine peridotite from the other sources.

The Lewisian complex's trace element geochemistry presents a number of distinctive features, some of which are attributable to the effects of high grade metamorphism. In particular, significant contrasts have been established between granulites and their retrogressive derivatives, which appear to have undergone high pressure and temperature metamorphism during the early Scourian or Badcallian and the more widespread "grey gneisses" of amphibolite facies that underwent lower temperatures and pressures during the same events. The granulites of the Scourian complex show a depletion in K, Rb, Cs, Th, U with higher than average crustal abundances of Ba, Sr, Zr, Ce, Y (Tarney 1976). These features are ascribed to the effects of granulite facies metamorphism expelling volatile and incompatible elements from the granulites. However, the ultramafic bodies altered to form steatites are all within the "grey gneisses", thus the depletions in these trace elements may not be as marked. In general the Lewisian complex has lower concentrations of U, K, Th, Be and Pb relative to the values of Zr, Sr, Ba, B and Y compared to units for the Moine and Dalradian (Johnstone et al 1979), features in which the Lewisian seem to differ from some Norwegian examples (Cooper & Field 1977).

In this study the U concentrations in the Lewisian sources are low, less than 20 ppb. This is lower than most of the other samples. However a number also have compatibly low values; zmc-1, zmc-2, msc-1, zuc-2, zfd-4. The samples from the Lewisian also show no significant depletion, with respect to the other samples, in the other incompatible elements analysed. There are a number of possible explanations for these features. Firstly, the steatites from ultrabasics within the "grey gneisses" of the Lewisian complex are considerably less depleted than the granulite areas. Also, soluble incompatible elements, such as Rb, Cs, and Pb, may reflect the concentration in the metasomatic fluids and not the general over concentration of the region, despite any removal of incompatible elements attributed to processes associated with dehydration (Heier & Adams 1965). This may also apply to U that is soluble as a CO_2 complex, conditions that may have been present during metasomatism (Henderson 1982).

The trace element concentrations demonstrate that the different regions do not have distinct trace element characteristics that can be easily quantified. It was thought that the different regions may have contained ultrabasics that were of different origin and therefore different trace element characteristics relating to those origins. There are a number of types of ultramafic associated with different tectonic settings, including komatiites, major layered intrusions, Alpine type ultramafics, zoned Alaskan ultramafic complexes and Appinite type ultramafics. Of most interest are the Alpine type ultramafics that appear to be the original parent ultramafics of most steatite bodies. Alpine ultramafics may be divided into ophiolitic suites and non-ophiolite Alpine peridotites. These types have different origins as is reflected in a number of features: non-ophiolite ultramafics are often highly deformed and rarely contain any cumulate textures. Most are of pyroxene composition indicating initial crystallisation was at high temperature. Some are garnet bearing (also indicating high temperature origin). Others contain bodies of basic material interpreted as partial melt products. All of these features suggest an upper mantle origin for this type of peridotite. The non-ophiolite peridotites are predominantly lherzolites, whereas the ophiolites are dominantly harzburgites and dunites. This difference is significant as lherzolites are much richer in fusible constituents than harzburgites and dunites. Thus lherzolites may be considered "fertile" or "undepleted" mantle whereas harzburgites and dunites are more likely to be melting residue cumulates.

The steatite from the Unst/Fetlar, Lizard and Anglesey ophiolites are clearly from ophiolitic Alpine type ultramafics. The origins of the ultramafics in the Lewisian complex are unclear, although Tarney & Weaver (1987) have suggested that they form fragments of oceanic floor intercalated tectonically with the continental crust in a subduction zone.

3.11 Conclusions

These analyses have demonstrated that ICP-MS offers great potential in trace element analysis for archaeological provenance studies. ICP-MS offers relatively rapid analysis capability for a wider range of elements with lower detection limits than many techniques conventionally used for chemical characterisation studies. Sample dissolution techniques have been evaluated and a method that results in total dissolution has been achieved. Analysis of standard reference material confirmed this procedure.

Elements that can be analysed in a multi-element semi-quantitative mode with some degree of precision have been identified. A large number of elements were analysed with reasonable precision, 20 with coefficients of variation of less than 10% and 34 less than 20%. Thus these results have allowed this provenance study to concentrate on these elements. The potential of these elements in provenancing steatite has been assessed through the structured statistical approach used in this study.

Analytical techniques such as ICP-MS are able to generate substantial volumes of data with complex relationships between analysed variables. Therefore a systematic approach to data analysis was required to enable an objective evaluation of the results to be made. This study has provided an example of a structured statistical approach to deal with the large data sets that may be created from ICP-MS analysis. ICP-MS has the advantage over techniques such as NAA in that the errors change predictably through the periodic table and with concentration. Thus the data lend themselves well to multivariate analysis, whose underlying assumptions are possibility not violated in the same manner that may occur with other analytical techniques with less predictable error structures.

The use of this structured statistical approach to the analysis of the data has enabled the techniques used to be evaluated with respect to complex multi-element data sets.

One of the aims of this chapter was to assess the statistical methods commonly used in the analysis of large data sets in which by their nature multivariate relations exist. There are no short cuts in the analysis of such data sets for data simplification to be reliable. Ideally a multitude of techniques should be used in a structured manner to establish areas of agreement and disagreement on which the final interpretation can be more reliably based.

The univariate and bivariate analysis have served a number of important functions. The methods used enabled the identification of elements that display some discriminating potential between the source groups. They also allow an assessment of the normality of the data to be made thus influencing decision of log transformation or standardisation important in any further multivariate analysis.

There is no single "best" data analysis method. Each technique has its strengths and weaknesses, for example it is clear that Discriminant Analysis is a very powerful tool, yet great care must be taken as it is very dependant upon the quality of the groups assigned to it. Principal Components Analysis does not require any preconceived judgement of the data structure, however problems may exist with the result presentation and the subjective decision as to how to define individual groups. Like PCA, cluster analysis strength lies in its ability to analyses a completely unknown data set about which no inferred knowledge is assumed. However there are a number of methodological problems, as yet unresolved, associated with cluster analysis.

The final part of this study was an assessment of how these methods had been successful in tackling the steatite provenance problem.

Univariate and bivariate analysis have demonstrated that there are no simple relationships between source group and the elemental concentrations in a large range of trace elements. However, a number of elements that allow the separation of the Lewisian sources have been identified. This source group may be resolved from all the other sources by the use of combinations of Sr, Nb, As and Ba. All these elements are analysed with a precision of greater than 20%. Differences between sources are greater than 20%. Thus the differences may be considered as genuine and not relics of poor precision. The fact that the different tectonic environments could not be separated from one another using conventional univariate and bivariate techniques was generally expected when the complexed nature of steatite formation and the trace element studies of Allen et al (1975) are considered.

The univariate and bivariate analysis indicated that a complex relationship may exist between the source groups and the trace element data. In order to investigate these possible relationships a number of Multivariate techniques were utilised. PCA, discriminant analysis and cluster analysis were used to assess the steatite provenance problem. These analyses demonstrated the highly structured nature of the data, thus giving confidence in the ability to resolve the group. The use of all the variables, although indicating this structured nature, is unable to fully resolve the groups. It has been demonstrated that the use of well-chosen variables in the analysis resulted in a higher proportion of the total variance explained by the initial principal components. Furthermore these same variables were able to place a high proportion of cases correctly in discriminant analysis. These techniques have enabled the identification of elements that show great potential in the separation of these geological groups.

The univariate/bivariate and multivariate analysis have all identified variables that demonstrate separation between groups or show great potential at resolving the group structure. From these analyses several elemental groups repeatedly appear to demonstrate these differences; REE and Y, LIL, PGE, and selected transition elements thus giving increased confidence to the assessment of these variables as the most likely to resolve steatite sources.

Both PCA and discriminant analysis using a number of different elemental groups are able to resolve the Lewisian group. The agreement of a number of techniques and using different elemental groups increases the confidence in the assessment of the Lewisian sources being substantially different from other sources. Although the other sources may not be resolved by this method the question of whether an artifact is of Lewisian origin may be answered.

The resolution of the Lewisian group is of particular importance in the understanding of the utilisation and movement of steatite on mainland Scotland, particularly prior to the Norse colonisations of much of northern Britain. During this period the utilisation of steatite is comparatively modest, but steatite artifacts show a distribution pattern that suggests that local Lewisian steatite was exploited. Steatite may also be able to give conclusive evidence of contact across Scotland during the Iron Age, a period when little is known about movement of goods and the links between the separate Iron Age provinces.

These analyses have identified a number of elements that exhibit discrimination potential in the case of steatite and in particular the Lewisian sources. Further analysis can concentrate on these elements coupled with further sampling of the Lewisian sources. This may allow a more precise characterisation of the Lewisian sources perhaps enabling further source resolution.

The techniques outlined in this chapter may form part of an overall steatite provenancing study. If provenancing methods are sought for complexed material such as steatite it is unlikely that any one technique will provide an answer to all the problems posed. It is more reasonable to assume that a number of techniques will be required and the combination of the results from these may enable archaeological assessment to be made of the utilisation of the material.

CHAPTER 4 : THE UTILISATION OF RARE EARTH ELEMENTS FOR THE CHARACTERISATION OF STEATITE SOURCES

4.1 Introduction

It was thought that the Rare Earth Elements (REE) might be of use to characterise the different steatite sources in Britain. Geochemical considerations suggest that this group of elements may be of great potential for provenance studies. As described in chapter 2, the different sources are alteration products of a range of different parental ultrabasic bodies which may be expected to have different REE profiles and the steatisation involves interaction with discrete fluids at different pressures and temperatures so resulting in different REE patterns. The REE were also identified by the analysis of the multi-elemental data as a major component of the total variance of the data. This is also a strong indication that the REE may be useful in discriminating between sources. It is therefore possible that individual quarry sites may have distinct chondrite normalised REE patterns, and this may provide a basis for linking artifacts to individual sources.

Before investigating the chondrite normalised REE patterns of different steatite sources it was important to develop an accurate method for measuring the REE in steatite. Previous studies (Buttler 1984, Moffat & Buttler 1986, Kemp & Williams 1991) have encountered problems due to the low REE concentrations found in most ultrabasic rocks and their resulting alteration products. It was therefore difficult to accurately measure the REE concentrations, with a reasonable degree of precision, that would enable the REE patterns to be investigated. Moffat & Buttler (1986) attempted to interpret REE results that can clearly be shown to be dubious, thus compromising their interpretation. Kemp & Williams (1991) using NAA overcame some of the problems that had previously been encounter by long irradiation and count times of black soapstone crosses from Africa. However, although some matches in patterns were possible and the method appeared very promising some 30% of samples were below detection limits and many were very close to these limits. It was thought that ICP-MS analysis offered many advantages; low detection limits, analysis of all 14 naturally occurring REE and the relative speed of analysis, over methods such as neutron activation analysis or XRF.

Once a method had been developed, the study set out to characterise a number of features of the British steatite sources. The initial aim was to define any differences in REE between source quarries. In the studies in North America by Allen *et al* (1975, 1978, 1982) and Allen & Pennell (1978) considerable variations in REE patterns from different steatite quarries were noted. It was hoped that similar variations could also be measured in steatite sources in Britain. Moffat

& Buttler (1986) suggested that as steatites are formed from similar ultrabasic units then no differences will be noted between different bodies. However, the different parent ultramafic bodies are of different ultramafic types formed in different tectonic settings and therefore will more than likely possess different REE patterns. Secondly, the REE profiles from within a single source would need to be characterised. In order to be a useful tool in provenancing studies the internal variation in REE patterns must be not as great as to include the variation, if any, noted between source quarries. Allen & Pennell (1978) and Rogers *et al* (1983) have shown that the REE concentrations vary within a single quarry, but the REE pattern itself shows little variation. Doubt has been cast on this premise by Moffat & Buttler (1986), who pointed out that all ultramafic complexes show wide internal variation in REE profiles. However, this problem may not be as severe as Moffat & Buttler suggested when dealing with the relatively small scale ultrabasic bodies that are hydrothermally altered in the formation of steatite. These implications for steatite provenancing are reasonable as general comments, but their basis was as a consequence of the dubious results of Moffat & Buttler (1986) obtained from Shetland steatite sources. This study sought to resolve this apparent conflict of published results from steatite sources, hence an assessment may be made as to REE usefulness for provenance studies.

If these two requirements, both inter-site and intra-site variability, can be assessed then their usefulness to a provenancing study of British sources can be appraised. This may lead to a form of classification based on the chondrite normalised REE patterns that will enable artifact comparison and thereby the ultimate artifact provenance to be determined. Ultimately the REE may form the basis of a provenancing method that enables artifacts to be assigned to individual quarry sites.

A review of the presentation of REE data and the use of REE to provenance archaeological material will be discussed in this chapter. This will then be related to the REE concentrations and chondrite normalised patterns within the different ultrabasic precursors and steatite itself, and their mobility during formation, with a view to describing the potential differences and similarities between and within sources. The sample preparation procedures and ICP-MS analysis developed for steatite analysis are then discussed. This is followed by a comparison of this technique with other methods of REE analysis. The results from the selected British steatite sources are then presented, discussed and classification systems suggested, along with the implication of these results for steatite provenancing.

4.2 Presentation and display of data

The method of plotting REE data is familiar to most geochemists, but it does deserve some explanation. The concentrations are generally normalised against a reference concentration. The reference concentrations are those in chondrite meteorites, in sedimentary "average rock", or those estimated for the Earth's crust. Normalisation to abundances in chondrite meteorites is the most common choice and the resultant graph is sometimes referred to as a Masuda-Coryell diagram after the authors who proposed this method (Masuda 1962, Coryell *et al* 1963). The advantages of this method are that the abundance variation between REE of odd and even atomic number is eliminated, this variation is a relic of nucleosynthesis. Also the extent of any fractionation amongst the various REE is discernible because there is considered to be no fractionation between light and heavy REE in chondrites. The plotting position for Eu sometimes lies away from the trend defined by the other REE on chondrite-normalised abundance diagrams. This departure is referred to as a *europium anomaly,* and in addition is noted as being positive if Eu_{cn} is greater than each of Sm_{cn} and Gd_{cn}, negative if vice versa. Similar anomalies are occasionally recorded for a few other REE, especially Ce.

Unfortunately, adoption of only one set of chondrite normalising concentrations has not been agreed. In this study the recommended chondrite concentrations based on a C1 meteorite of Boynton (1984) was used.

4.3 Provenancing Utilising Chondrite Normalised REE Patterns

REE despite their similar chemical behaviour may be fractionated one from another by several petrological and mineralogical processes. This results in a wide range of chondrite normalised REE patterns that are process controlled. While the concentrations are of importance, it is the pattern that is characteristic of the processes that have effected the rock. Thus in provenancing studies the REE concentrations may change due to mineral phase differences in samples but the chondrite normalised REE pattern is of use in characterisation of sources and their related artifacts.

4.4 The Natural Variability of REE Concentration and Chondrite Normalised Patterns in Ultrabasic Rocks

The majority of ultrabasic rocks are peridotites and pyroxenites of several distinct types (Wyllie 1967). This review will concentrate only on the ultrabasic types that are of most importance in the formation of steatites. While there are some textural and compositional similarities among these different types the two main types will be discussed separately:

1. Alpine peridotites occurring as isolated masses.
2. Peridotites forming the basal tectonic unit of ophiolite sequences.

4.4.1 Alpine peridotites

In general, alpine peridotites are dominated by rock of lherzolite and harzburgite compositions, with lesser amounts of dunite and pyroxenite. In most alpine peridotites the aluminous phase is spinel rather than plagioclase or garnet, but in some areas such as Norway, garnet lherzolites dominate.

i) Lherzolites

Spinel lherzolites form the bulk of the ultramafic masses at The Lizard in Cornwall, Mount Albert in Quebec and Tinaquillo in Venezuela. These all are strongly depleted in Light Rare Earth Elements (LREE) relative to chondrites (Haskin *et al* 1966). Frey (1969, 1970a) demonstrated that the REE abundances in The Lizard rocks and constituent minerals varied considerably, although the peridotites have LREE/HREE abundance ratios less than that of chondrites. This led to the interpretation that these peridotites formed as residues from partial melting. More recently more REE data have been published from many alpine peridotites (mostly spinel bearing); Ronda, Spain (Suen & Frey 1977, 1987, Menzies *et al* 1977), Beni Bouchera, Morocco (Loubet *et al* 1975, Menzies *et al* 1977, Loubet & Allègre 1980), Lherz, France (Loubet *et al* 1975, 1980), several locations in the Alps (Loubet *et al* 1975, 1980, Menzies *et al* 1977, Ottonello *et al* 1984,), and Liguria, Italy (Ottonello *et al* 1979, 1984). Ranges of chondrite normalised REE abundances are shown in figure 4.1 - 4.4.

Figure 4.1 Range of chondrite normalised REE abundances in lherzolites from the Ronda massif. Data from Suen & Frey (1977, 1987), Menzies *et al* (1977).

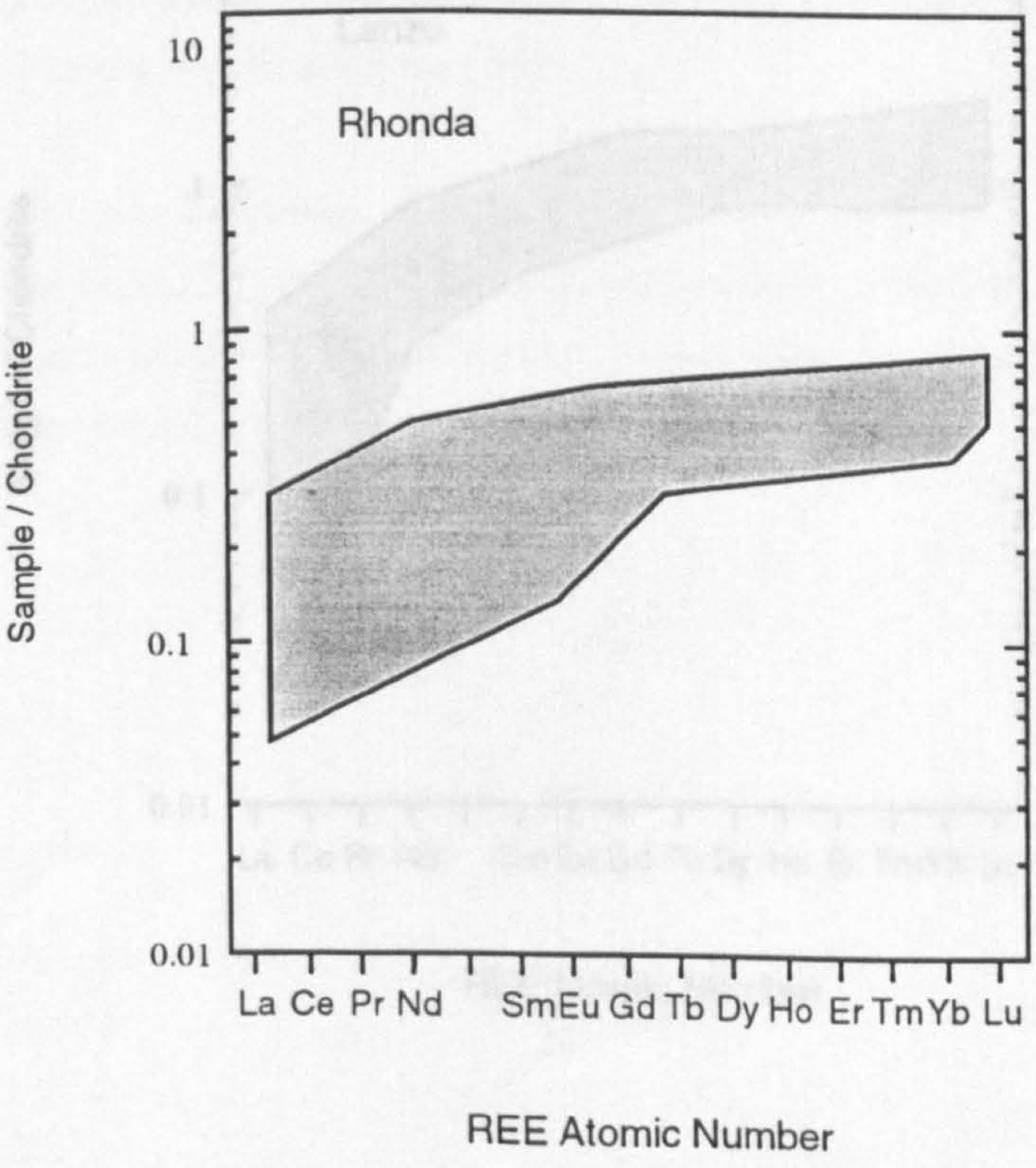


Figure 4.2 Range of chondrite normalised REE abundances in lherzolites from the Lherz massif and other massifs in the eastern Pyrenees. Data from Loubet *et al* 1975, 1980).

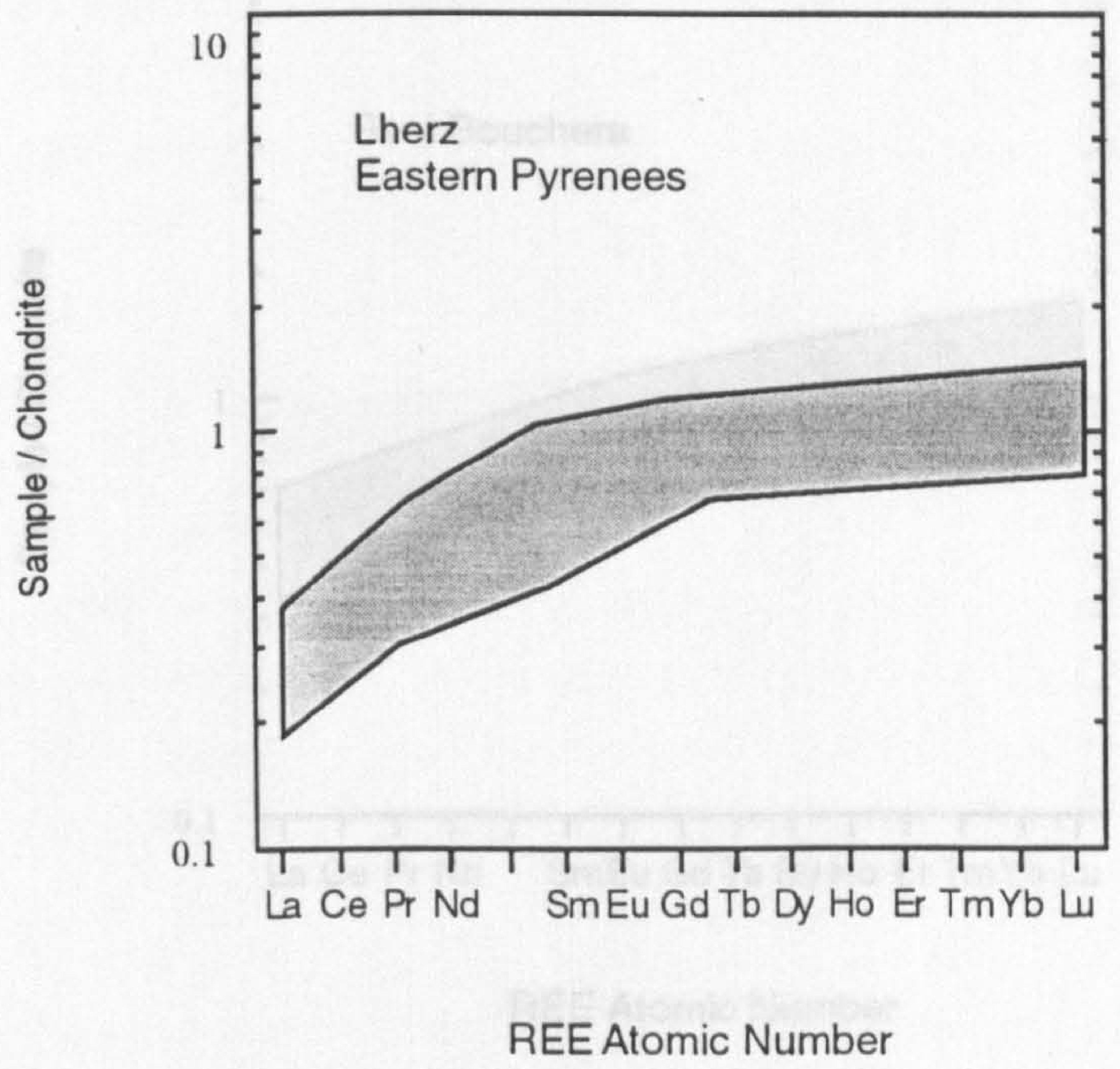


Figure 4.3 Range of chondrite normalised REE abundances in lherzolites from the Balmuccia, Baldissero and Lanzo massifs. Data from Loubet *et al* (1975, 1980), Menzies *et al* (1977), Ottonello *et al* (1984).

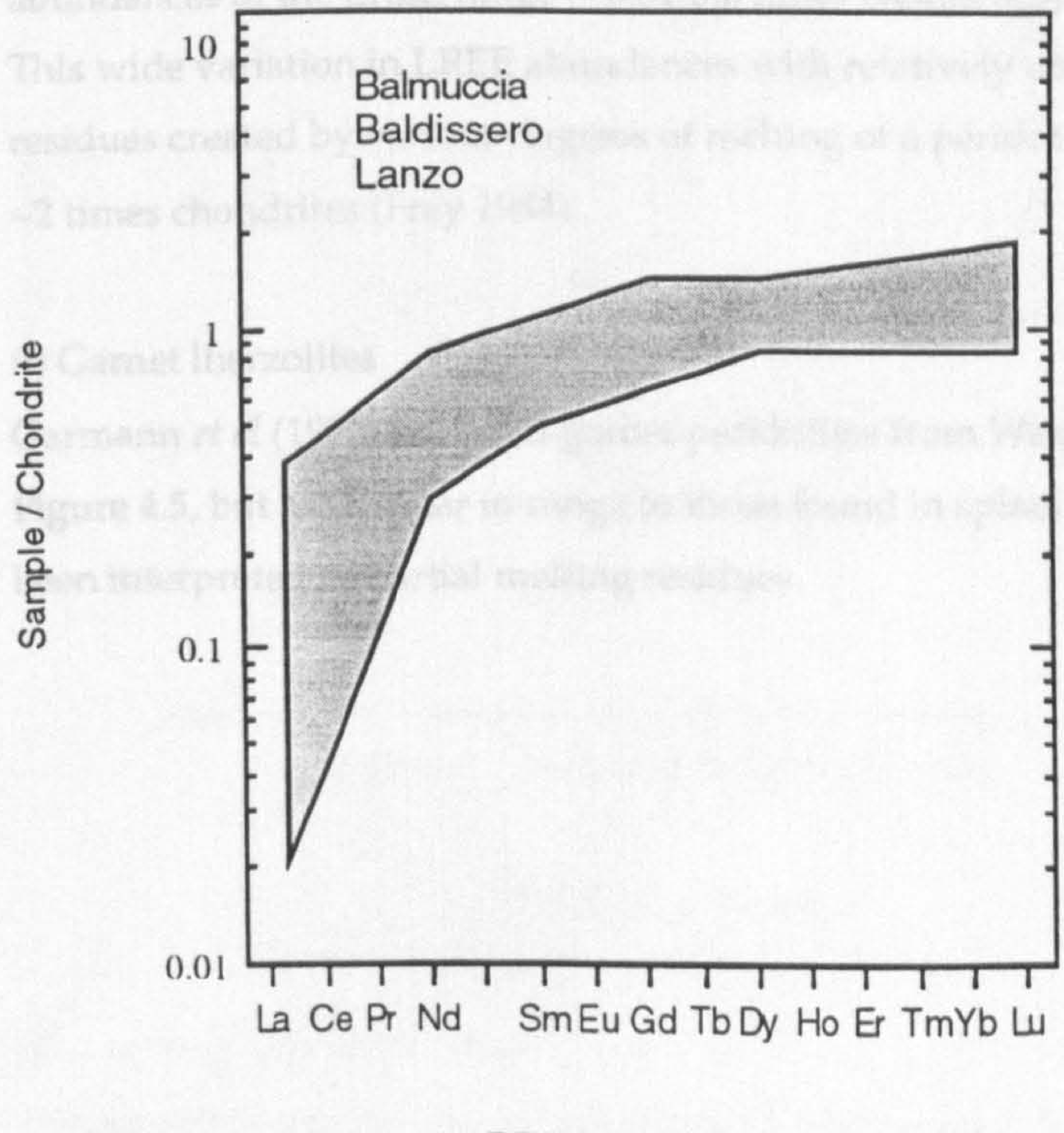
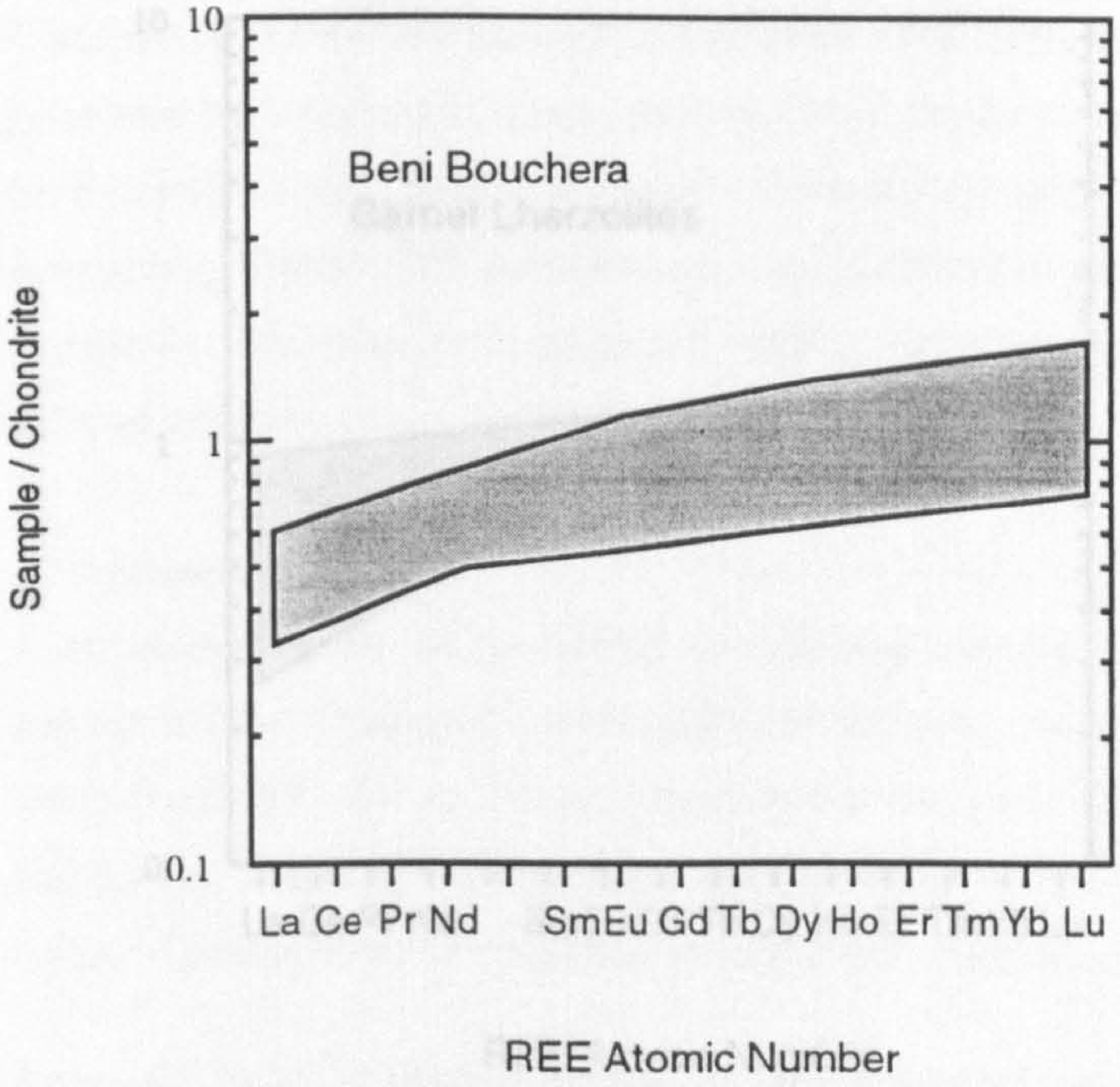


Figure 4.4 Range of chondrite normalised REE abundances in lherzolites from the Beni Bouchera massif. Data from Loubet *et al* (1975, 1980).



It is evident that all these alpine peridotites are characterised by LREE depletion compared to chondrites, and that the HREE abundances typically range from 1 to 2 times chondrites. The abundances of the LREE range (~0.01-0.6 times chondrites) much more widely than the HREE. This wide variation in LREE abundances with relatively uniform HREE content is expected for residues created by various degrees of melting of a peridotite with uniform REE abundances, ~2 times chondrites (Frey 1984)

ii) Garnet lherzolites

Garmann *et al* (1975) analysed garnet peridotites from West Norway. The data are scattered, Figure 4.5, but are similar in range to those found in spinel lherzolites. These patterns have also been interpreted as partial melting residues.

Figure 4.5 Range of chondrite normalised REE abundances in garnet lherzolites from West Norway. Data from Garmann *et al* (1975).

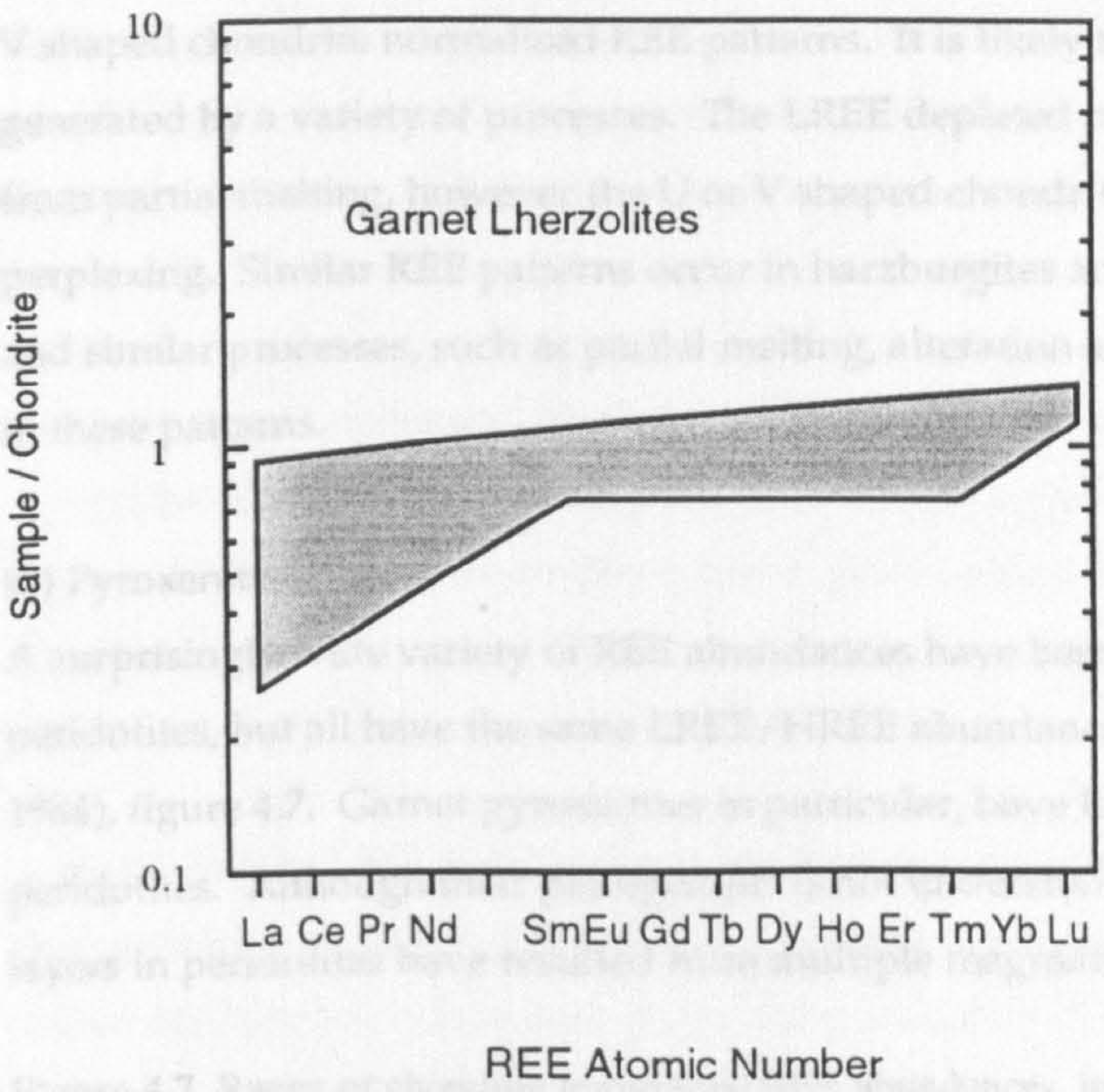
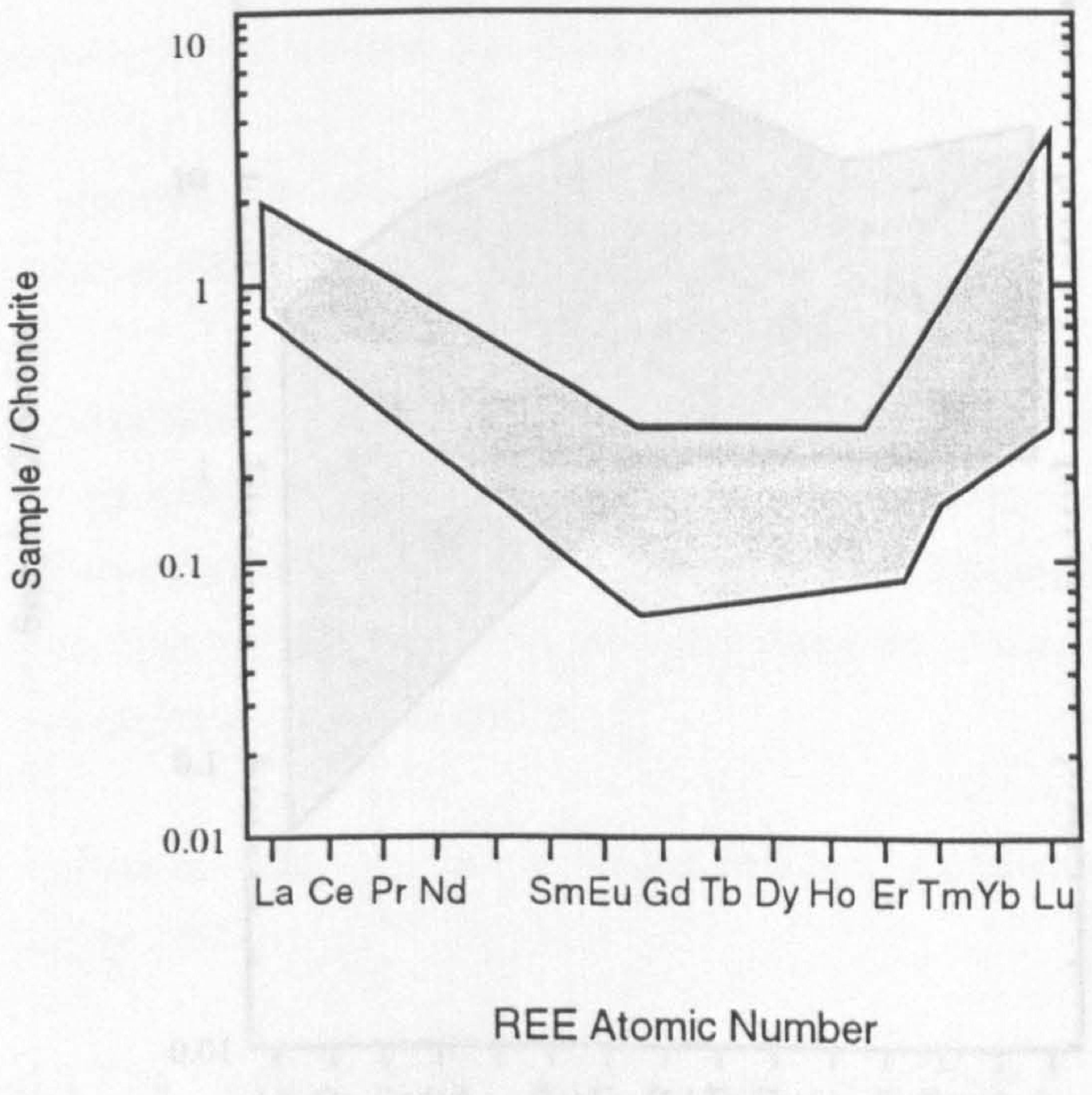


Figure 4.6 Range of chondrite normalised REE abundances in harzburgites and dunites. Data from Frey (1984).



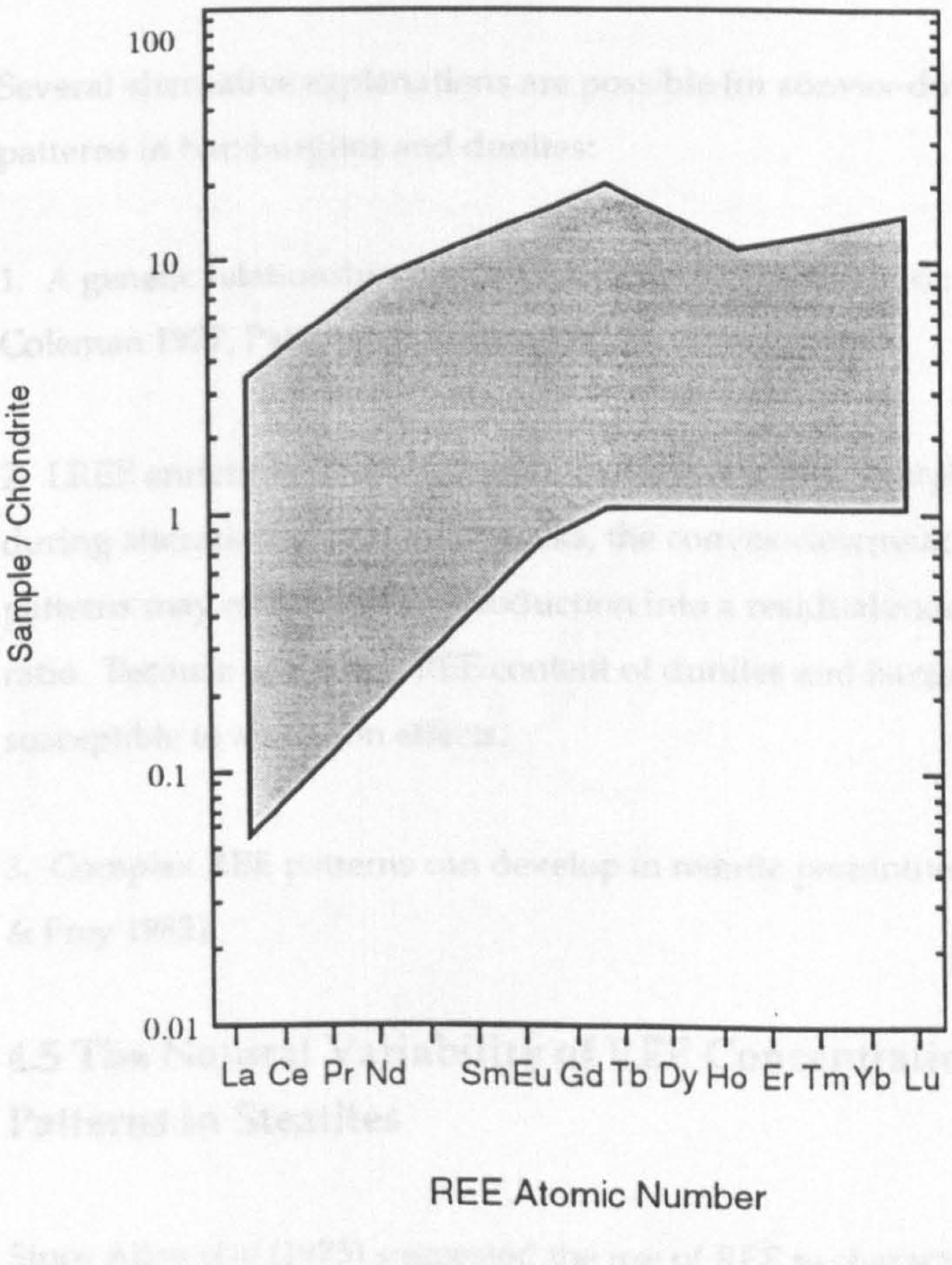
iii) Harzburgites and Dunites

Harzburgites and dunites are dominant in many alpine peridotites, a number of these have been analysed for REE (Frey 1984). These ultrabasics have some of the lowest REE contents found in peridotites, since clinopyroxene is the major REE host phase in most peridotites, the low REE abundances (~0.01-0.2 times chondrites) in these clinopyroxene-poor peridotites are not surprising. However, they display a variety of chondrite normalised REE patterns, figure 4.6. Some have LREE depleted patterns similar to those of lherzolites, whereas others have U or V shaped chondrite normalised REE patterns. It is likely that pyroxenites and dunites can be generated by a variety of processes. The LREE depleted patterns probably represent residues from partial melting, however the U or V shaped chondrite normalised REE patterns are more perplexing. Similar REE patterns occur in harzburgites and dunites from ophiolite sequences and similar processes, such as partial melting, alteration and mantle metasomatism, may result in these patterns.

iv) Pyroxenites

A surprisingly wide variety of REE abundances have been found in pyroxenites from alpine peridotites, but all have the same LREE/HREE abundance ratios less than chondrites (Frey 1984), figure 4.7. Garnet pyroxenites in particular, have LREE/HREE ratios less than the host peridotites. Although their petrogenesis is not understood in detail, it is evident that mafic layers in peridotites have resulted from multiple magmatic events in the mantle.

Figure 4.7 Range of chondrite normalised REE abundances in pyroxenites. Data from Frey (1984).



4.4.2 Ultramafics associated with ophiolites

Metamorphic peridotites form the basal member of ophiolite sequences, their textures reflect a mantle history of subsolidus recrystalisation. Harzburgite tends to dominate ophiolite basal sequences, whereas lherzolite is the major component of alpine peridotites discussed previously.

Similar to harzburgites and dunites from isolated peridotite masses, the harzburgites and dunites from ophiolites have very low REE contents, typically ~0.001-0.5 times chondrites (figures 4.8 - 4.9). Rare lherzolites occur in basal ophiolite sections, having similar REE abundances and patterns to lherzolites from alpine peridotites. Consequently similar petrological inferences can be made.

Interpretations of REE patterns from harzburgites and dunites are more difficult because of their unexpected convex-downwards, chondrite normalised REE patterns. These show preferential depletion in intermediate atomic number REE (figure 4.9), with La/Sm greater than chondrites.

Several alternative explanations are possible for convex-downward chondrite normalised REE patterns in harzburgites and dunites:

1. A genetic relationship between the ultrabasics and basic rocks in ophiolites (Frey *et al* 1971, Coleman 1977, Pallister & Knight 1981).

2. LREE enrichment results from alteration and metamorphism. If the LREE are mobilised during alteration of ultramafic rocks, the convex-downwards chondrite normalised REE patterns may reflect LREE introduction into a residual rock with a low LREE/HREE abundance ratio. Because of the low REE content of dunites and harzburgites they are particularly susceptible to alteration effects.

3. Complex REE patterns can develop in mantle peridotites by mantle metasomatism (Hickey & Frey 1982).

4.5 The Natural Variability of REE Concentration and Chondrite Normalised Patterns in Steatites

Since Allen *et al* (1975) suggested the use of REE to characterise steatite sources, a number of steatite bodies have been analysed for REE. If the REE are to be useful in characterisation of steatite sources then the REE patterns must show differences between separate quarries.

Figure 4.8 Range of chondrite normalised REE abundances in lherzolites harzburgites and dunites from ophiolites. Data from Frey *et al* 1971, Coleman 1977, Pallister & Knight 1981.

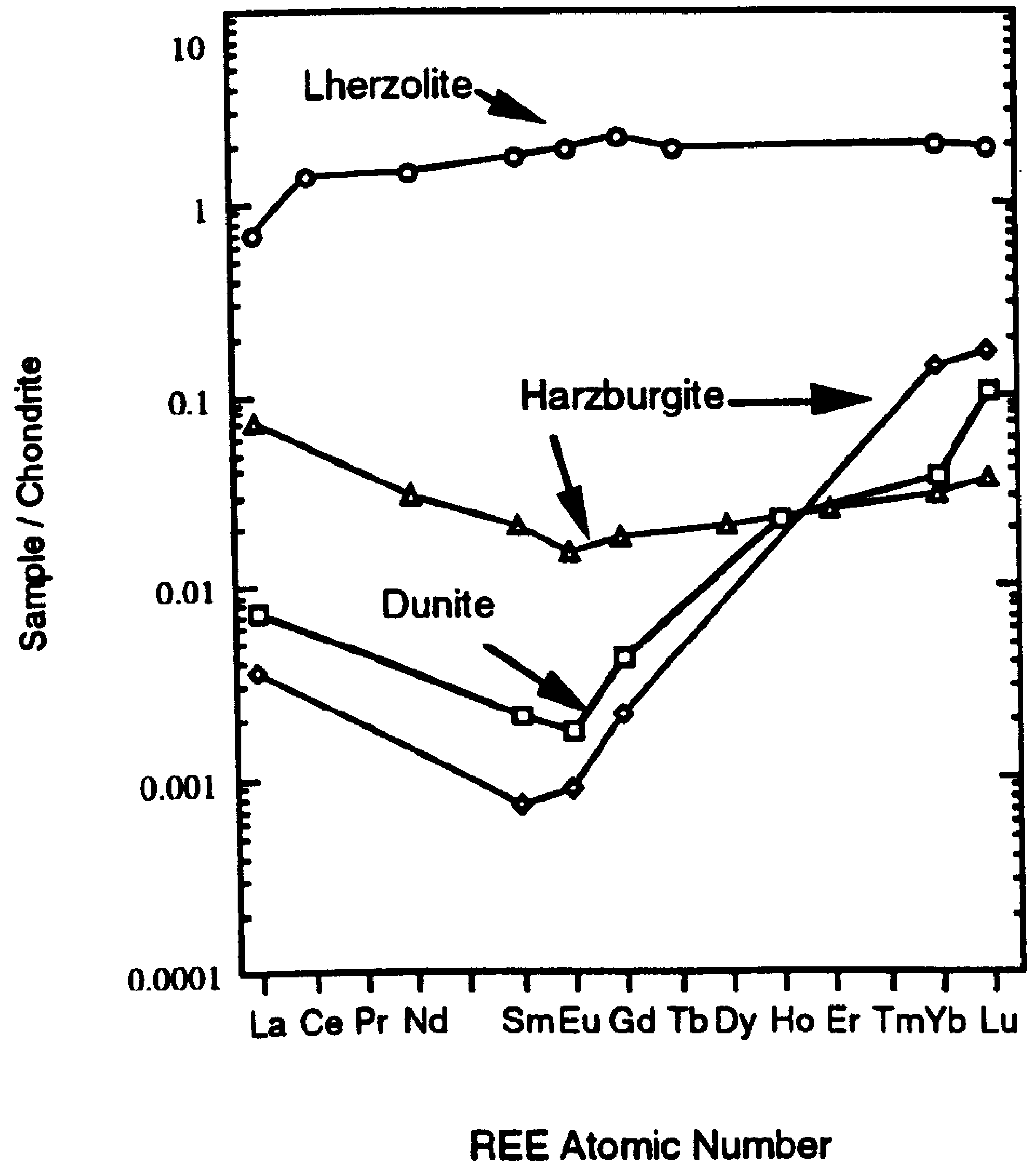
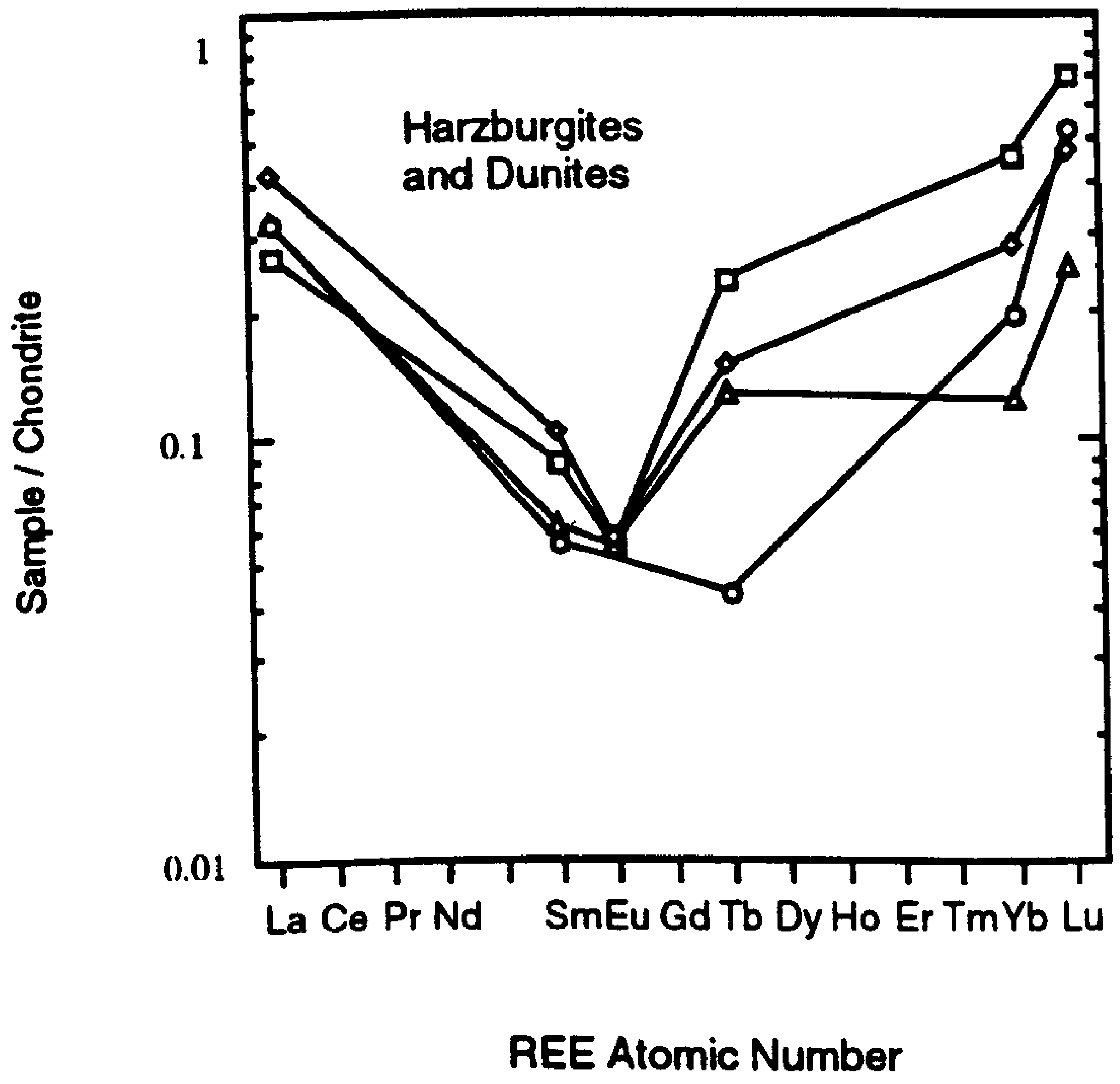


Figure 4.9 Range of chondrite normalised REE abundances in harzburgites and dunites from ophiolites. Data from Frey (1984).



The processes that result in steatite formation may lead to similar REE patterns for all sources. It is unfortunate that no REE concentrations have been published from North American steatite sources. However, a number of the chondrite normalised REE patterns can be compared to examine variability in REE between source sites, figures 4.10 - 4.12.

These chondrite normalised patterns show that there is considerable variation between different steatite sources in North America. There are no common REE patterns. Most show LREE enriched trends, although others have flat and V-shaped patterns. Concentrations range from 700 times chondrites to 0.1 times chondrites for LREE and from 50 times chondrites to 0.05 times chondrites for HREE.

Prior to this work the REE data from Shetland steatite sources (Buttler 1984, Moffat & Buttler 1986) was limited and of poor quality, figures 4.13 - 4.14. The low concentrations, coupled with poor precision of the NAA techniques used, result in plots in which no patterns can be determined. However, the overall concentrations appear to be lower than North American sources, ranging from 6 times chondrites to 0.05 times chondrites. Although the overall patterns cannot be determined from these results, the patterns that are not possible can be documented. The results from Hubie, Fethaland, Hillswick Ness and Clibberswick are unable to reveal any clear pattern, however the samples from Cunningsburgh in general show HREE depletion. This is probably the only reliable trend that can be observed as many elements show anomalous concentrations when chondrite normalised. These anomalous results are hard to

Figure 4.10 Chondrite normalised REE abundances in a range of steatites from eastern North America, (▼) Montgomery County MD, (▲) Jackson Hill GA, (□) Albemarle-Nelson County Virginia, (○) Watuga County NY, (*) Westfield MA.

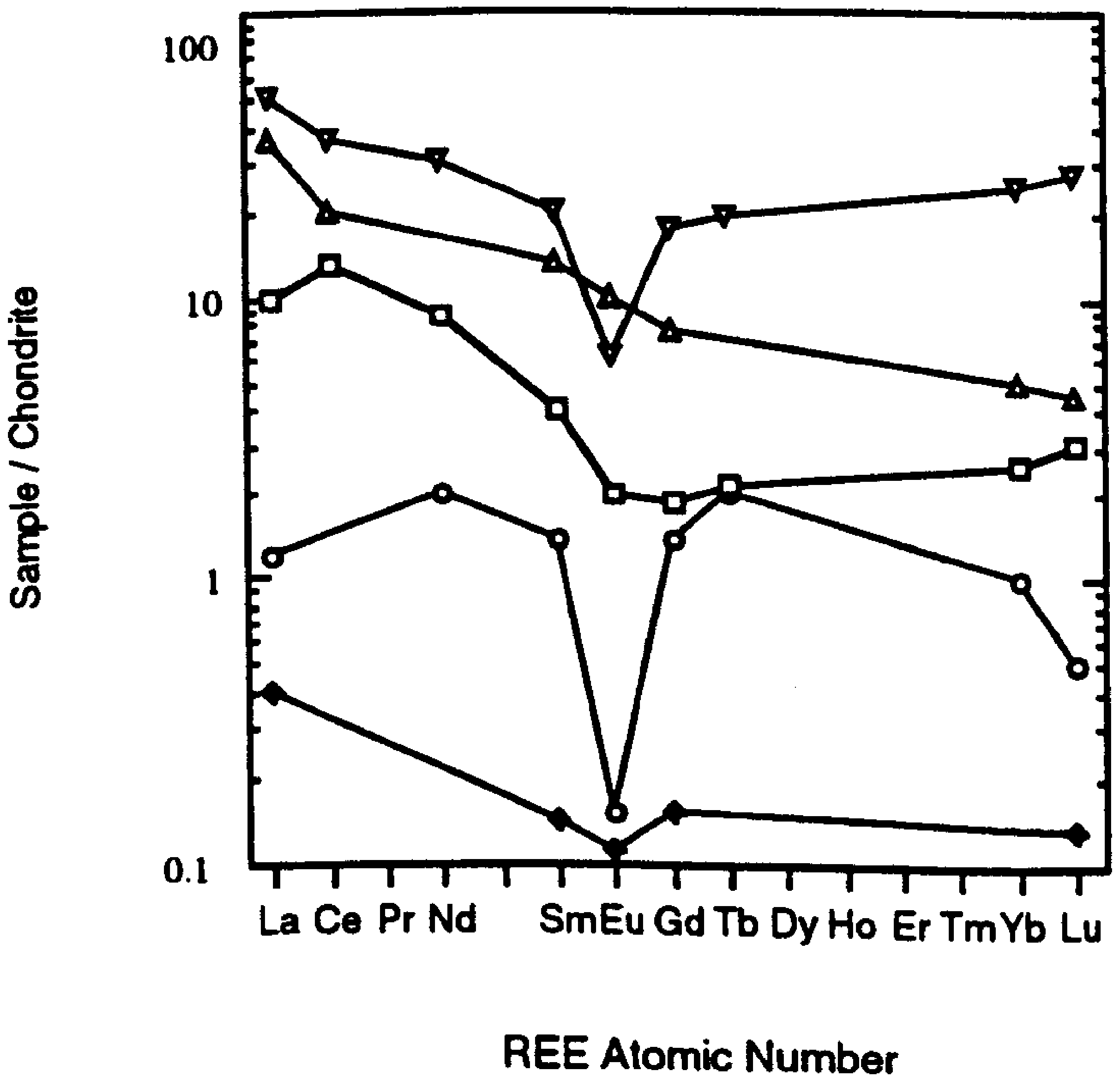


Figure 4.11 Chondrite normalised REE abundances in a range of steatites from eastern North America, (◆) Madison County VA, (□) Albemarle County VA, (○) Campbell County VA, (▲). Chester County PA.

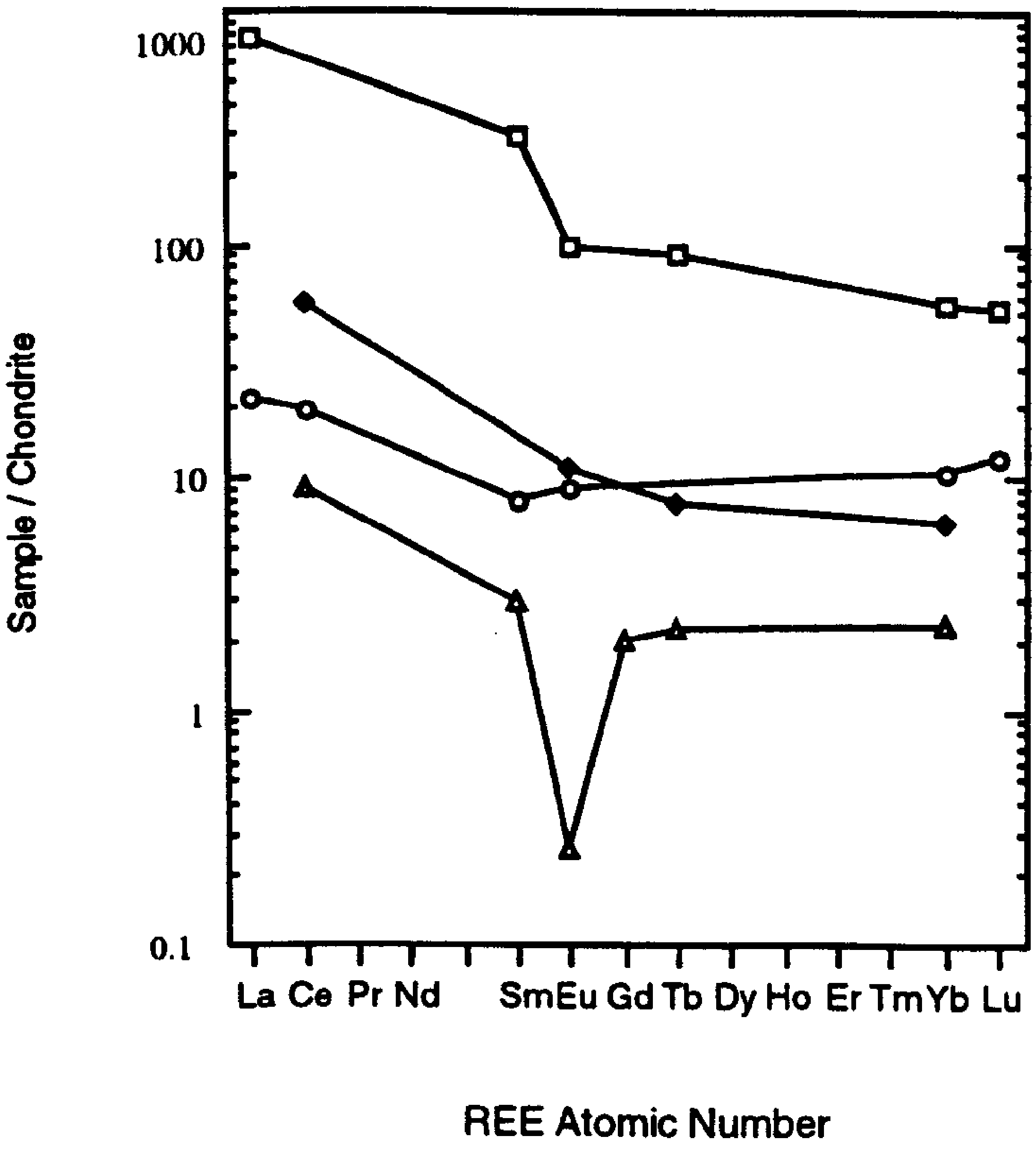


Figure 4.12 Chondrite normalised REE abundances in a range of steatites from Newfoundland. Data from Rogers *et al* 1983.

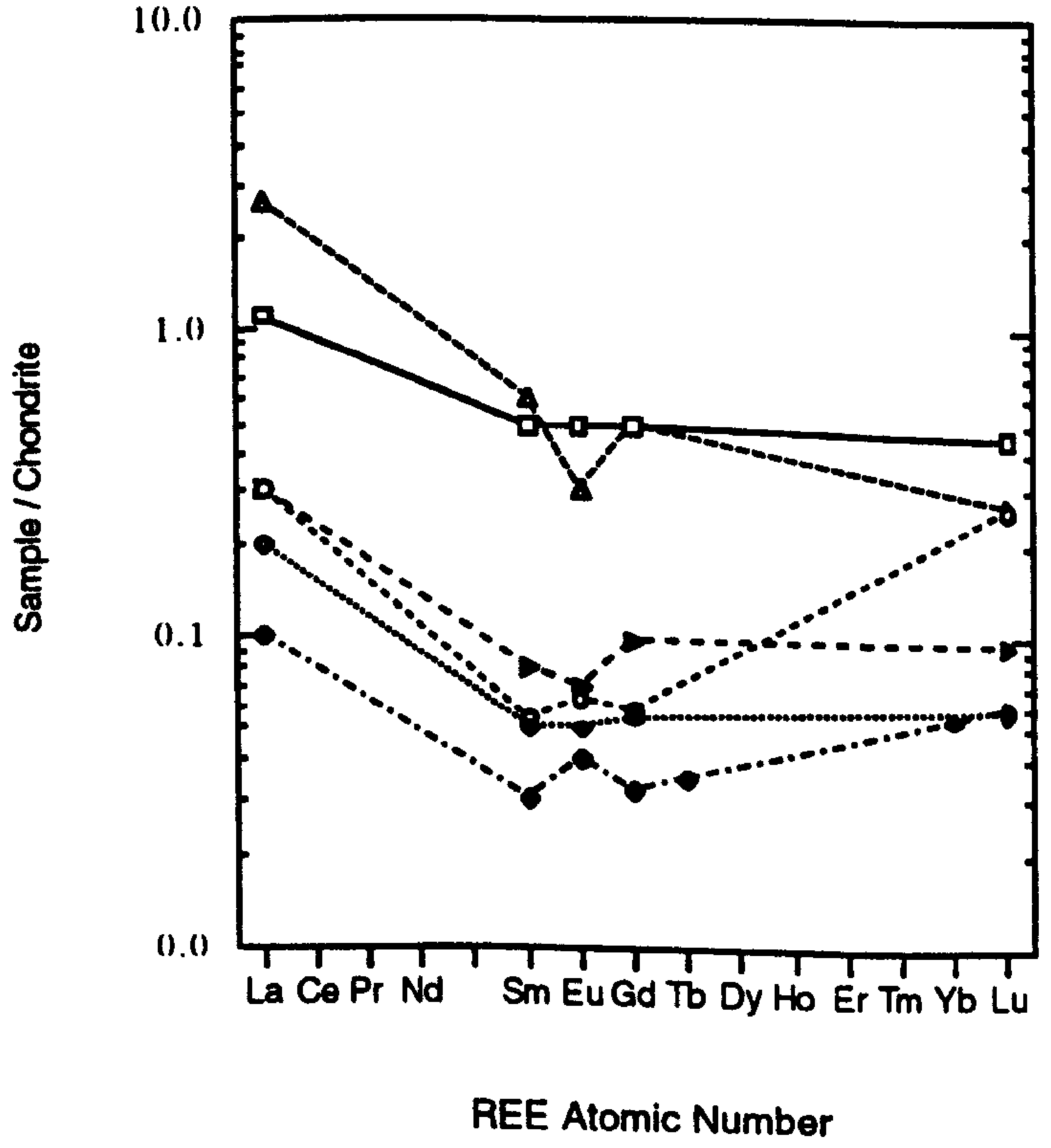


Figure 4.13 Chondrite normalised REE abundances in steatite from Cunningsburgh, Shetland. Typical errors are shown. Data from Moffat & Buttler 1986.

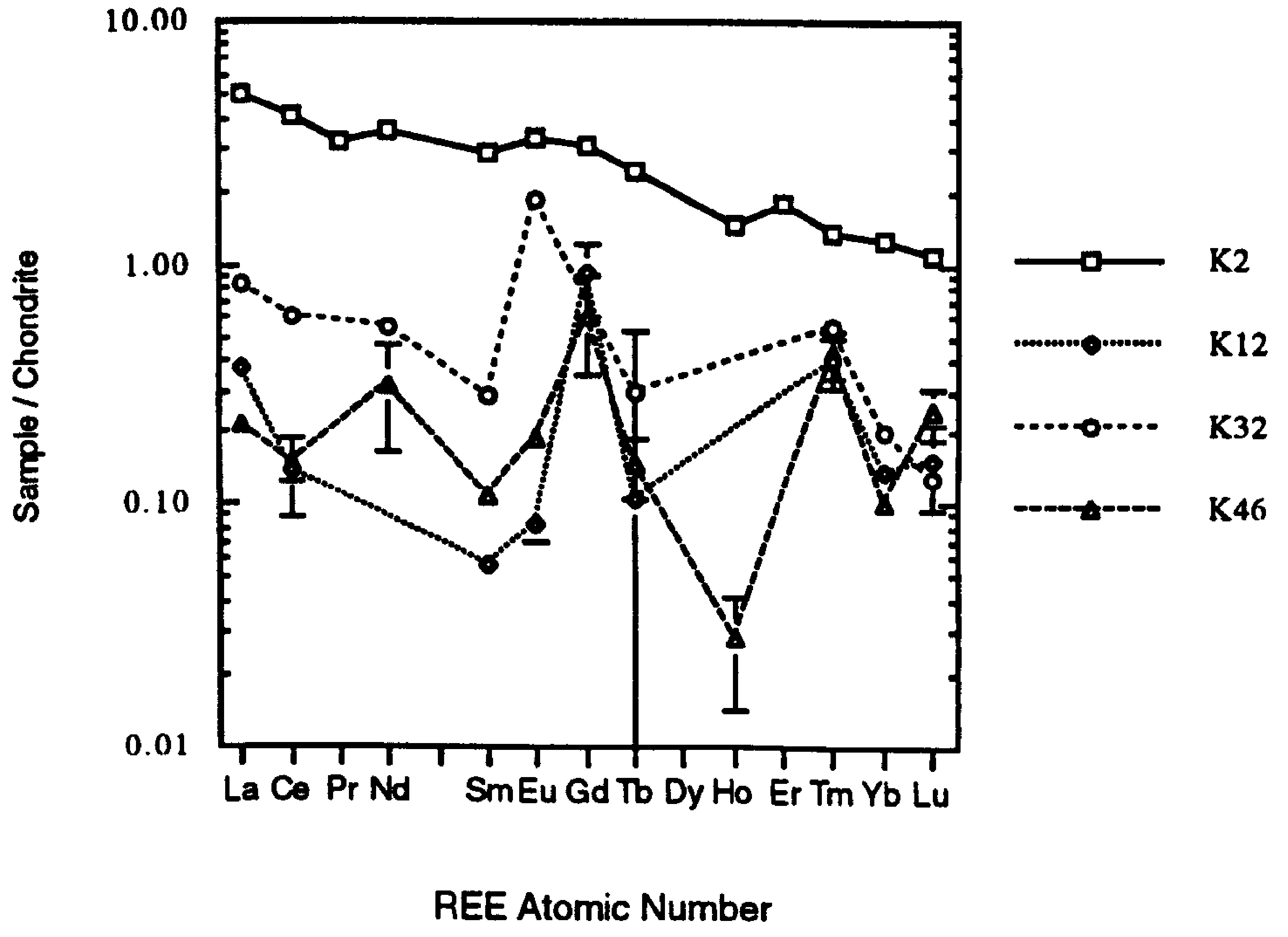
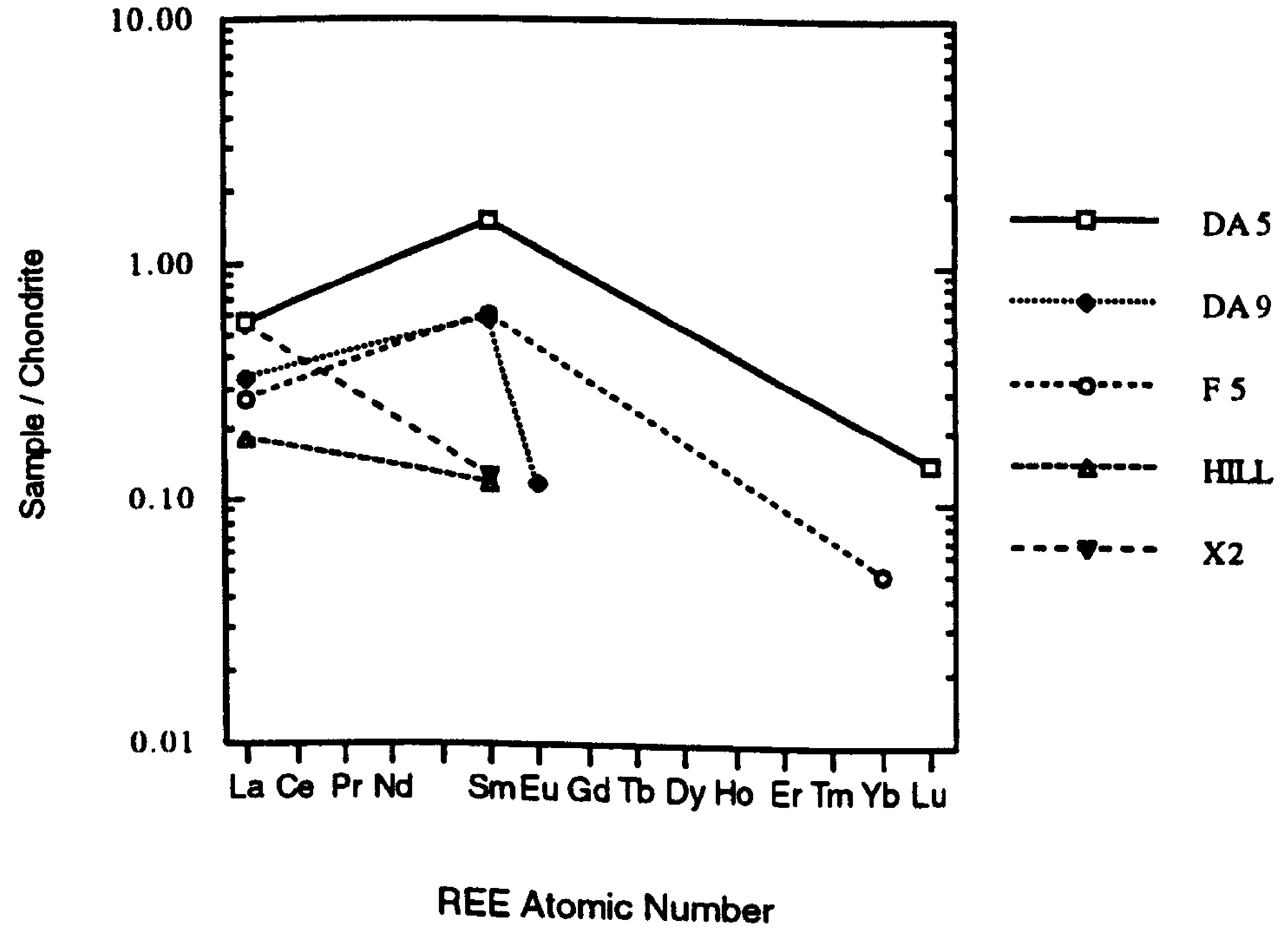


Figure 4.14 Chondrite normalised REE abundances in steatite from Hubie, Fethaland, Hillswick Ness, Clibberswick; Shetland. Data from Moffat & Buttler 1986.



explain, if they represent real phenomena and are not a product of analytical errors. These patterns will be further discussed along with the results of this study.

These differences in REE abundances within steatites are important for characterisation of sources as it is evident that all steatites do not have similar patterns and concentrations. The steatisation processes that have produced the different sources have not resulted in similar chondrite normalised REE patterns.

4.6 The Mobility of the Rare Earth Elements

It has been demonstrated that the precursor ultrabasic rocks from which steatite is formed have a range of REE patterns. However a greater range of REE patterns is possible if the REE are mobile during the various steatite formation processes. Therefore REE mobility, or lack of it is important to the overall possible range of REE patterns in steatite.

It has become evident from studies on oceanic and continental crust that there is no simple relationship between the degree of mobility of the REE, metamorphic grade, or the type of rock being altered. The overall gain or losses of the REE during metamorphism or alteration will be a function of the relative importance of several factors:

1. The abundances of the REE in the unaltered rock, their distribution and sites of concentration in the mineral phases, and the relative stability of the mineral phases with respect to the fluid.

2. The concentration of REE in the fluid, partition coefficients of the REE between the mineral phases and the fluid, and the ability of the fluid to transport the REE in/out of the system.

3. The ability of the secondary mineral phases formed during the alteration to accommodate the REE released from the original mineral phases.

4.6.1 Rare Earth Element Mobility during Serpentinisation

The possibility of REE mobility during serpentinisation has been recognised for a long time. However, the effects of this alteration have not been thoroughly documented. Frey & Suen (1983) studied Ronda peridotites ranging from <5% to ~30% serpentine and found no correlation between REE abundances and degree of serpentinisation. This conclusion supports Loubet *et al* (1975) assumption that serpentinisation has no significant effects on REE abundances. However, Eu^{2+} shows preferential mobility during serpentinisation (Sun & Nesbitt 1978), which may explain any Eu anomalies. Moreover, there is evidence that REE, especially the LREE, can be mobilised during hydrous alteration and metamorphism of peridotites. Frey (1969) inferred that LREE enrichment of peridotites was a result of LREE transport by metasomatic fluids. Others have also argued for similar phenomena during ultrabasic alteration (Condrie 1971, Suen *et al* 1979). However, the relative LREE enrichment in peridotites may be a result of LREE enrichment in clinopyroxene (McDonough & Frey 1989).

Negative Ce anomalies have been reported for several serpentinised peridotites (Neal & Taylor 1989). Ottonello *et al* (1979) concluded that Ce could be preferentially leached from a rock during hydrothermal alteration.

4.6.2 Rare Earth Element Mobility during Steatisation

There is much debate as to the mobility of REE during hydrothermal metasomatic processes (Grauch 1989). For instance, Muecke *et al* (1979) reported almost unchanged REE concentrations across a metabasite-epidosite contact, and Hajash (1984) demonstrated that hydrothermal alteration of basalts had little effect on REE abundances. On the other hand significant quantities of REE, especially LREE, can be introduced during metasomatism. Martin *et al* (1978) showed significant increases in LREE abundances with increasing degree of fenitisation, while in other cases during Boron metasomatism, REE may be lost from a body (Alderton *et al* 1980). Leroy & Turpin (1988) showed that REE may be leached or concentrated in one body depending on the prevailing redox conditions.

There is little data on REE mobility during steatisation of serpentinites and peridotites, however a number of points can be made from the available data. REE mobility has been described from metasomatic zoned ultramafics (Fowler *et al* 1983). They suggest that substantial REE mobility occurred during metasomatism, especially of the middle and HREE. They demonstrated that REE are lost during metasomatism, in marked contrast to the enrichment described by Martin *et al* (1978). A similar overall loss of REE is also noted by Allan & Pennell (1978) during the alteration of a serpentinite block.

Complexing has long been recognised (Mineyev 1963) as a significant factor in REE mobility / transport, and the importance of pH and the presence of certain ligands; notably F^-, Cl^-, CO_3^{2-}. Unfortunately there is often little direct evidence of which ligand or ligands were introduced in a given metasomatic event. Fowler *et al* (1983) suggest that carbonate ligands are probably not significant in REE transport as CO_2 contents are low and dolomite/calcite are only observed as minor phases. While this may be true for the body they studied carbonate ligands cannot be ruled out for all cases of steatisation as dolomites are often major components in steatites. Fowler also suggests that Eu anomalies are a result of relatively low oxygen fugacity that allowed a significant proportion of Eu to remain in a bivalent state.

It may be concluded that at present the evidence suggests that the REE are mobile during steatisation, although this may not be the case for all metasomatic alterations involving the formation of steatite.

4.7 Summary of REE Patterns and Concentration within Ultrabasics and Steatites

It is evident from this review of patterns and concentrations of REE in the parental ultrabasics and the subsequent alteration product, that the REE patterns and concentrations demonstrate a considerable variation. This has important implications for provenancing, as probable variations between individual bodies or quarries can be demonstrated. It is probable that quarry sites will possess a range of different REE patterns thus making characterisation of quarry sites possible.

The evidence that the REE appear to be mobile during steatisation is important, as this increases the possible concentrations and patterns seen within steatite sources from the limited number of the original parental ultrabasics. These variations in both the ultrabasics and steatite sources are likely to be seen in sources of steatite in Britain, and it is these variations, principally in REE patterns, but also in concentrations, that are considered possible in characterising these steatite sources.

4.8 Sample Preparation and Dissolution

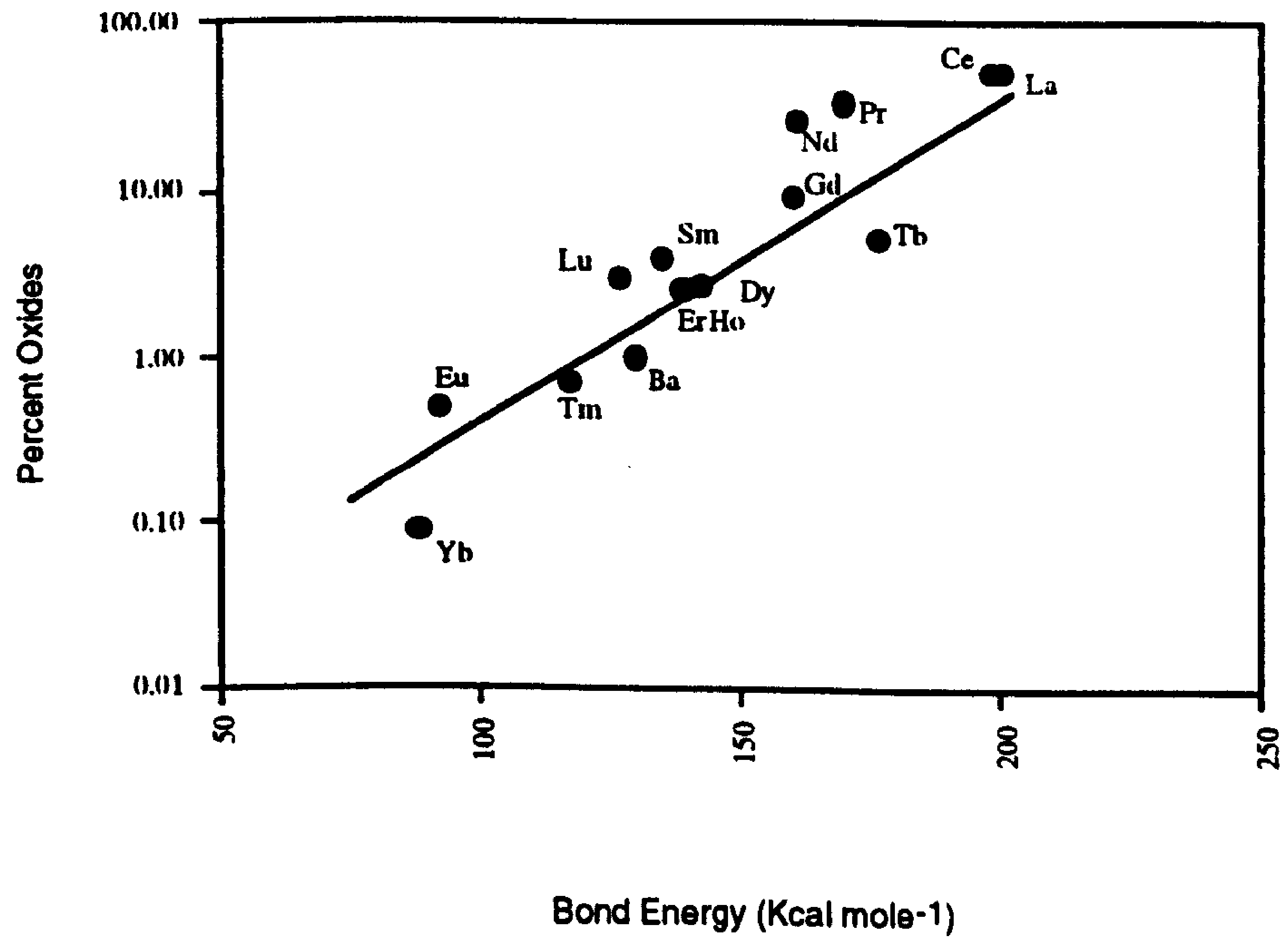
The samples were cleaned of all weathered material with a diamond saw to obtain clean blocks of approximately 100g. These were then crushed and milled to 150µm. The samples that were used in the analysis were further ground to 53µm using an agate mortar and pestle. The sample dissolution was identical to the method used for the multi-element analysis using PFA teflon screw-top beakers (Savillex) described in section 3.4.

4.9 Rare Earth Element Analysis by ICP-MS

The REE are a difficult element group to quantify by many instrumental techniques and consequently their ease of determination by ICP-MS has received much attention (Jarvis *et al* 1992). The ICP-MS spectra are simple to interpret, as each REE has at least one isotope free from isobaric overlap and sensitivity is relatively uniform from ^{139}La to ^{175}Lu (Jarvis 1989b). The major potential analytical problem encountered is the level of refractory oxide formation (Longerich *et al* 1987). Since the REE form a continuous group from 139 to 175 *m/z*, the formation of LREE oxide species could produce significant interferences on the middle to

HREE. In many sample types the concentration of the LREE is considerably higher than the HREE and therefore the potential for serious interferences is increased. The relative level of oxide formation is in general a direct function of the oxide bond strength of the parent element. Figure 4.15 shows the variation of percentage oxide as a function of bond strength. However, instrumental operating conditions and basic instrumental design can significantly affect the oxide level. Date and Hutchison (1987) report levels of 0.05-0.5% although Longerich *et al* (1987) quote higher figures of 0.1-70%. On most instruments oxide levels are considered to be in the region of 1% (Jarvis *et al* 1992).

Figure 4.15 Variation of percentage oxide as a function of oxide bond strength (after Longerich *et al* 1987)



Accurate REE data have been reported for bulk rock samples that have been taken through a mixed acid digestion with no separation of the REE from their matrix (Doherty & Vander Voet 1985), Longerich *et al* (1987), Date & Hutchison (1987), Lichte *et al* (1987), Jarvis (1988, 1989b), Doherty (1989). The REE may also be isolated from the matrix using ion exchange separation (Jarvis 1988).

Sample introduction used the aspiration of liquid nebulisation of aqueous samples, described by Jarvis *et al* (1992). The instrumental operating conditions for REE determination are given in table 4.1. The isotopes used for the determination of the REE are shown in table 4.2. In general the most abundant isotope is used where it is free from isobaric overlap.

Table 4.1 Instrumental operating conditions for REE determination

Forward power	1300 W
Reflected power	< 5 W
Nebuliser gas flow rate	0.751 min^{-1}
Coolant gas flow rate	131 min^{-1}
Auxiliary gas flow rate	01 min^{-1}
Sample uptake rate	0.5 ml min^{-1}
Nebuliser	De Galan / Meinhard concentric
Spray chamber	Water cooled
Ion lenses	Optimised on ^{140}Ce
Scan range	100 - 189.18 amu
Number scan sweeps	400
Dwell time	160 µs
Number of channels	1024
Points per peak	5
Sweeps results averaged from	3

Table 4.2 Isotopes used in ICP-MS determination of REE

Element	Isotope	Abundance (%)	Comment
La	139	99.9	Most abundant free isotope
Ce	140	88.5	Most abundant free isotope
Pr	141	100	Mono-isotopic
Nd	146	17.2	Most abundant free isotope
Sm	152	26.7	Most abundant isotope
Eu	153	52.2	Most abundant isotope
Gd	157	15.7	Most abundant free isotope
Tb	159	100	Mono-isotopic
Dy	162	25.5	Most abundant free isotope
Ho	165	100	Mono-isotopic
Er	166	33.4	Most abundant isotope
Tm	169	100	Mono-isotopic
Yb	174	31.8	Most abundant isotope
Lu	175	97.4	Most abundant free isotope

Two standard solutions were used following the method of Doherty (1989) using Ru and Re as internal standards that allow correction of non-spectroscopic errors related to the matrix of the sample.

The detection limits for all fourteen naturally occurring REE are typically between 0.01 - 0.1 ng ml^{-1} (Jarvis *et al* 1992).

4.9.1 Comparison of Analytical Performance with some Other Techniques

A comparison of analytical performance of ICP-MS and some other analytical techniques commonly used for the determination of the REE are shown in table 4.3. The lower detection limits (using 3σ standard deviation of the background) are lower than those achieved by INAA and are typically one or two orders of magnitude lower than ICP-AES and XRF. Quantitation limits (10σ standard deviations, quoted as ppm in the solid) are for a dilution factor after pre-concentration (5X approximately).

Table 4.3 A comparison of detection limits for ICP-MS and other analytical techniques

Element	Mass (*m/z*)	ICP-MS *		ICP-AES †	INAA §	XRF #
		Detection limit (ng ml^{-1})	Quantitation limit (μg g^{-1})	Quantitation limit (μg g^{-1})	Quantitation limit (μg g^{-1})	Quantitation limit (μg g^{-1})
La	139	0.070	0.00125	0.044	0.83	1.17
Ce	140	0.09	0.0015	0.145	2.5	1.10
Pr	141	0.09	0.0015	0.065	n.d.	1.03
Nd	146	0.15	0.0030	0.085	7.7	0.87
Sm	147	0.15	0.0025	0.031	0.17	0.77
Eu	153	0.05	0.0010	0.005	0.08	0.73
Gd	157	0.1	0.0014	0.035	6.5	0.67
Tb	159	0.03	0.0005	n.d.	0.15	0.67
Dy	163	0.1	0.0018	0.011	n.d.	0.63
Ho	165	0.03	0.0005	0.010	2.83	0.60
Er	166	0.05	0.0010	0.019	n.d.	0.57
Tm	169	0.09	0.0002	n.d.	0.57	0.57
Yb	172	0.05	0.0010	0.004	0.23	0.57
Lu	176	0.04	0.0008	0.004	0.17	0.50

Detection limits are 3σ standard deviations of blank intensities. Quantitation limits are equal to 10σ standard deviation. n.d. = not determined

* This work

† Jarvis & Jarvis (1988)

§ Potts (1987)

Robinson *et al* (1988)

4.9.2 Rare Earth Element Pre-Concentration

Initial sample results following standard dissolution showed that the low abundance elements of the group in many of the samples were below 0.1 ng ml^{-1}, when samples were dissolved to produce a maximum of 0.2% salt concentration for sample introduction into the ICP-MS. In order to reduce the final dissolution and maintain a salt level of less than 0.2% the REE had to be separated from the other constituents and pre-concentrated. Ion exchange chromatography procedures have been used for a number of years (Strelow & Jackson 1974, Walsh *et al* 1981) for the pre-concentration of the REE. Recently organic solvent extraction techniques have been developed (Weiss *et al* 1990). The limiting factor in all these methods is the procedural blanks.

Pre-concentration also has the advantage that it removes many of the higher abundance elements that result in matrix effects during ionisation, and a significant reduction in interferences from oxides.

A number of techniques were developed and REE recovery assessed using standard reference material.

Method 1. Separation of the REE was achieved based on the standard cation exchange chromatography techniques. The solution was loaded onto a preconditioned cation exchange column containing 10 ml Bio-Rad AG50W X 8, 200-400 mesh resin. The sample was then loaded in 2 ml of 2.5 *M* HCl , washed with 2 ml of 2.5 *M* HCl and eluted with 56 ml of 2.5 *M* HCl. The REE were stripped from the column using 50 ml of 6 *M* HCl and evaporated to dryness.

Method 2. The REE separation from the bulk rock sample was carried out using an adaptation of the method of Hooker *et al* (1975) and Thirlwell (1982). This involved an anion-exchange column, pre-equilibrated in 5 ml of 90% CH_3COOH-10% 5 *M* HNO_3 mixture. The REE were loaded in 75% CH_3COOH-25% 5 *M* HNO_3 mixture onto the resin bed for sorption, 2 ml of wash solution (90% CH_3COOH-10% 5 *M* HNO_3) were passed through and discarded. The separation was then achieved with 50 ml 90% CH_3COOH-10% 5 *M* HNO_3 mixture as eluant. The REE were then stripped off the column with 15 ml of 0.05 *M* HNO_3.

The concentration of standard reference rock achieved using these methods as well as standard dissolutions are given in table 4.4. The second method of Hooker *et al* (1975) and Thirlwell (1982) obtained substantially higher recoveries than the first method. These recoveries were considered high enough to be used in further quantitative analysis of steatite source material. Complete procedural blank levels for both methods were below 0.01 ng/ml in all cases.

Table 4.4 Comparison of pre-concentration methods used in this study. Concentration in ppm of GSP-1 reference rock material.

Element	Ref 1	A		B		C		D	
La	184	173.81	±0.06	175.62	±0.06	175.02	±0.04	138.60	±0.09
Ce	399	405.02	±0.18	419.91	±0.19	385.15	±0.15	308.69	±0.25
Pr	52	51.46	±0.06	53.62	±0.05	48.93	±0.04	33.97	±0.04
Nd	196	191.33	±0.18	200.64	±0.21	198.06	±0.12	159.22	±0.31
Sm	26.2	24.17	±0.03	25.31	±0.02	24.89	±0.01	19.47	±0.05
Eu	2.3	2.27	±0.01	2.33	±0.01	2.10	±0.01	1.46	±0.02
Gd	12.1	14.20	±0.03	16.31	±0.05	11.93	±0.02	8.23	±0.06
Tb	1.34	1.49	±0.003	1.52	±0.01	1.25	±0.003	0.77	±0.006
Dy	5.5	5.94	±0.004	6.00	±0.005	5.22	±0.003	3.28	±0.005
Ho	1.01	0.91	±0.001	0.89	±0.010	0.92	±0.001	0.62	±0.009
Er	2.7	2.25	±0.007	2.29	±0.011	1.32	±0.005	0.22	±0.008
Tm	0.38	0.32	±0.001	0.32	±0.005	0.32	±0.001	0.22	±0.001
Yb	1.7	1.52	±0.008	1.49	±0.006	1.47	±0.008	1.12	±0.009
Lu	0.21	0.19	±0.001	0.19	±0.002	0.18	±0.002	0.11	±0.003

Ref 1 Data from Govindaraja (1989)
A & B Standard dissolution no pre-concentration.
C Pre-concentration method 2.
D Pre-concentration method 1

4.10 Results

The REE results for the selected British steatite sources are given in Appendix D. These results show that, as expected, steatites have very low concentrations comparable to those reported for Shetland steatite sources by Moffat & Buttler (1986). Many of these concentrations are below the quantitation limits of commonly used techniques for REE determination; ICP-MS without pre-concentration, ICP-AES (Jarvis & Jarvis 1988), INAA (Potts 1987) and XRF (Robinson *et al* 1988). Thus pre-concentrations and ICP-MS offer a relatively rapid method for REE determination in concentration between 0.01 and 0.1 times chondrites, especially when compared to previously used isotope dilution techniques.

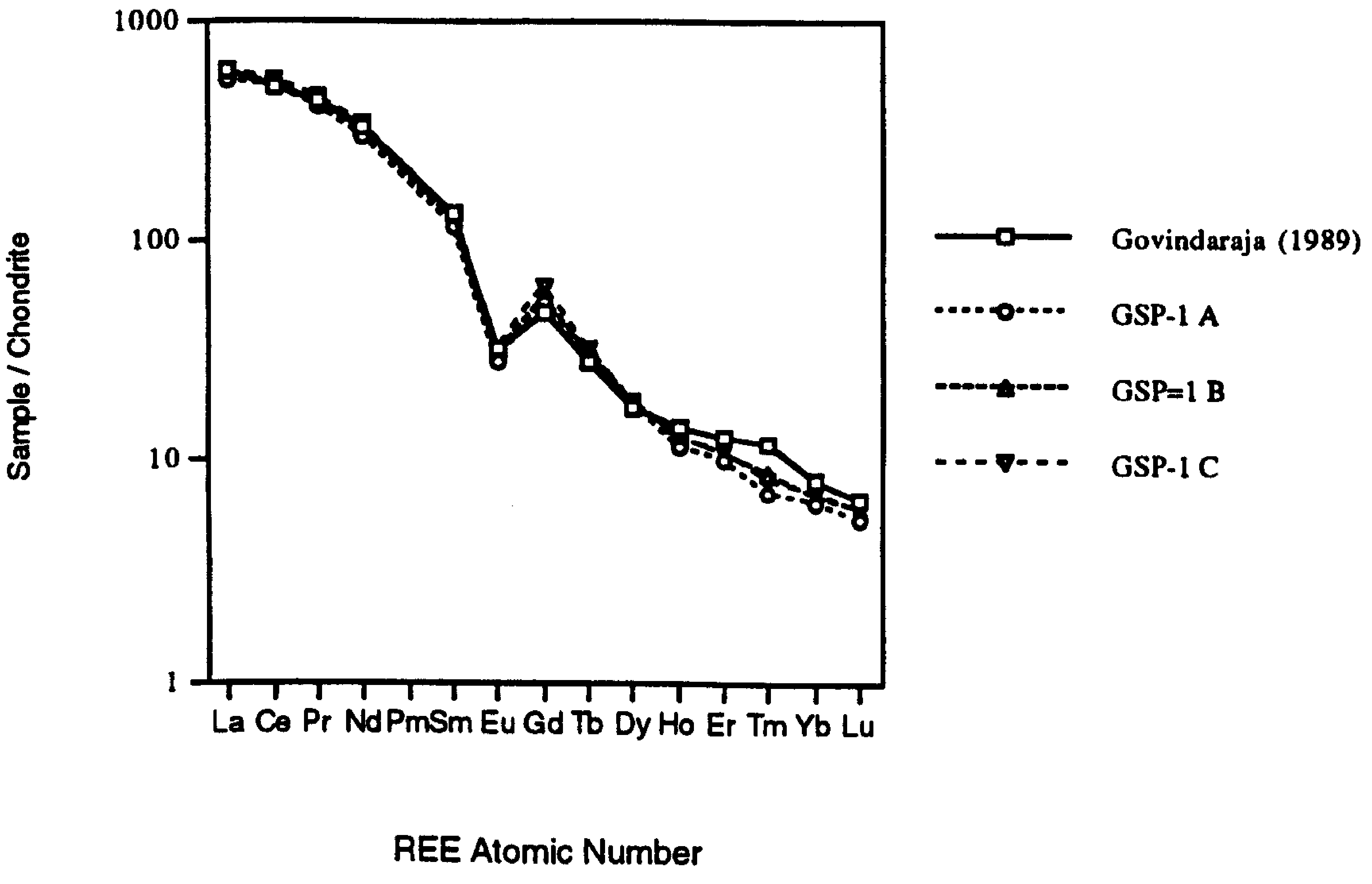
During the period of the analyses standard reference materials were analysed in order to characterise the precision within sample runs and during the period of the analysis. Analyses of standard reference materials analysed throughout the program are given in Appendix D. The precision over the period of the analysis was generally better than 7% RSD. A single individual sample run was characterised by six analyses of standard reference material, Appendix D, the precision was generally better than 5% RSD.

An assessment of the analytical accuracy may be made by comparison of the measured values with compilation of Govindaraja (1989) , although many of the REE values reported have a great deal of uncertainty, due largely to the relatively small data sets used in the compilation. However, the ICP-MS data compares favourably with the limited number of values reported by Govindaraja (1989).

An addition assessment of analytical accuracy may be made by normalising the REE data to chondritic abundances and plotting the results against atomic number, figure 4.16. Due to the coherent behaviour of this group of elements, a smooth curve should result for all elements except Ce, and Eu which because of their different oxidation states may display anomalous behaviour. The chondrite normalised REE abundances for the reference material produce smooth curves.

These standard reference material results are able to characterise the precision of the analysis throughout the period of the steatite sample analysis and give some idea of the accuracy. The chondrite normalised REE pattern is less affected than the absolute concentration by poorer precision. The accuracy and precision were considered adequate for REE analysis at the low abundances found in most steatites, while also allowing any differences in concentration and chondrite normalised REE pattern to be noted.

Figure 4.16 Chondrite normalised REE abundances for reference material GSP-1. Reference values of Govindaraja (1989) are plotted with values obtained during this study.



4.11 The use of REE to Provenance Steatite

To demonstrate that the REE could be useful in characterising different steatite bodies they needed to exhibit a number of properties. Firstly, the REE had to show differences between the separate steatite sites. The nature of these differences could be concentrations or the overall REE profile. Secondly, these differences must be greater than any internal variation measured within a single quarry.

4.12 Discussion of Results

The chondrite normalised REE patterns for a number of the samples; Clibberswick, Fethaland, Corrycharmaig, Gew-graze, and Porth-Delise, show characteristic LREE depleted patterns compared to chondrites, figures 4.17 - 4.22. These patterns are similar to REE patterns of upper mantle rocks, such as lherzolite and pyroxenite, one of steatite's possible parental ultrabasics. These LREE depleted patterns have been interpreted as the product of various degrees of partial melting of upper mantle material (Frey 1969).

Figure 4.17 Chondrite normalised REE abundances in steatite from Clibberswick, Unst, Shetland. Typical errors are shown.

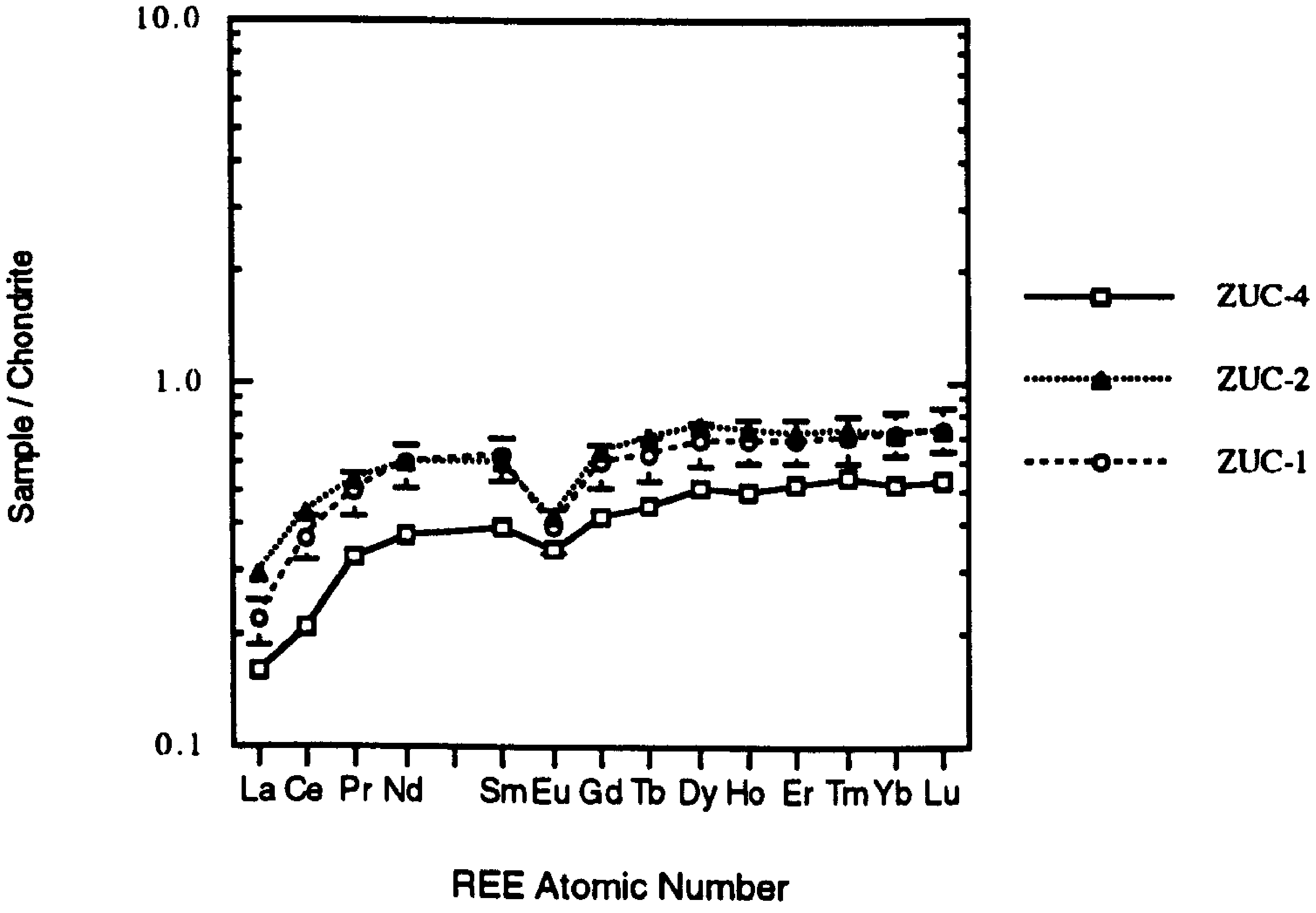


Figure 4.18 Chondrite normalised REE abundances in steatite from Fethaland, North Roe, Shetland. Typical errors are shown

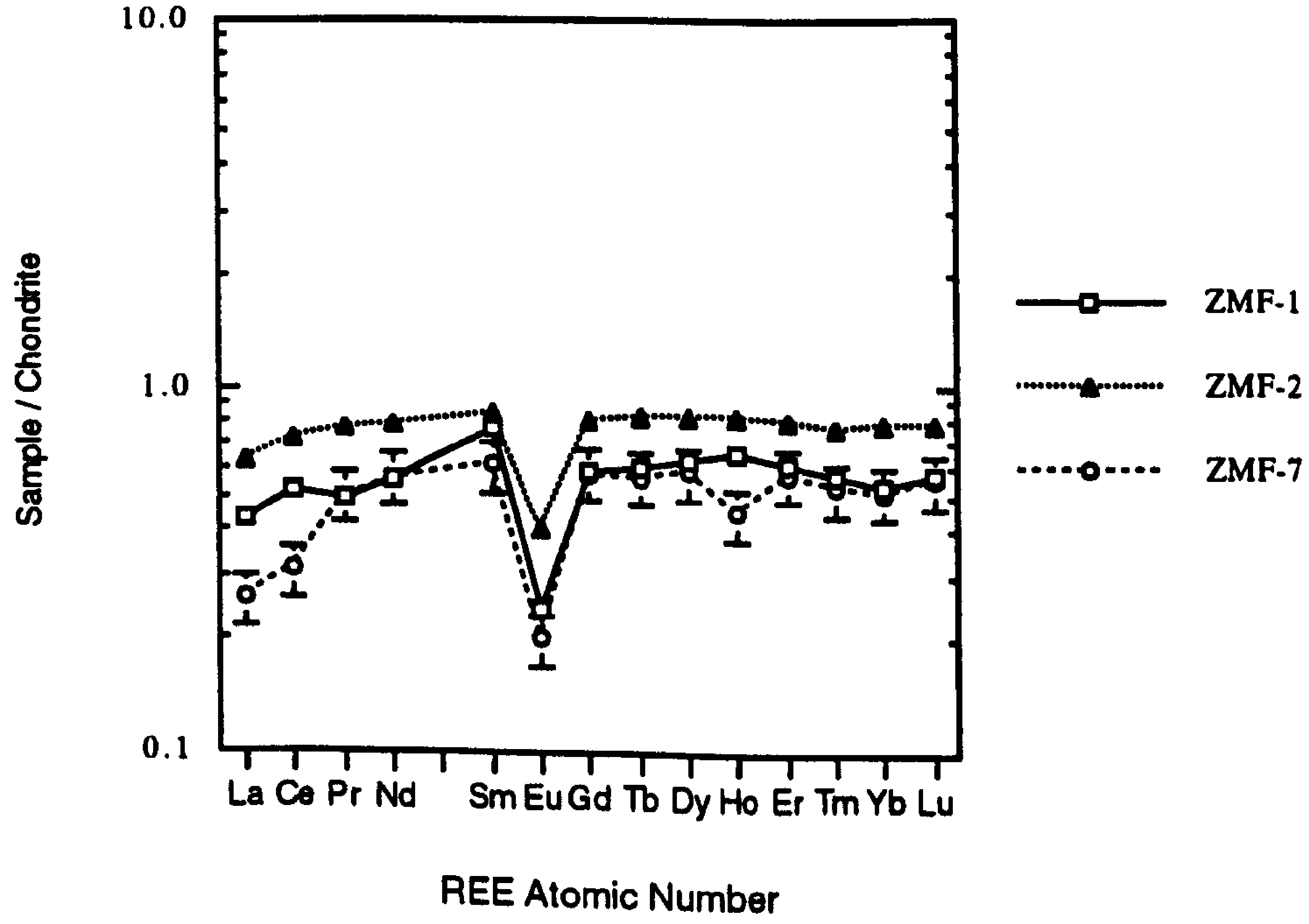


Figure 4.19 Chondrite normalised REE abundances in steatite from Corrycharmaig. Typical errors are shown.

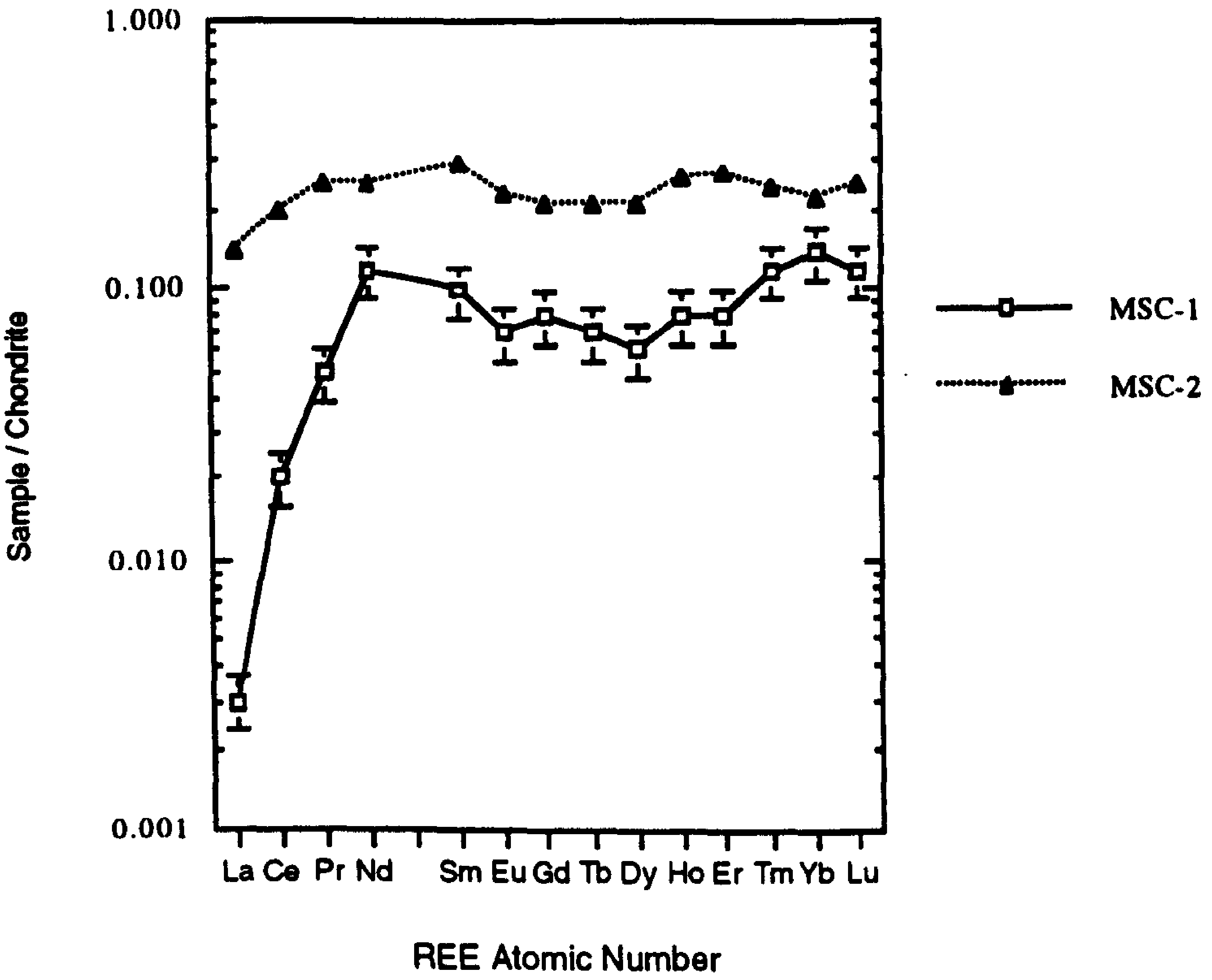


Figure 4.20 Chondrite normalised REE abundances in steatite from Gew-graze, Cornwall. Typical errors are shown.

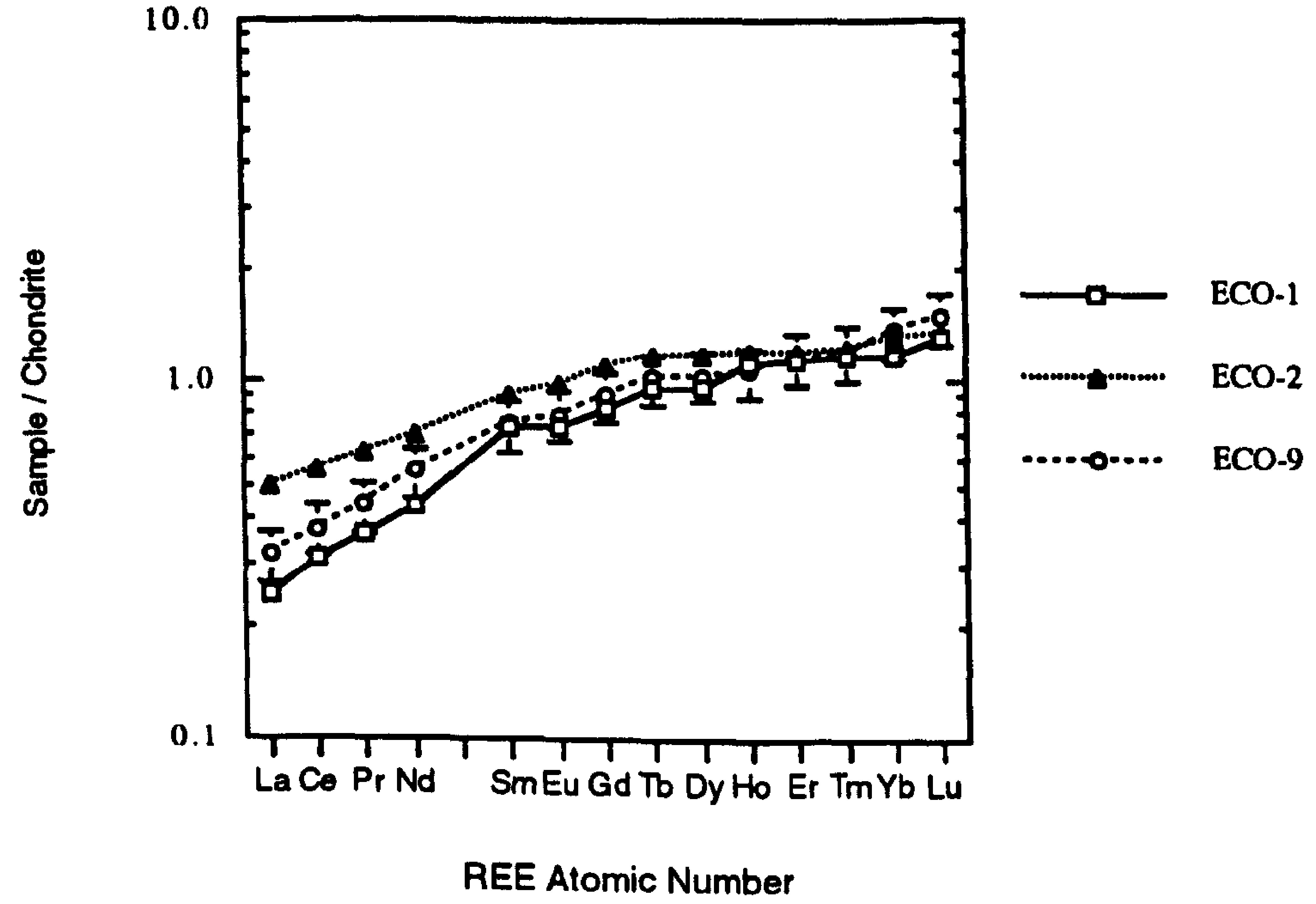


Figure 4.21 Chondrite normalised REE abundances in steatite from Porth-delise, Anglesey. Typical errors are shown.

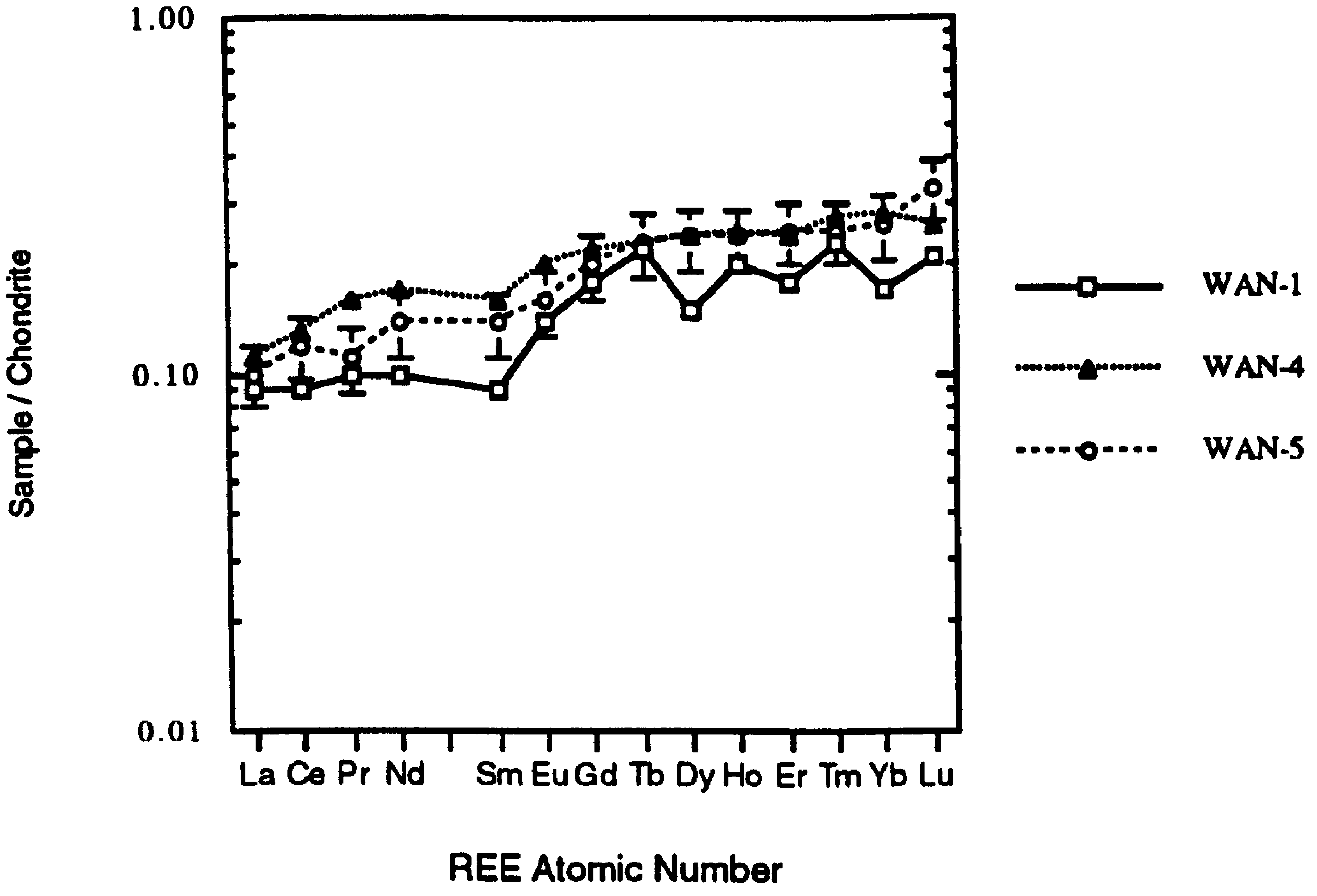
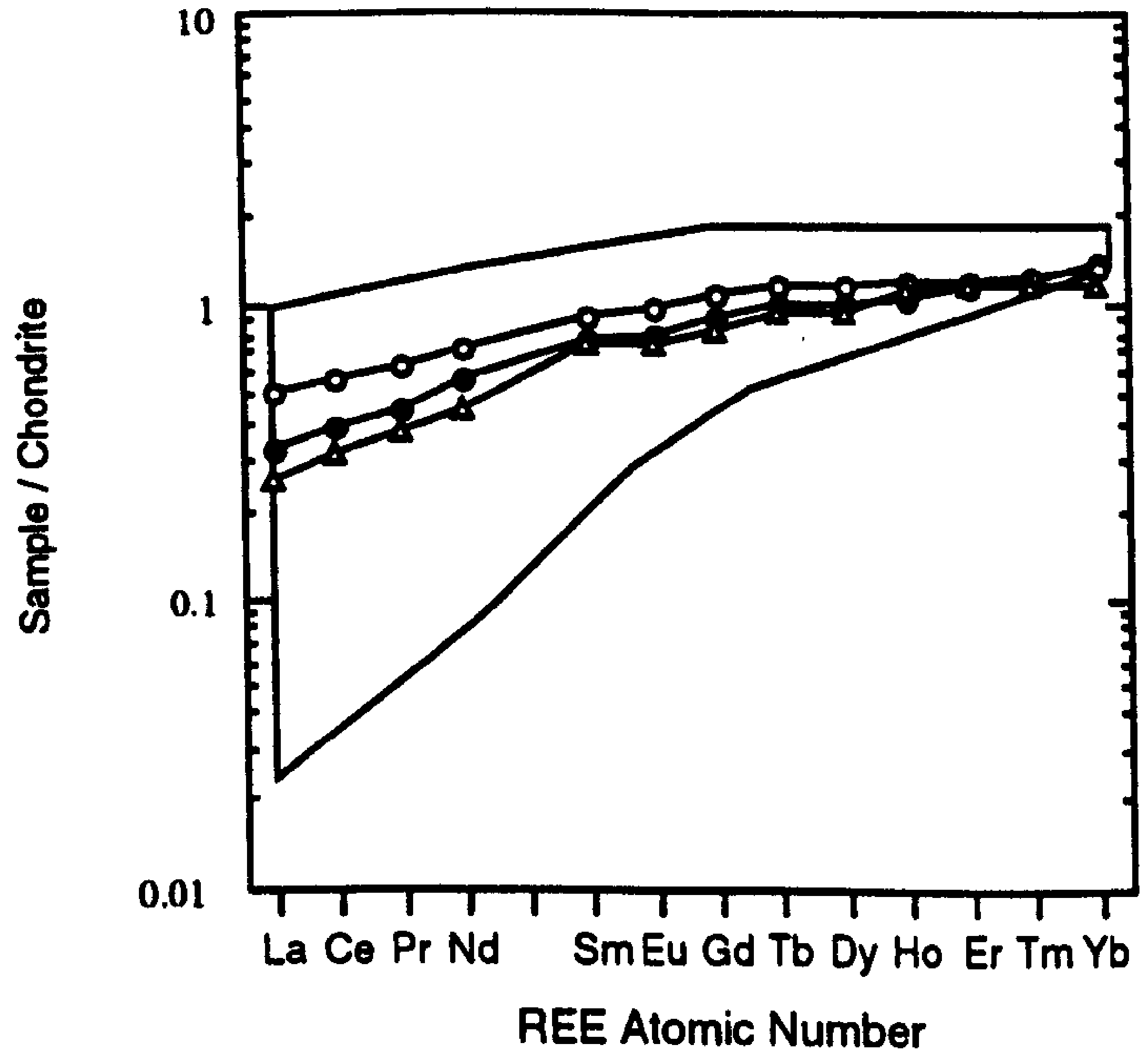


Figure 4.22 Chondrite normalised REE abundances of steatite from Gew-graze, Cornwall, shade area shows the range of abundances of Lizard peridotites, data Frey(1969).



The samples from Gew-graze (Cornwall) also show similar LREE depleted patterns to those of peridotites from Cornwall reported by Frey (1969), figure 4.22.

In all of these analyses the REE abundances range from, 0.003 to 0.6 times chondrite for the LREE and 0.1 to 1 times chondrite for the HREE. These are in general lower than the average for lherzolites and pyroxenites. It is probable that these REE patterns reflect the original REE patterns of the precursor ultrabasic that was altered to form the steatite. In these cases it may be possible that none or little fractionation and general REE mobility occurred, with the exception of Eu which in samples from Clibberswick, shows redox effects. This general immobility was probably a result of the local fluid characteristics, which may not have allowed REE mobility, see section 4.6.2. The apparent lower REE abundances in these samples than those of average lherzolites and harzburgites may reflect the samples taken or, alternatively, lower REE concentrations in the alteration products as a result of few lattice sites for the REE in steatite and/or the removal of REE by the fluid from grain boundary sites in the original ultrabasic material.

Samples from different source localities also have chondrite normalised REE patterns similar to those of ultramafic rocks. Samples from Cunningsburgh and Loch na h'Oidhche have V-shaped chondrite normalised patterns similar to those seen in harzburgites and dunites, figures 4.23 - 4.24. As with the previously discussed samples these patterns probably reflect original ultrabasic chondrite normalised REE patterns. However these sample patterns are not as characteristic of the formation processes as those from lherzolites and pyroxenites. The V-shape is not very distinct and there are other possible processes that could result in a similar pattern.

Chondrite normalised REE patterns for the rest of the samples analysed do not reflect patterns that are similar to those known from ultrabasic material, figures 4.25 - 4.33. In these cases it must be assumed that the process of steatisation, since it is unlikely that serpentinisation had any large effect (see section 3.6), resulted in REE mobility and fractionation. Most of these chondrite normalised REE patterns have LREE/HREE ratios greater than that of chondrites. The degree of this LREE enrichment is extremely variable from different source localities. The REE concentration range from 0.05-80 times chondrites for LREE and 0.02-2 times chondrites for HREE. In general these samples show an enrichment in LREE compared to the range of original ultrabasics and a depletion or no change in HREE.

Figure 4.23 Chondrite normalised REE abundances in steatite from Loch na h'Oidhche, Fisherfield Forest. Typical errors are shown.

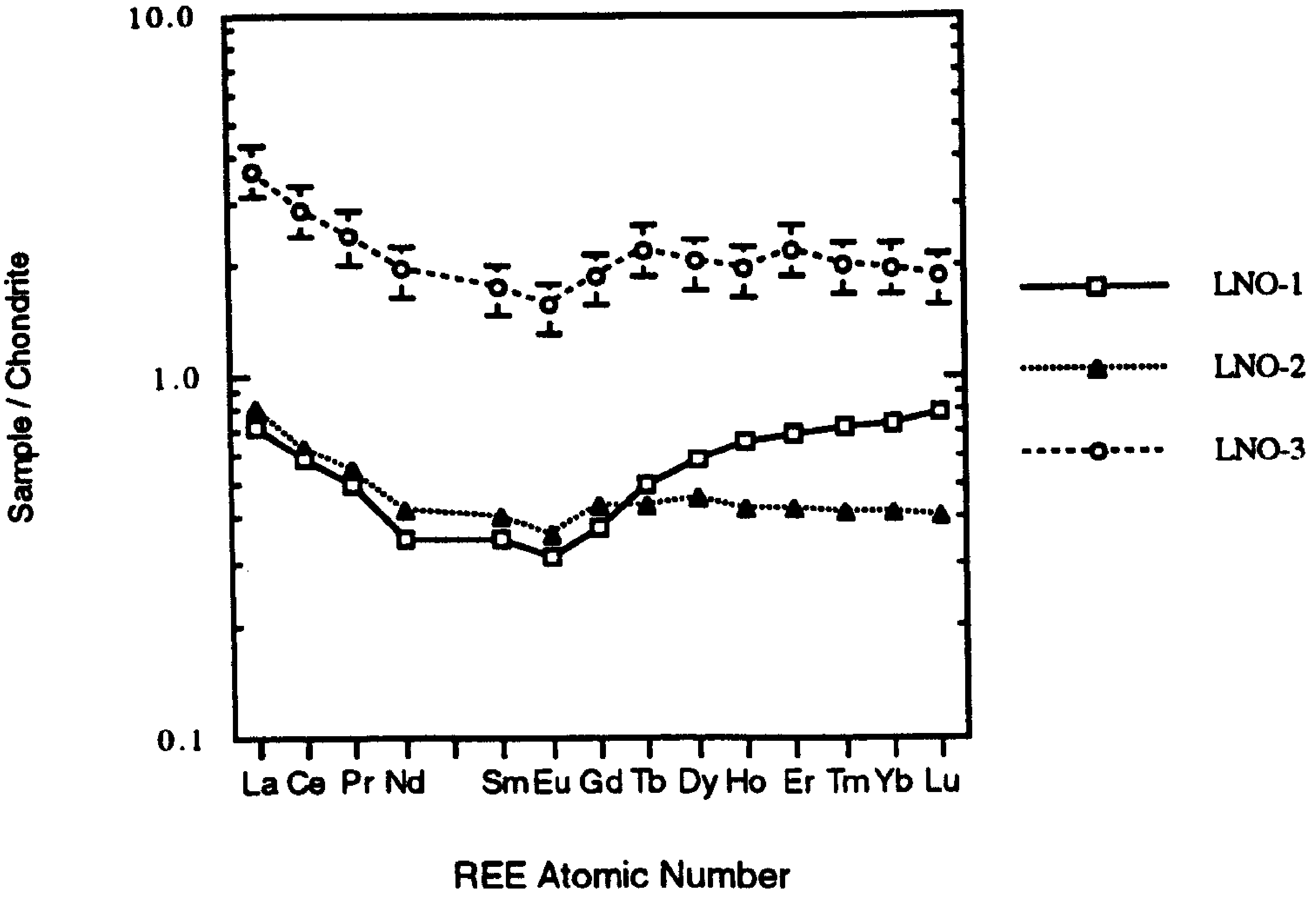


Figure 4.24 Chondrite normalised REE abundances in steatite from Cunningsburgh, Dunrossness, Shetland. Typical errors are shown.

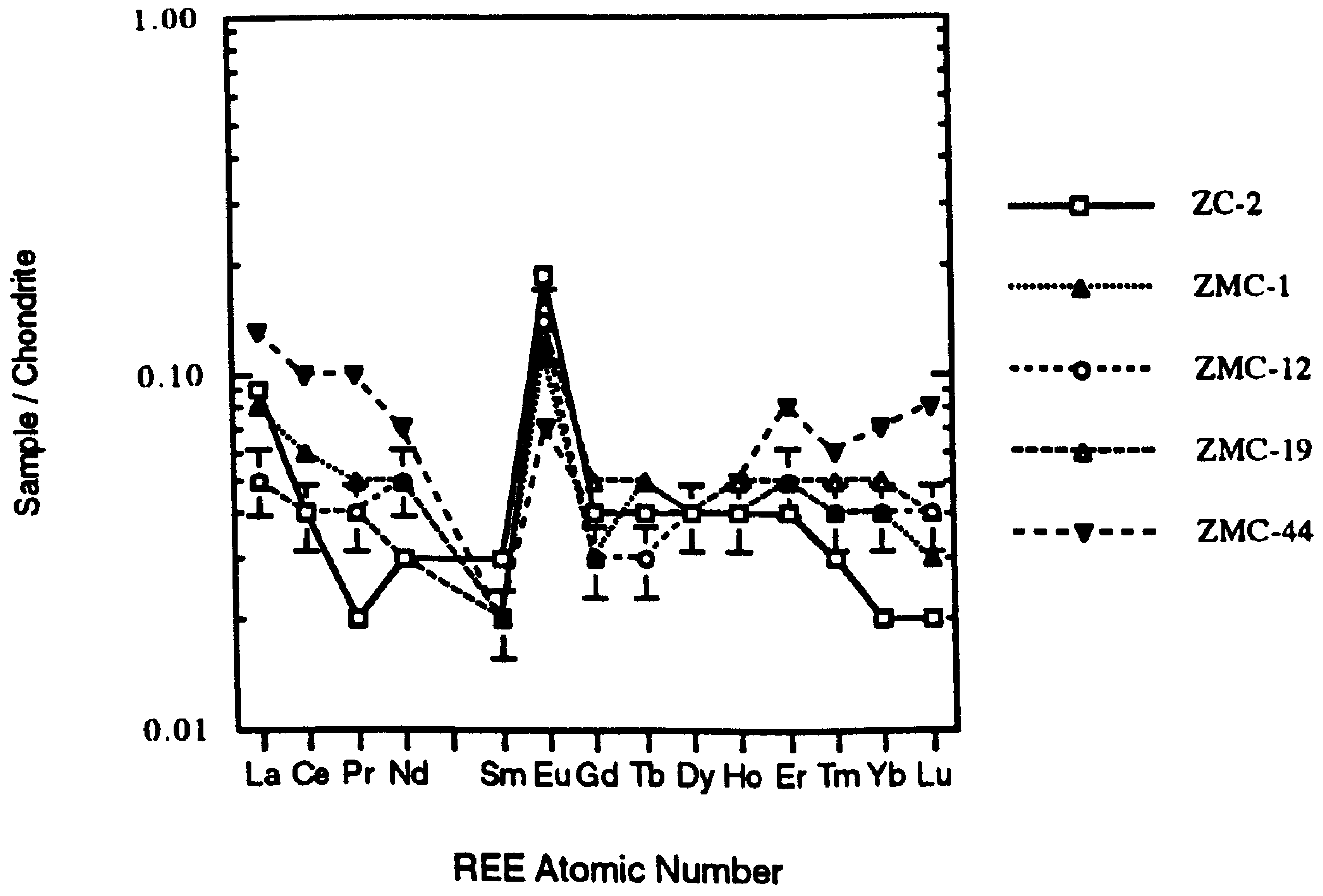


Figure 4.25 Chondrite normalised REE abundances in steatite from Eilean Glas, Scalpay, Harris. Typical errors are shown.

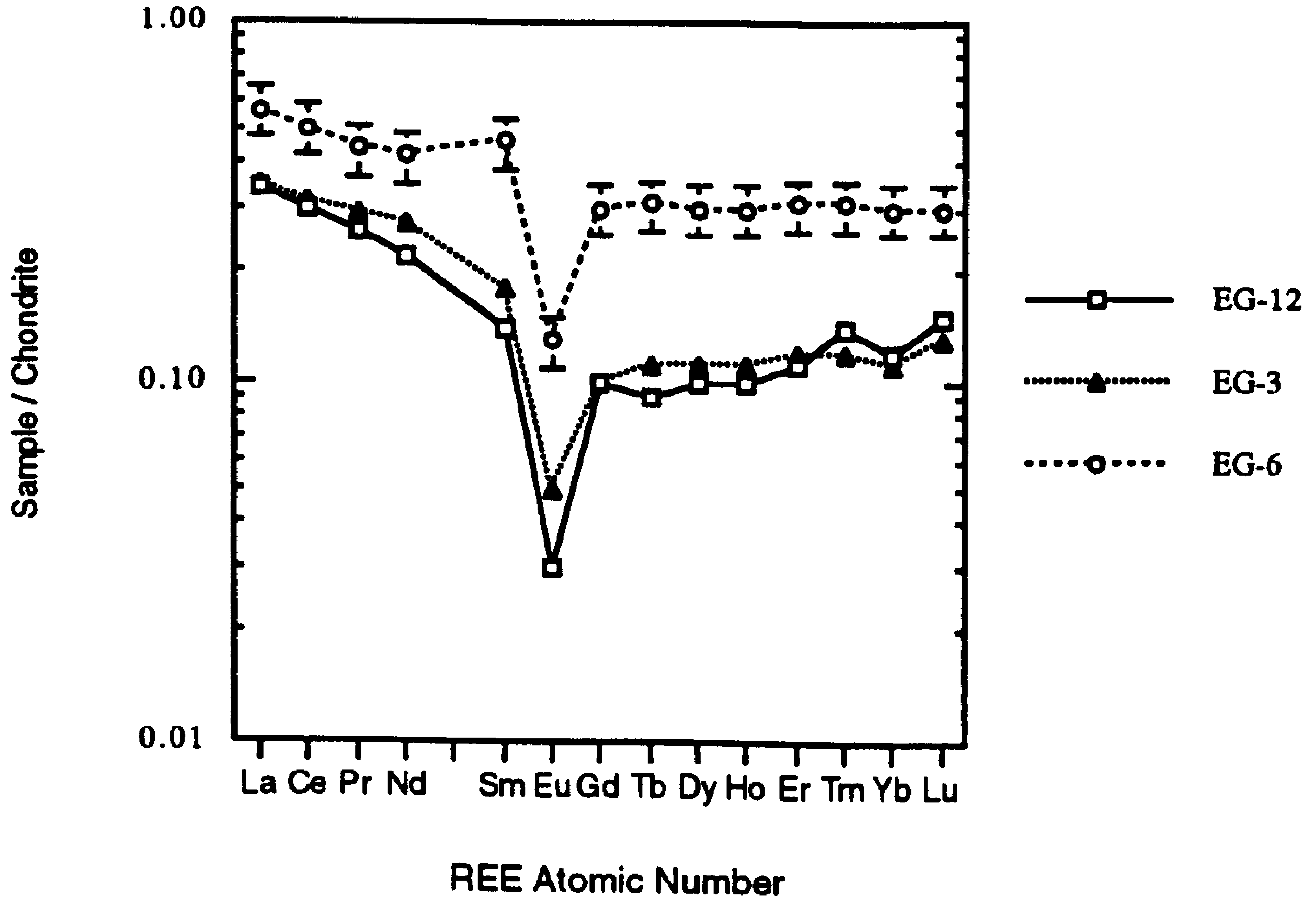


Figure 4.26 Chondrite normalised REE abundances in steatite from Ardintoul, Glenelg. Typical errors are shown.

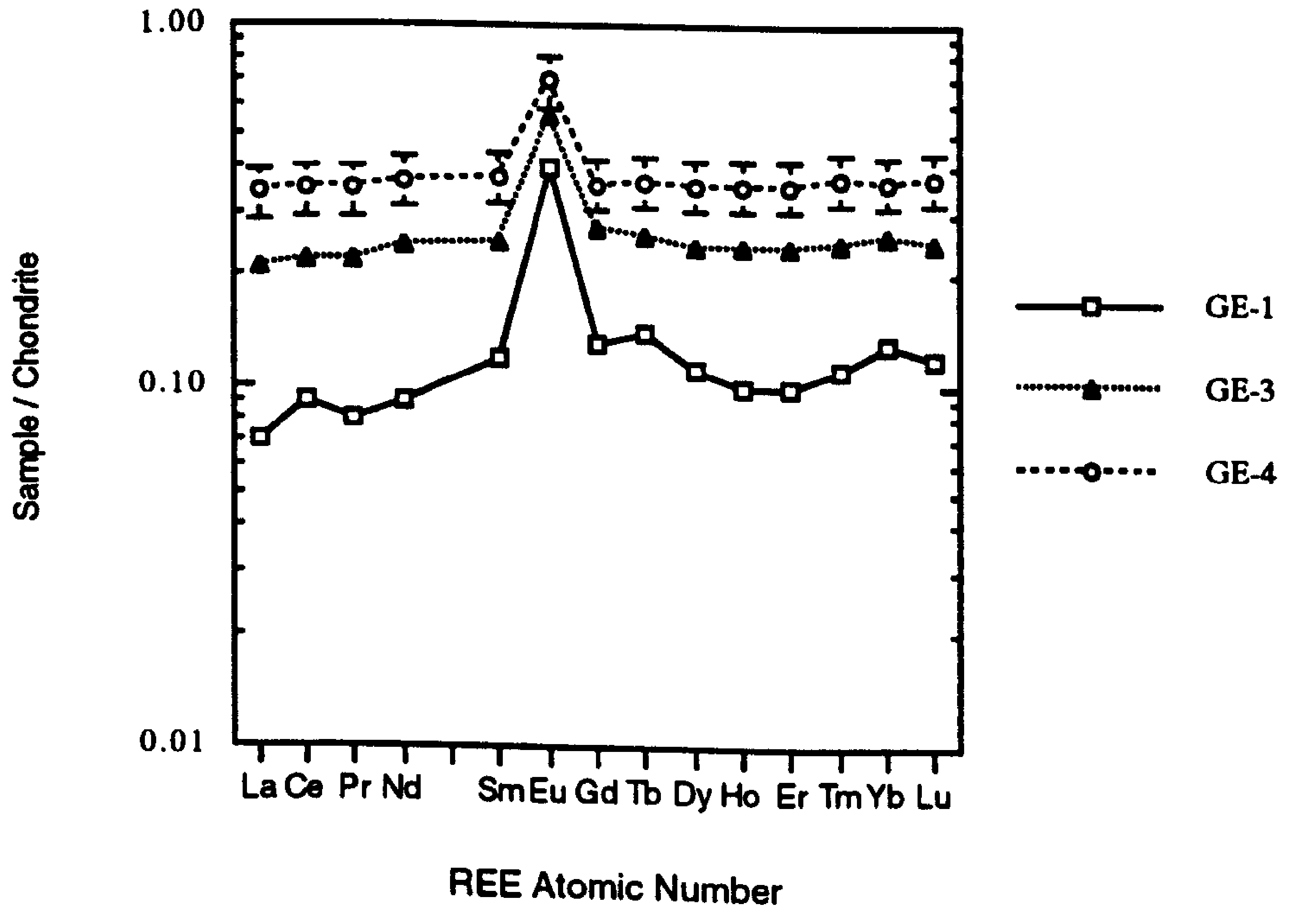


Figure 4.27 Chondrite normalised REE abundances in steatite from Damshead quarry, Portsoy. Typical errors are shown.

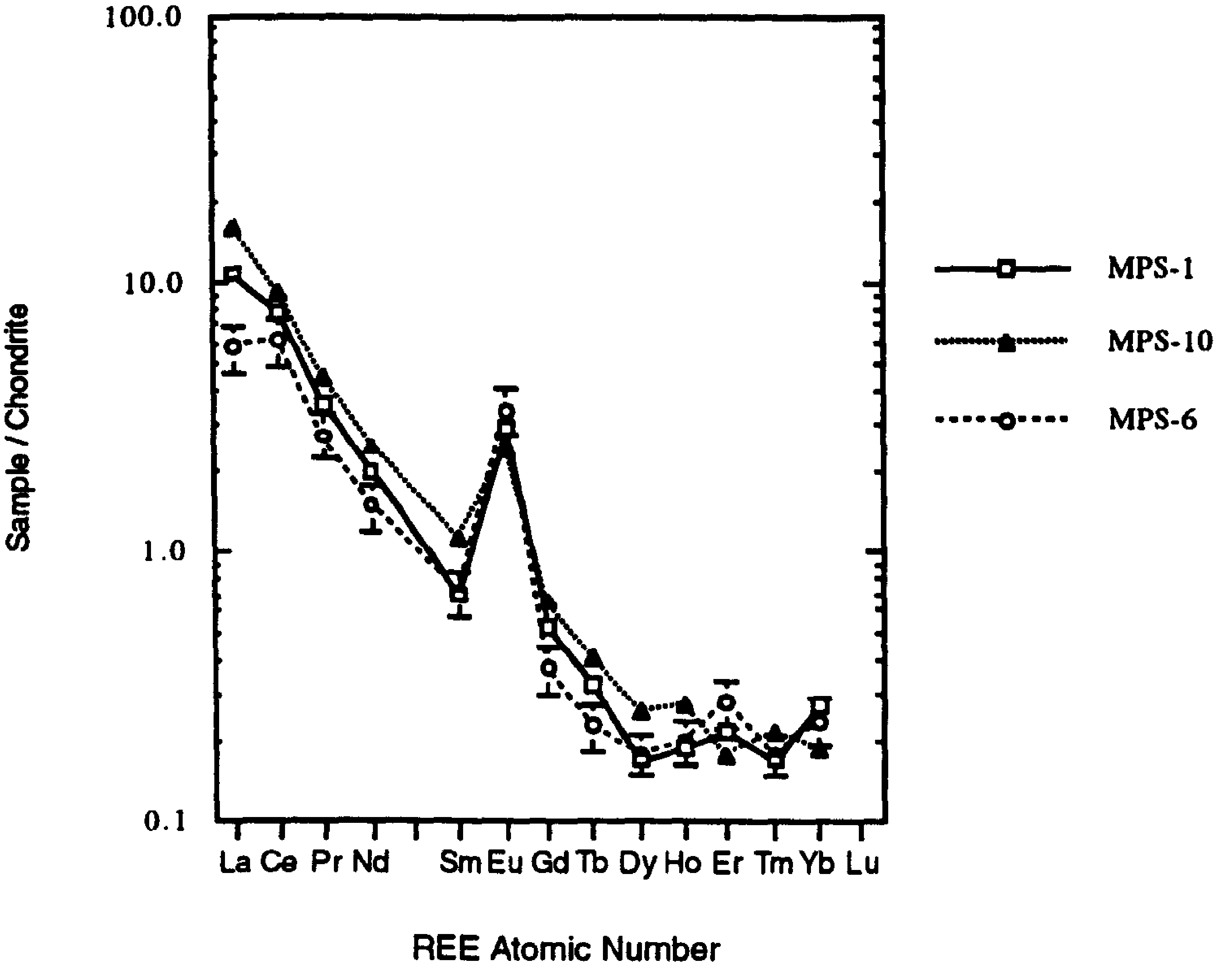


Figure 4.28 Chondrite normalised REE abundances in steatite from Toward/Inellan. Typical errors are shown.

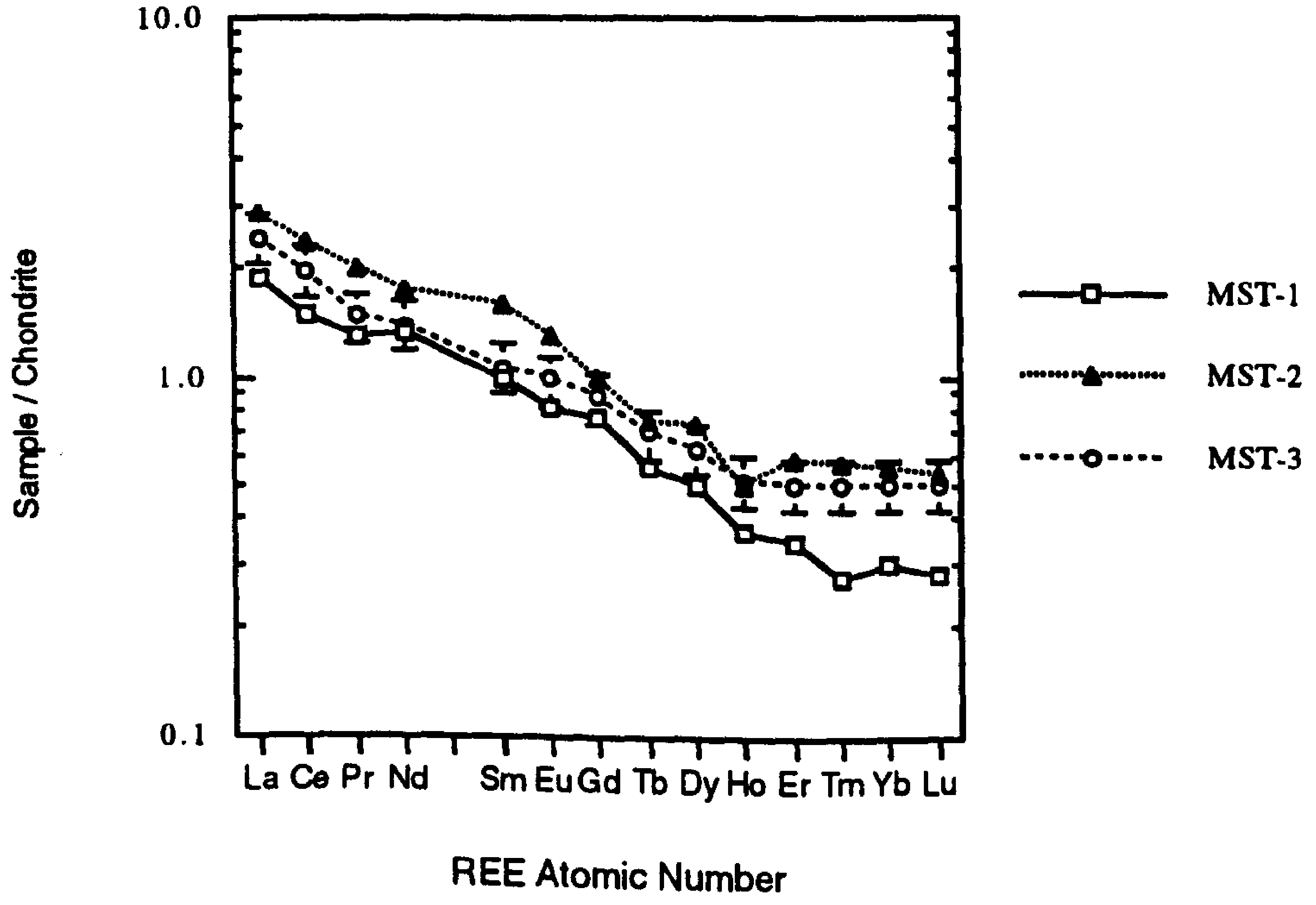


Figure 4.29 Chondrite normalised REE abundances in steatite from Dammins, Hubie, Fetlar, Shetland. Typical errors are shown

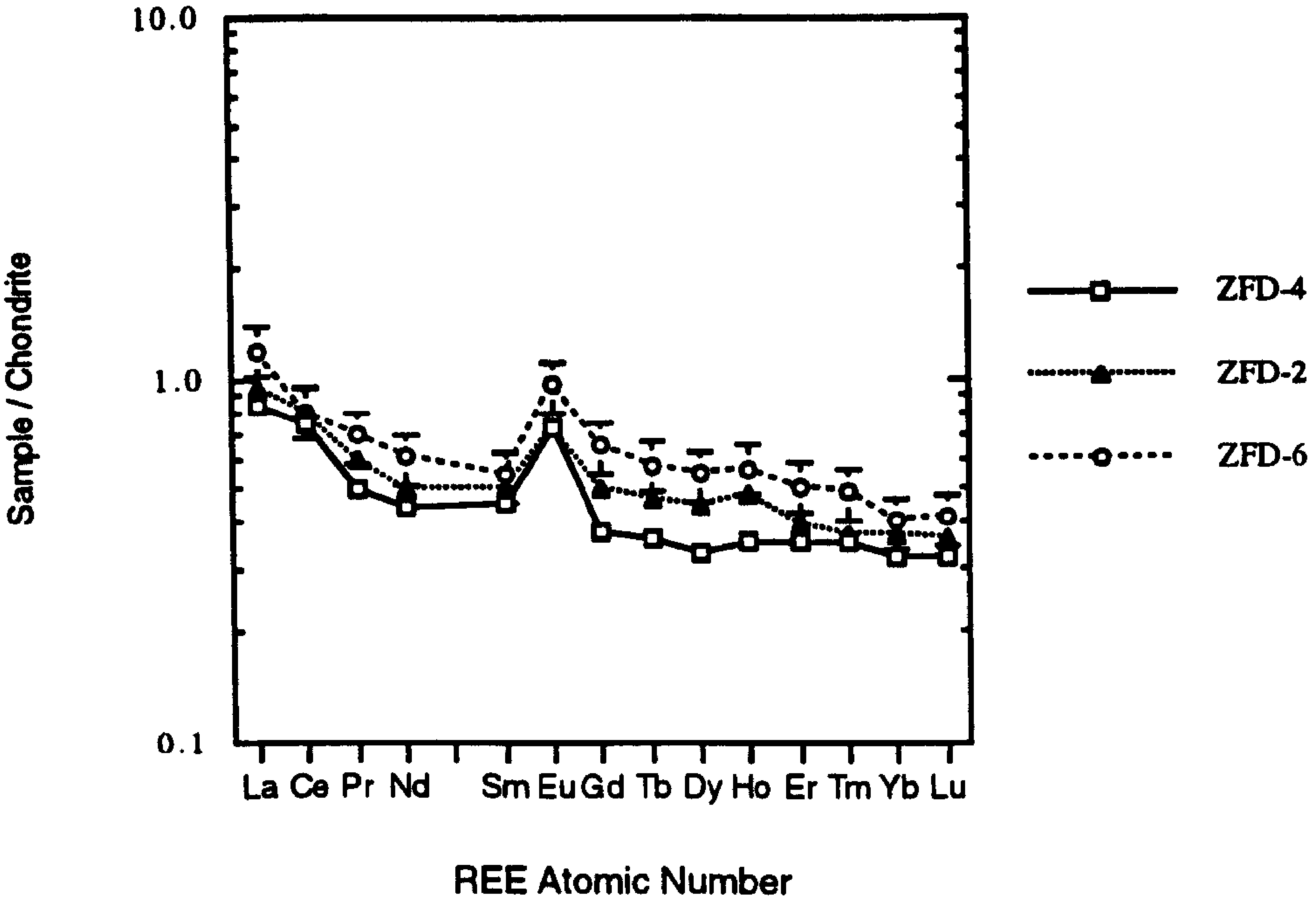


Figure 4.30 Chondrite normalised REE abundances in steatite from Cleber Geo, Hillswick Ness, Shetland. Typical errors are shown

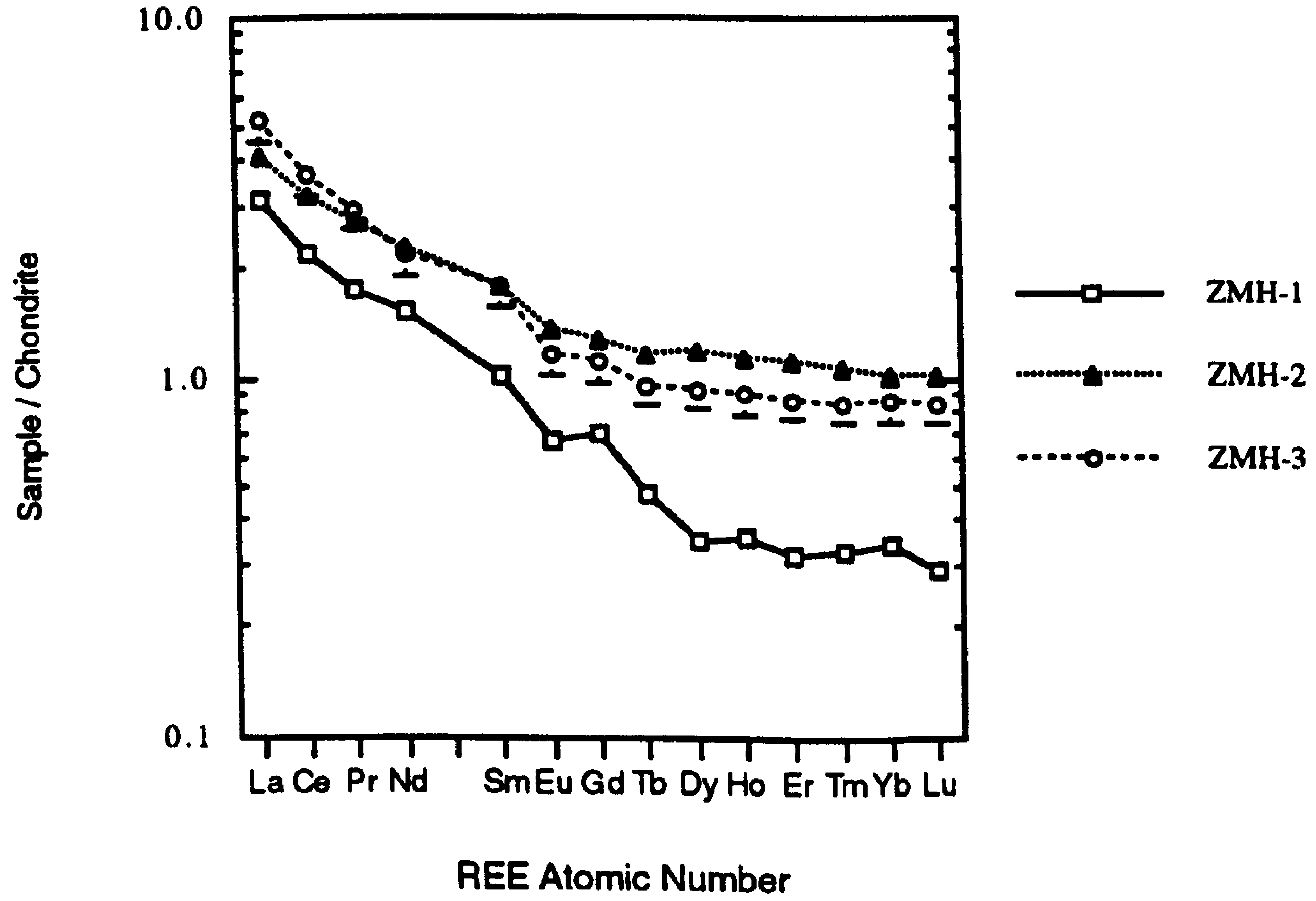


Figure 4.31 Chondrite normalised REE abundances in steatite from Orra Wick, Shetland. Typical errors are shown

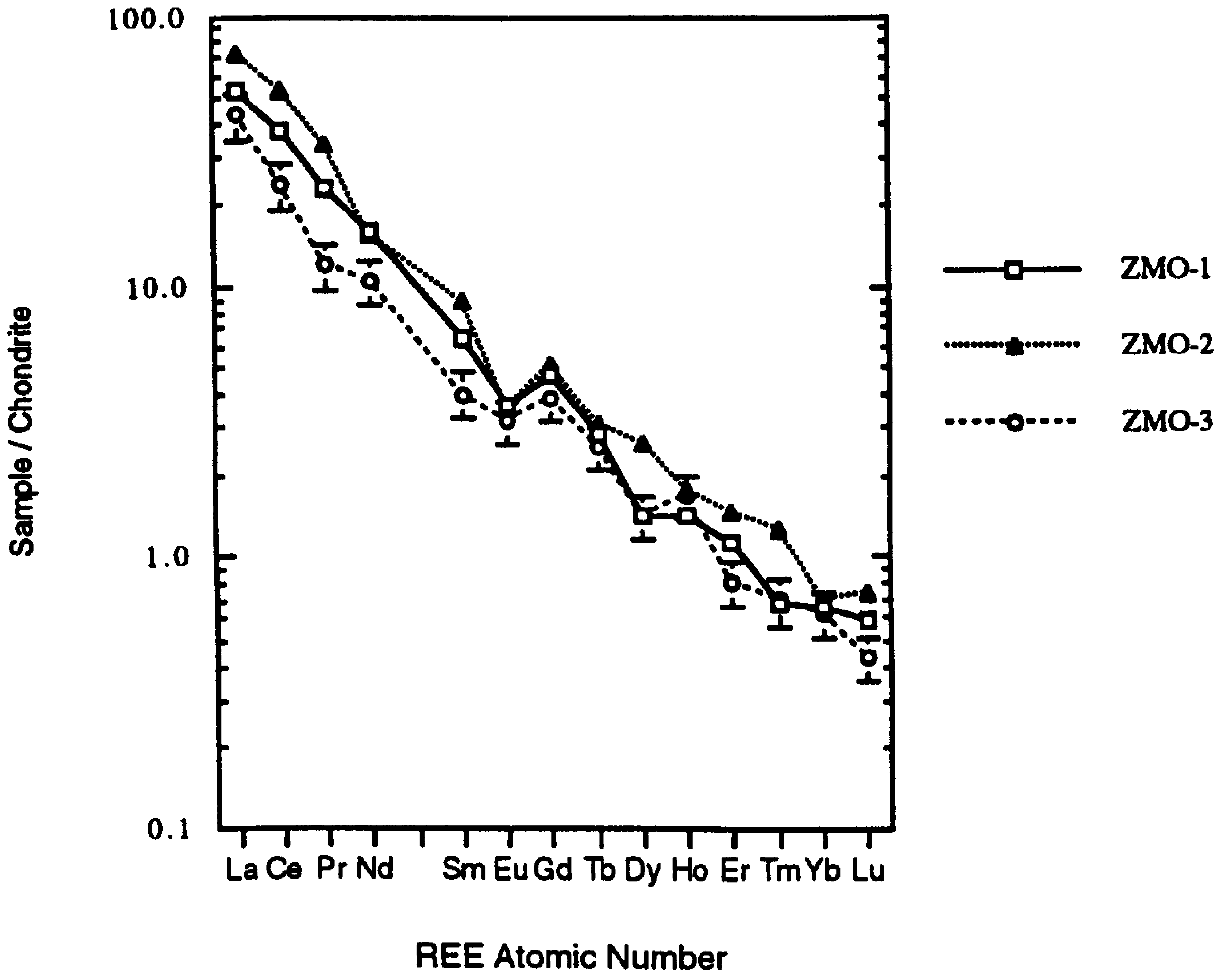


Figure 4.32 Chondrite normalised REE abundances in steatite from Belmont, Unst, Shetland. Typical errors are shown

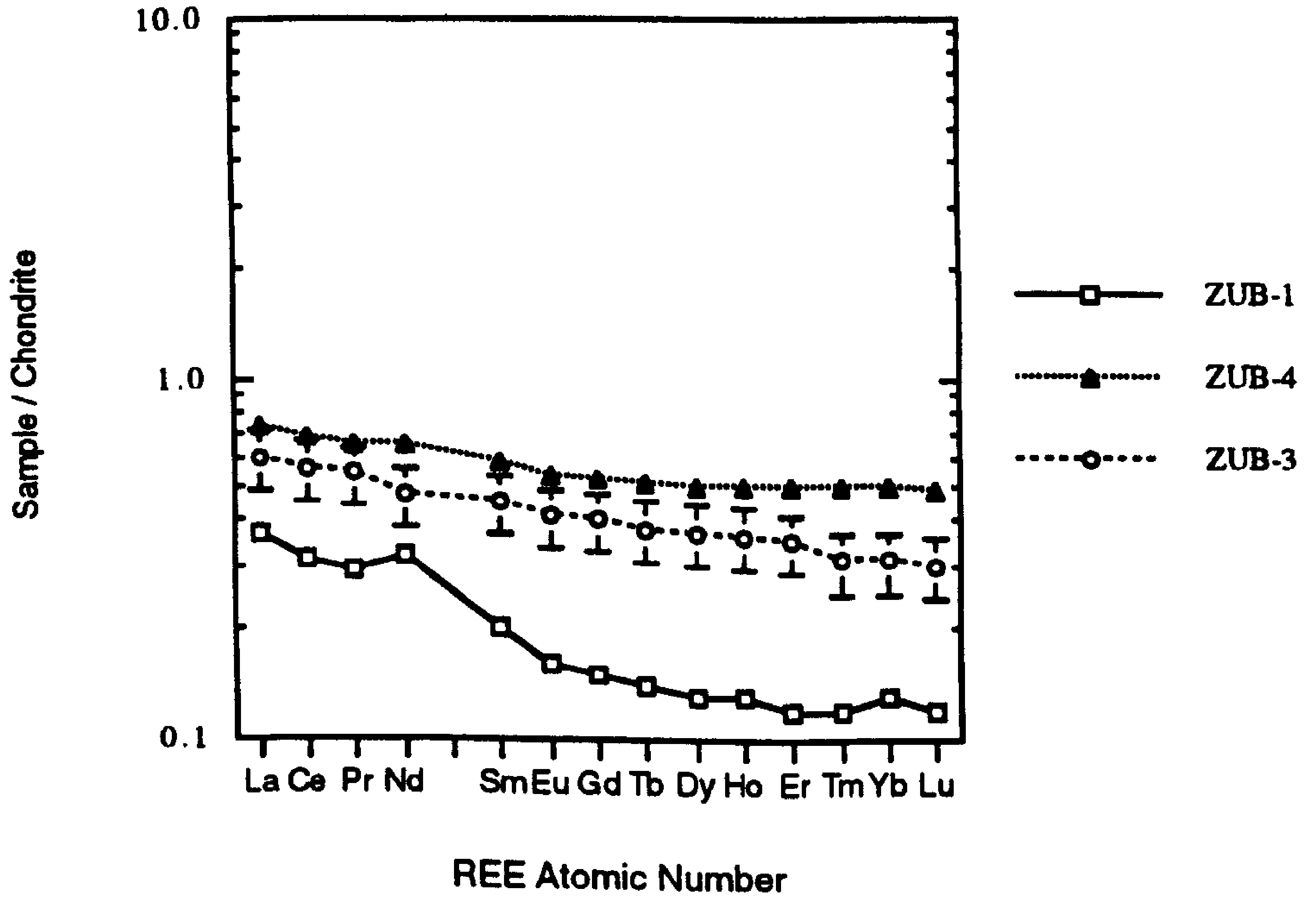
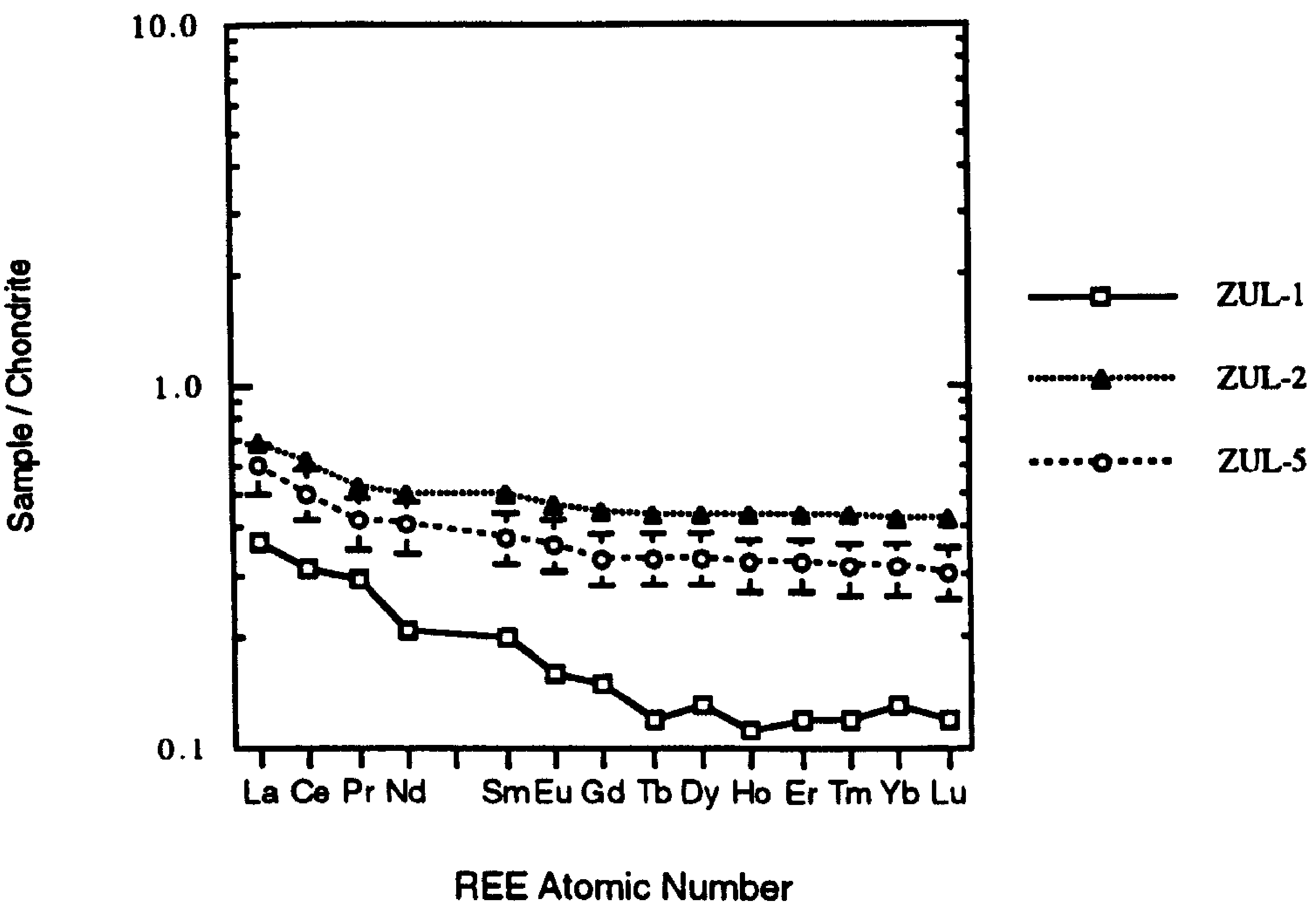


Figure 4.33 Chondrite normalised REE abundances in steatite from Gorsendi Geo, Lund, Unst, Shetland. Typical errors are shown



The original chondrite normalised REE patterns of the parent ultrabasic may easily be altered during steatisation as the original ultrabasics have very low REE abundances, typically less than chondrites. Therefore it would require little metasomatic fluid with a REE concentration of normal continental crust to radically alter the REE pattern of the alteration product. The REE abundances now seen in these steatites are a combination of the REE abundances and patterns within the original ultrabasic, the metasomatic fluid and the partition co-efficient between the rock and fluid. Any depletion in REE from the original ultrabasic may be a result of the lack of available structural sites in steatite in a similar manner to that reported in ultramafic pods by Fowler *et al* (1983).

These chondrite normalised REE patterns are similar to a number of those reported in North America, figures 4.10 - 4.12. Many of the samples analysed by Allen *et al* (1975), Allen & Pennell (1978), Allen *et al* (1978) and Rogers *et al* (1983) show similar characteristic LREE enriched patterns. It is probable that similar processes to those that resulted in the British steatite produced these REE patterns.

A number of these patterns can also be compared with known REE results from the limited study by Buttler (1984) and Moffat & Buttler (1986), figures 4.13 -4.14. Although their results suffer from poor precision some comparisons can be made. The results from the Cunningsburgh samples are similar in concentration to those obtained by Moffat & Buttler. They also exhibit the LREE enrichment and generally flat HREE profile. The samples also show the positive Eu anomaly of Moffat & Buttler K32. The anomalous behaviour of individual elements that Moffat & Buttler noted is not seen in these samples to the same extent as that seen in K12 and K46 although a small negative Ho anomaly can be seen in zc-2 and zmc-1. These anomalies are difficult to explain geochemically. Williams (1977) demonstrated that the REE did not fractionate during steatisation in an ultramafic body in the USA. A process that fractionates Gd and Ho seems unlikely during steatisation, which occurs under conditions that are not particularly unusual in natural systems.

Samples analysed from Fethaland are slightly lower in concentration than those reported by Moffat & Buttler. They only managed to detect three REE, which tends to indicate that the REE patterns analysed in this work do not contradict possible patterns from their results. REE patterns from the samples from Hillswick Ness show a LREE enriched pattern, this is not seen in the Moffat & Buttler sample, which has lower REE abundances. Samples from Dammins and Clibberswick are lower in concentration than those reported by Moffat & Buttler and no overall pattern can be recognised from only 2 REE results. These differences are difficult to explain, however Moffat & Buttler were working at their limit of detection for many of the REE and errors were as large as 50%.

An important fact in any provenancing study is the degree to which the provenancing parameter is representative of individual sources. In this case the chondrite normalised REE patterns of the samples analysed are considered to be representative of the quarries. It must be noted at this stage that only steatite from the ultrabasic alterations was analysed, and that no attempt has been made in this study to characterise the full extent of REE variability throughout a number of zoned bodies. A similar sampling strategy has been used for steatite sources in America (Allen *et al* 1982). However, it has to be assumed that the REE patterns are representative of the individual quarries. There are a number of reasons that this assumption will hold true. Firstly, an individual steatite body is formed from an ultramafic mass that has a small internal variation in REE concentration and similar chondrite normalised pattern. Secondly, the formation processes will essentially be the same across the body, and since it is these processes that control the REE pattern, the chondrite normalised REE pattern of the resulting steatite will be similar within a single quarry. Thirdly, as the REE patterns can be explained geochemically and samples agree with known REE patterns (Gew-graze and peridotites from The Lizard), some degree of certainty can be assumed. Lastly, Williams (1977) demonstrated that the REE partition co-efficients are similar for the constituents of steatite and the fluid, therefore gross changes in mineralogy across the steatite would not result in changes in the REE. This last tenet has to be considered only true for the body Williams studied, which contained little carbonate. However it may be the case that it holds true for many steatite bodies. Much more work will have to be done before this can be ascertained.

The results from the British steatite sources show that there is variation in the REE abundances, but the overall chondrite normalised REE patterns change little within the quarry, and in all cases this internal variation of REE patterns is relatively small when compared with the overall variation between sources. Thus the British evidence supports the theory that the REE patterns appear to be representative of individual quarry sites. The full range of internal variation can not be commented on from these results. It will require a detailed analysis of quarries before this will be possible.

It has been established that in any provenancing study the variables used in discrimination of source materials must show differences between sources and these differences must be greater than any differences seen within any quarry sites. I will deal with differences seen between the quarry sites first.

It has already been argued that the chondrite normalised REE patterns are the important factor and that the actual REE concentrations although important are less significant. The chondrite normalised REE plots, figures 4.17-4.33, clearly show that there are major differences in the REE patterns between the samples analysed from a number of different steatite sources in Britain. This is consistent with the variability noted in steatite sources from Northern America (see section 4.5). The results show a number of different types of REE pattern. Although this may oversimplify the data the REE patterns have been classified into a number of different types in order to make comparisons and discussion easier. Four basic types of REE patterns are proposed:

1. LREE depleted
2. LREE enriched
3. V-shaped REE pattern
4. Flat REE pattern i.e. no depletion in LREE or HREE

A further sub-division of these basic types can be made if the Eu values are considered. If the Eu behaves anomalously, an Eu anomaly, seen in the chondrite normalised REE pattern can be used in the sub-division. Thus in each of the four basic types there are three sub-divisions:

1. No Eu anomaly
2. Positive Eu anomaly
3. Negative Eu anomaly

From this classification system all samples may be assigned a type and sub-division, table 4.5. Samples from the different quarries fall into a wide range of groups and sub-divisions.

Table 4.5 Classification of chondrite normalised REE patterns from analysed steatite quarries based on visual inspection of REE patterns.

Chondrite normalised REE pattern	**Eu Anomaly** positive	negative	none
LREE depleted		ZUC ZMF	MSC ECO WAN
HREE depleted	MPS	EG ZMH ZMO	MST
V-shaped	ZMC		LNO
Flat	GE ZFD		ZUL ZUB

The method of placing a chondrite normalised REE pattern into curve type and extent of Eu anomaly is rather subjective. In order to allow greater description of these patterns, a number of chondrite normalised ratios can be utilised. The $(La/Lu)_{cn}$ ratio gives a measure of the overall slope of the normalised plot and thereby an extent of fractionation of the LREE and HREE. The $(La/Sm)_{cn}$ and $(Gd/Lu)_{cn}$ ratios give comparable information for the LREE and HREE respectively. The plotted position for Eu sometimes lies away from the trend defined by the other REE on chondrite normalised abundance diagrams. The extent of the anomaly is defined by the ratio $(Eu/Eu^*)_{cn}$, where Eu is the europium concentration and Eu* is the value obtained at the Eu position by interpolation between the plotted points for Sm and Gd. These and similar ratios are useful in defining the nature of a chondrite normalised plot of REE abundances. However, care must be exercised when using these results. For example the $(La/Lu)_{cn}$ ratio of some ultrabasics is close to one, but this gives no indication of the marked concave nature of some of these chondrite normalised plots. Spurious results may severely affect the ratios and so give a false impression of a pattern that would be apparent on any plot.

In general a $(La/Lu)_{cn}$ ratio of between 0.7 and 3 describes a relatively flat chondrite normalised REE pattern, a lower ratio describes LREE depletion and a higher HREE depletion. The $(La/Sm)_{cn}$ and $(Gd/Lu)_{cn}$ ratios describe the slope of their respective parts of the REE curve, values between 0.85 and 1.5 describe flat curves, lower values a positive slope and conversely higher values a negative slope. A Eu anomaly is apparent for values greater than 1.2 and less than 0.8.

Table 4.6 Chondrite normalised ratios for samples analysed.

Sample	La_{cn} / Lu_{cn}	La_{cn} / Sm_{cn}	Gd_{cn} / Lu_{cn}	Eu_{cn} / Eu^{*}_{cn}
ZUC-4	0.3	0.41	0.8	0.83
ZUC-2	0.39	0.48	0.87	0.68
ZUC-1	0.3	0.35	0.79	0.65
ZMF-1	1.16	0.56	1.58	0.36
ZMF-2	0.91	0.75	1.18	0.48
ZMF-7	0.47	0.42	1.05	0.34
MSC-1	0.01	0.03	0.63	0.78
MSC-2	0.56	0.49	0.86	0.93
ECO-1	0.19	0.34	0.64	0.94
ECO-2	0.38	0.56	0.82	0.96
ECO-9	0.21	0.42	0.61	0.96
MPS-1	25.74	15.38	1.25	4.79
MPS-10	79.45	14.15	3.29	2.72
MPS-6	23.08	8.07	1.47	6.32
EG-12	2.27	2.38	0.64	0.25
EG-3	2.69	1.97	0.79	0.35
EG-6	1.87	1.21	0.99	0.34
ZMH-1	10.9	3.13	1.45	0.78
ZMH-2	4.06	2.28	1.25	0.88
ZMH-3	6.05	2.89	1.3	0.8
ZMO-1	90.66	8.07	8.36	0.65
ZMO-2	97.81	7.97	7.18	0.5
ZMO-3	99.72	10.54	9.13	0.81
MST-1	6.71	1.91	2.75	0.93
MST-2	5.38	1.79	1.86	1.01
MST-3	4.88	2.28	1.77	1.01
ZC-2	4.5	3.46	2.29	6.02
ZMC-1	2.67	3.56	1.03	3.92
ZMC-12	1.25	2.28	0.75	5.14
ZMC-19	1.25	2.3	1.17	3.91
ZMC-44	1.63	6.17	0.54	2.23
LNO-1	0.92	2.06	0.48	0.86
LNO-2	2.01	1.98	1.07	0.87
LNO-3	1.96	2.12	1.01	0.86
GE-1	0.58	0.58	1.02	3.28
GE-3	0.84	0.81	1.06	2.15
GE-4	0.89	0.9	0.95	1.88
ZFD-4	2.66	1.89	1.19	1.76
ZFD-2	2.64	1.9	1.37	1.47
ZFD-6	2.93	2.21	1.61	1.61
ZUL-1	2.98	1.88	1.28	0.91
ZUL-2	1.62	1.41	1.05	1.01
ZUL-5	1.97	1.55	1.11	1.01
ZUB-1	2.98	1.48	1.24	0.92
ZUB-4	1.54	1.27	1.09	0.96
ZUB-3	2.01	1.33	1.32	0.97
WAN-1	0.43	0.92	0.86	1.02
WAN-4	0.42	0.7	0.84	1.06
WAN-5	0.3	0.71	0.6	0.94

Classification can now be made on the basis of these ratios. Additional types of curves can be defined by the use of these ratios. The LREE depleted and HREE depleted can both be divided in two types, concave and straight. The overall shape can be defined as (see figure 4.34 for diagrammatic representation of type):

LREE depletion concave (A)	$(La/Lu)_{cn}$	< 0.7
	$(La/Sm)_{cn}$	< 0.85
	$(Gd/Lu)_{cn}$	0.85 - 1.5
LREE depletion linear (B)	$(La/Lu)_{cn}$	< 0.7
	$(La/Sm)_{cn}$	< 0.85
	$(Gd/Lu)_{cn}$	< 0.85
HREE depletion concave (C)	$(La/Lu)_{cn}$	> 0.7
	$(La/Sm)_{cn}$	> 0.85
	$(Gd/Lu)_{cn}$	0.85 - 1.5
HREE depletion linear (D)	$(La/Lu)_{cn}$	> 0.7
	$(La/Sm)_{cn}$	> 0.85
	$(Gd/Lu)_{cn}$	> 0.85
V-shaped (E)	$(La/Lu)_{cn}$	0.7-3
	$(La/Sm)_{cn}$	> 1.5
	$(Gd/Lu)_{cn}$	< 0.85
Flat (F)	$(La/Lu)_{cn}$	0.7-3
	$(La/Sm)_{cn}$	0.85-1.5
	$Gd/Lu)_{cn}$	0.85-1.5
Curvilinear (G)	$(La/Lu)_{cn}$	0.7-3
	$(La/Sm)_{cn}$	< 0.85 or >1.5
	$Gd/Lu)_{cn}$	0.85-1.5

Figure 4.34 Diagrammatic representation of the types of chondrite normalised REE patterns used for classification during this study. A - LREE depleted concave, B - LREE depleted linear, C - HREE depleted concave, D- - HREE depleted linear, E - V-shaped, F - flat, G - curvilinear.

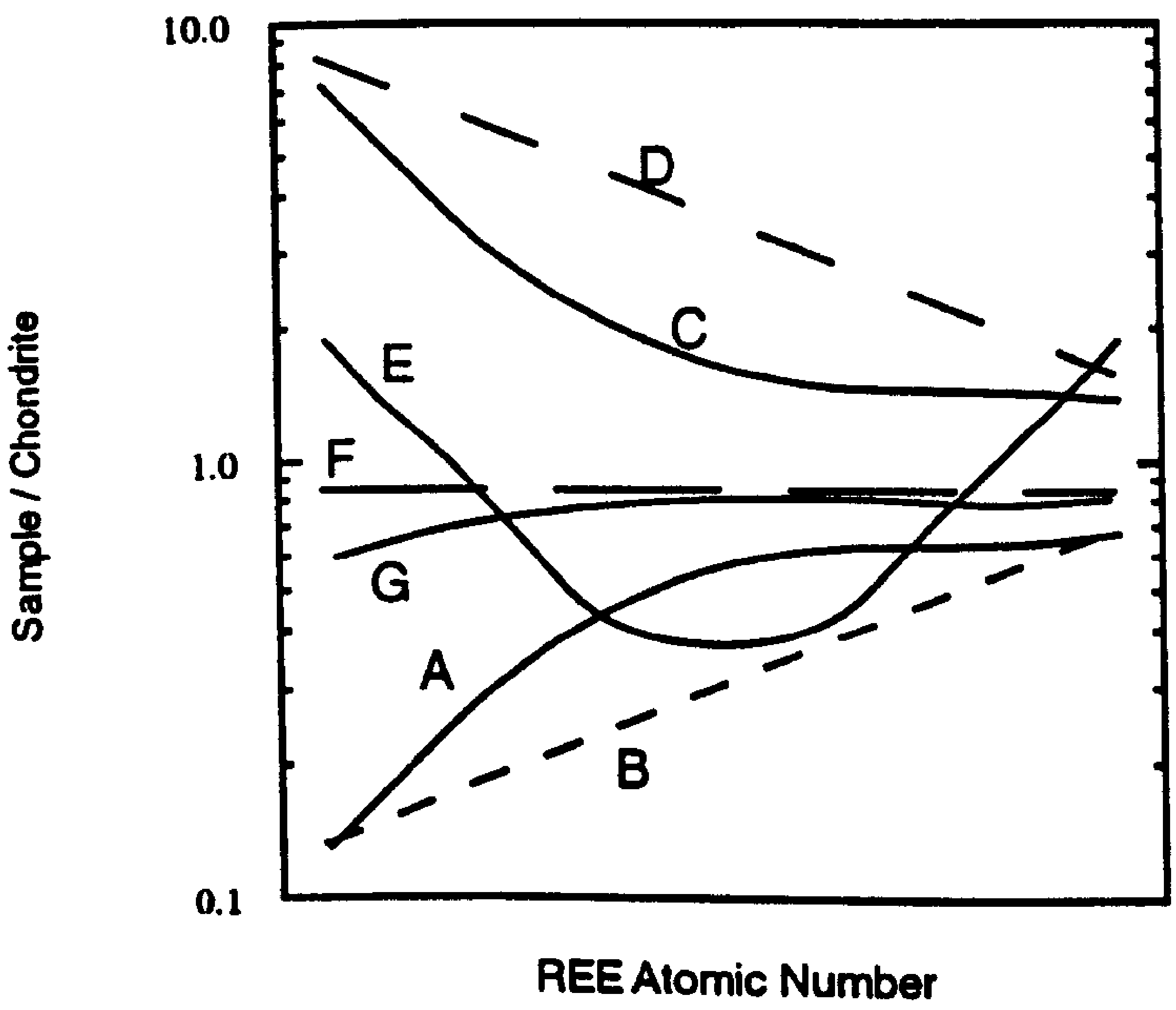


Table 4.7 Classification of chondrite normalised REE patterns based on chondrite normalised ratios.

Chondrite norm. REE pattern Type	Sample
LREE depleted concave (A)	zmf-7
LREE depleted straight (B)	zuc-4 zuc-2 zuc-1 msc-1 msc-2 eco-1 eco-2 eco-9 wan-4 wan-5
HREE depleted concave (C)	zmh-1 zmh-2 zmh-3 mps-1 mps-6
HREE depleted straight (D)	zmo-1 zmo-2 zmo-3 mst-1 mst-2 mst-3 mps-10 zc-2
V-shaped (E)	zmc-12 zmc-44 lno-1
Flat (F)	zub-1 zub-4 zub-3 zul-1 zul-2 zul-5
Curvilinear (G)	zmf-1 zmf-2 eg-12 eg-3 eg-6 zmc-1 zmc-19 lno--2 lno-3 ge-1 ge-3 ge-4 zfd-4 zfd-2 zfd-6

The Eu_{cn}/Eu_{cn}^* ratio is able to categorise the Eu anomaly. Both extent and direction of the anomaly are recorded thus allowing a further parameter to be used in classification.

Table 4.8 Classification of samples based on Eu anomaly.

Eu Anomaly	Sample
Positive	zuc-2 zuc-1 zmf-1 zmf-2 zmf-7 msc-1 eg-12 eg-3 eg-6 zmh-1 zmh-3 zmo-1 zmo-2
Negative	mps-1 mps-6 mps-10 zc-2 zmc-1 zmc-12 zmc-19 zmc-44 ge-1 ge-3 ge-4 zfd-4 zfd-2 zfd-6
None	zuc-4 msc-2 eco-1 eco-2 eco-9 zmo-3 mst-1 mst -2 mst-3 zmh-2 lno-1 lno-2 lno-3 zul-1 zul-2 zul-5 zub-1 zub -3 zub-4 wan-1 wan-2 wan-3

In general this classification system appears to categorise most of the samples into the type that would be expected from a visual examination of the chondrite normalised REE patterns. The combination of ratio values results in more than the original four types of curve suggested from visual inspection. This may in some cases aid characterisation of source material and thus allow fewer options of source for artifacts. However the use of large numbers of curve types does present problems. A number of samples are classified into types that are not expected from visual examination. This is principally a function of the error from a single point used in the chondrite normalised ratio, that may result in a ratio that suggests a pattern that is not a true reflection of the overall REE pattern, see figure 4.25, Sm value eg-12, that suggests a much flatter pattern than the overall LREE trend. Another problem arises from the fact that in some cases the curves from a single quarry site are not assigned to a single class of curve when from visual inspection the curves all appear to show the same basic pattern. This can be seen in samples zmf, see figure 4.18, these samples are classified into different types by the ratio parameters. This is a result of errors on a point used in the ratio as mentioned above and as with any classification system similar patterns may be separate purely on the position of the break point between two groups. These problems could largely be eliminated if the number of types of curves were reduced. However, this would reduce the value of the classification as the number of potential sources for any artifact would increase.

Unlike much of the NAA work on steatite (Allen *et al* 1982, Rogers *et al* 1983 and Moffat & Buttler 1986) ICP-MS is able to analyse all of the REE. Therefore the chondrite normalised REE abundance patterns have considerably more detail than is apparent from NAA results. This is particularly important in two respects. Firstly, the patterns are less susceptible to bias that may be introduced by analytical error if single points are used to define the REE pattern. Secondly, all the information contained in the curve may be used for comparison. This is especially useful in describing any depletion or enrichment in the LREE.

Visual inspection of the chondrite normalised REE curves, comparison of artifacts to known source material, assisted by the classification system, is probably the optimum method of source assignment of artifacts.

One major challenge of geochemical provenancing is evident from these results. This is that a number of sources have similar REE patterns, thus making provenancing between these sources difficult if not impossible. However, although the chondrite normalised patterns may be similar the information may still be of some use. The absolute concentration may be able to discriminate between sources, if this is not possible and no positive identification of the source can be made the REE is able to restrict the number of potential sources, information that would potentially be useful if a number of techniques are used to determine the ultimate provenance.

Having established that considerable differences exist between different steatite source samples, the second tenet of any provenancing study must be examined, the internal variation within a single source. It has been previously argued that although the REE concentration may show some variation, the chondrite normalised REE patterns are similar within a single source. Williams (1977) demonstrated that the REE although varying in absolute concentration across a zoned ultramafic body, the chondrite normalised REE pattern remained essentially unchanged. Williams suggests that partitioning of the REE is even between the phases present. However, it is likely that the REE will be present in Ca sites within mineral phases and to a lesser extent along grain boundaries/defect sites. The availability of these sites will control the overall REE concentrations. If the REE within steatites reflect the original ultrabasic REE pattern then the REE abundances will reflect the available sites in the newly formed steatite. The REE appear to be mobile in some cases during serpentinisation/steatisation. A number of steatite samples display REE patterns that are not patterns seen in ultrabasics. A REE pattern, controlled by the concentration and relative proportions of the REE in the original ultrabasic and the metasomatic fluid and concentration controlled by the availability of sites, seems likely, as many of the samples from a single source of the non-ultrabasic type patterns show similar REE patterns. The REE patterns within a steatite body may be similar, as REE vary little over small areas within ultrabasics and REE concentrations and the extent of any fractionation will be relatively homogeneous within the metasomatic fluid. However, a more detailed study of fluid/rock interactions and the effect on the REE is needed to test this theory.

Examination of the chondrite normalised REE plots, figures 4.17-4.33, demonstrates that although the REE concentrations vary, the patterns remain unchanged within a steatite body. These patterns vary by up to a factor of 5.7 (chon. norm. abundances) in the most extreme cases, lno and ge. Although in general most variations are of the order of a factor of 2. The evidence of the $(La/Lu)_{cn}$, $(La/Sm)_{cn}$, $(Gd/Lu)_{cn}$ and (Eu/Eu^*) ratios also confirms these findings.

4.13 Conclusions

It has been established that the REE could potentially be useful in characterising steatite sources. These sources are thought to display differences in chondrite normalised REE patterns. The ultrabasic rocks of which steatites are alteration products show characteristic chondrite normalised REE patterns that reflect the formation processes and environments. As with all REE work, the patterns are more characteristic than the absolute REE concentration. There are a number of different REE patterns seen in the ultrabasic material that are a product of different formation histories. It is therefore probable that the parent material for steatite formation have a range of chondrite normalised REE abundances. Thus if the REE remain unchanged by the processes leading to steatite formations a wide range of chondrite normalised REE patterns will be evident in steatites. If the REE are mobile during steatisation, as seems probable in some cases, then the REE abundances and patterns in steatite will be dependant on the REE concentration and patterns within the parent ultrabasic and the metasomatic fluid, and the partition coefficient between them. This range of original REE abundances may allow a greater range of chondrite normalised REE patterns in the final steatite than would have been the case had steatite been formed from only a single type of parental material.

Previously analysed steatites also show variation in chondrite normalised REE patterns and abundances. It has been argued that this is a reflection of different steatite bodies having a range of different ultramafic precursor material and different formation processes and conditions resulting in the formation of steatite. These factors have resulted in a diverse range of chondrite normalised REE patterns from different steatite bodies. This is an essential requirement for any provenancing study.

On an analytical side, the REE are present in very low abundances, as would be expected for the alteration product of ultrabasics. The detection of REE is analytically challenging at these levels. Buttler (1984) considered these levels below detection limits for standard INAA and RNAA methods. Even using ICP-MS most samples require pre-concentration before analysis. Other methods such as isotope dilution are time consuming and expensive, thus limiting their potential for large scale studies. A pre-concentration method has been developed and analysis of International References Materials demonstrate that both accuracy and precision are suitable for REE determination at the low levels seen in many steatites thus allowing comparison of samples.

In order to obtain a useful REE pattern not all the REE need to be determined. However it is considered for the abundances found in steatite, at least La, Ce, Nd, Sm, Eu, Gd and at least two of the other HREE (preferably Tb and Lu), need to be analysed. Ideally all REE should be determined in order to give as much information about the REE pattern as possible and to minimise the effect of poor precision. ICP-MS using pre-concentration techniques is probably the best method to obtain the detection limit and range of elements required.

A range of steatite samples from British sources has demonstrated that the REE vary in abundance within a single quarry site. However the chondrite normalised REE patterns show this variation in abundance but their patterns alter little. It has been established that the internal variation in chondrite normalised REE pattern is much less than the variation between all different steatite sources. However, it would be useful if the internal variation could be characterised in greater detail in order that an accurate assessment of internal variation could be made.

It has been argued that the chondrite normalised REE patterns and not solely the REE concentrations in samples from the British steatite sources are representative of the quarry site as they reflect the geological formation processes of the body. These processes are believed to be consistent within a body and the separate bodies are the result of differing processes thus different REE patterns are seen. These results are extremely promising for source characterisation as individual quarries may be distinguished. This may potentially enable artifacts to be provenanced to individual quarry sites.

However, there are a number of problems associated with the characterisation of British sources. Firstly, this study only analysed a selection of the steatite sources within Britain, although these represent all the major quarry sites. Therefore more work will have to done to complete the data base. Until this has been completed no definite provenances can be established, as sources that have not been analysed may have similar patterns to those already determined, without limitations being placed on the results. Secondly, a number of quarries show similar REE patterns. Thus these quarries are indistinguishable from one another by the use of REE patterns alone. However, this only occurs in a limited number of cases, and even in these cases the REE pattern may not be able to positively identify the quarry, it is still able to restrict the number of possible quarry sites.

Chondrite normalised REE patterns can be classified into a number of different types. This may be done on the basis of visual inspection and by the use of a number of chondrite normalised ratios. There are problems associated with both of these techniques, however it is thought that a combination of both is the optimum method for pattern comparison.

Sample homogeneity may also be an important factor. Samples of about 100g were used in characterisation of quarries. This is too large a sample to be taken from artifacts. It will be important to study any fractionations or major changes in concentrations if the sample size is reduced. Sample size is less important when patterns are used for characterisation, however these problems will be further discussed in the final chapter.

It has been established that considerable differences in the chondrite normalised REE patterns exist between steatite sources and these sources show little internal variation in REE pattern. Thus the REE may prove a particularly powerful tool enabling characterisation of the source material and ultimately steatite artifact provenancing. REE are especially useful as they may be able to provenance material to the individual quarry. Provenancing will require all the steatite sources to be analysed, this will be a long process due to the large number of Scandinavian steatite sources. However, the ultimate reward for this will allow much to be learnt about trade and cultural contacts in the Northern Atlantic region over long periods of prehistory and early history.

CHAPTER 5 : THE UTILISATION OF STRONTIUM, ARGON AND LEAD ISOTOPES FOR THE CHARACTERISATION OF STEATITE SOURCES.

5.1 Introduction

This study sought to characterise different steatite sources and source areas by the use of several isotope methods. Principally Sr isotopes have been examined in this chapter, but initially feasibility studies of argon and lead have also been evaluated. The potential of stable oxygen and hydrogen, and platinum group elements (PGE) have also been examined. It has already been established that steatite sources are found in a number of tectonically separate environments of Britain, see chapter 2. These different tectonic regions have a considerable range of ages; the Lewisian 2 700 - 2 900 Ma (Park 1991), the Moine 800 - 1 000 Ma, the Dalradian 600 - 800 Ma, the Unst ophiolite 490 Ma (Spray & Dunning 1991) and The Lizard complex 375 Ma (Davis 1984). These different tectonic environments and ages could result in the steatites having a Sr and Ar isotopic composition characteristic of their location. If this were the case this would be important as it would be able to separate some of the major quarry sites in Britain and Scandinavia.

The complex formation processes will probably result in a wide range of Pb, δD and $\delta^{18}O$ isotope values from different sources. Thus these isotope systems may have great potential for source characterisation. The PGE were identified by PCA, see section 3.9, as a major component of the variance in the data set. Coupled with potential known geochemical difference, these elements may provide valuable source characterisation information.

In this chapter the principles of Sr isotope techniques will be reviewed, their previous use for archaeological provenance studies, the characteristic of steatite precursors and the effect of steatisation on the Sr isotopic composition. This will then be followed by application of Sr isotope analysis to British steatite sources in order to assessing their potential for distinguishing between sources. A representative sample group was analysed and their results are discussed in order to enable characterisation both between source variability and within site variation. Thus the implication for archaeological provenance studies may be assessed.

The potential of Ar, Pb, PGE, δD and $\delta^{18}O$ will be discussed in a further section and their potential for source characterisation assessed. Future areas for work will be suggested.

5.2 Principles of strontium isotopes

Natural Sr consists of four stable isotopes ^{88}Sr, ^{87}Sr, ^{86}Sr, ^{84}Sr, in relative abundances of approximately 0.826, 0.070, 0.099, 0.006 respectively. However, isotopic composition of natural Sr varies since ^{87}Sr is a decay product of ^{87}Rb (half life = 4.88×10^{10}yr.) whilst the other isotopes of strontium are stable. The present day (measured) ^{87}Sr/^{86}Sr ratio of a rock sample is a function of the samples initial ^{87}Sr/^{86}Sr, its Rb/Sr and its age. These are related to each other by the following equation:

$$(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{measured}} = (^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_i + (^{87}\mathrm{Rb}/^{86}\mathrm{Sr})(e^{\lambda t} - 1)$$

when λ = decay constant of ^{87}Rb = 1.42×10^{-11} and t = age of sample
$(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_i = (^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ at time t.

The highest present day ^{87}Sr/^{86}Sr ratios are therefore found in rocks that are old, have high Rb/Sr and that were themselves derived from a source with high ^{87}Sr/^{86}Sr at the time of the rock's formation (i.e. have high $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_i$). These are typically granites and sediments (or their metamorphic equivalents) and are usually found in the upper continental crust. Conversely, the lowest present day ^{87}Sr/^{86}Sr ratios are found in rocks that are young, have low Rb/Sr and which were derived from sources with low $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_i$. Such rocks are typically ultramafic or mafic and are mantle derived.

Consequently if the fluids that produce steatite in diverse locations have different ^{87}Sr/^{86}Sr ratios, or the steatites themselves had different Rb/Sr ratios, or were of different ages then each body (or at least groups of geologically related bodies) may have characteristic present day ^{87}Sr/^{86}Sr ratios.

5.3 The use of Strontium Isotopes in Archaeological Provenancing

Measurements of Sr isotope ratios have been used in a number of archaeological provenancing problems involving lithic materials. Gale (1981) demonstrated that different obsidian sources in the eastern Mediterranean had different isotopic signatures. Gale at al (1988) showed that different sources of Mycenean gypsum could be distinguished by Sr isotopes and material from Mycenean palaces could be linked to these quarries.

5.4 Characteristics of Steatite precursors

In general the ^{87}Sr/^{86}Sr isotopic composition of ultrabasic rocks would be expected to be low, relative to metasediments and other units associated with steatites, as most are considered to have an upper mantle origin and have low Rb/Sr ratios. However, early work by Stueber (1965) demonstrated that there is considerable variation in strontium isotopic ratios in ultramafic bodies. Menzies and Murthy (1978) reported whole rock samples of harzburgite and dunite define a range of $^{87}Sr/^{86}Sr$ from 0.7063 to 0.7290, with an average of 0.7110. Complex genetic models resulted (Bonatti *et al* 1978) to account for the marked discordance between alpine peridotites ($^{87}Sr/^{86}Sr$ 0.7065-0.7290) and oceanic basalts ($^{87}Sr/^{86}Sr$ 0.7020-0.7040). Much of this early work concluded that there was no relationship between oceanic basalts and alpine peridotites.

More recent studies (Polvé & Allègre 1980) demonstrated that lherzolites have whole rock $^{87}Sr/^{86}Sr$ isotope ratios with a range 0.7022 to 0.7059, values that are similar to those of oceanic basalts. Within each ultramafic body a range of values was noted; Lherz 0.70265-0.70413, Freychinede 0.70301-0.70459, Lanzo 0.70263-0.70458, Beni Bouchera 0.70216-0.70390. In all cases the strontium concentrations are low (ca. 10 ppm) and fairly homogeneous. Samples also show low $^{87}Rb/^{86}Sr$ ratios, 0.009-0.05 from Lherz is typical.

Pyroxenites gave higher values that those of lherzolites with some overlap ($^{87}Sr/^{86}Sr$ ratio 0.7031-0.7114). The greater scatter in values has been attributed to differentiation, the higher values representing garnet clinopyroxenite that are considered to be the most differentiated samples. In general the $^{87}Sr/^{86}Sr$ isotopic ratio correlated with the degree of differentiation of the rock as defined petrographically (Polvé & Allègre 1980).

Menzies & Murthy (1978), Polvé & Allègre (1980) and Menzies (1984) demonstrated that fresh clinopyroxenes from harzburgites and dunites have low $^{87}Sr/^{86}Sr$ isotopic ratios, 0.7020-0.7050, suggesting a genetic link to MORB type basalts. These values differ markedly from observed whole rock samples confirming that radiogenic Sr is added to peridotites during hydrothermal alteration or serpentinisation. Reisberg *et al* (1980) reported values of 0.70205±2 to 0.70338±4 from peridotites from the Ronda ultramafic complex. Unfortunately there is little Sr data on serpentinites.

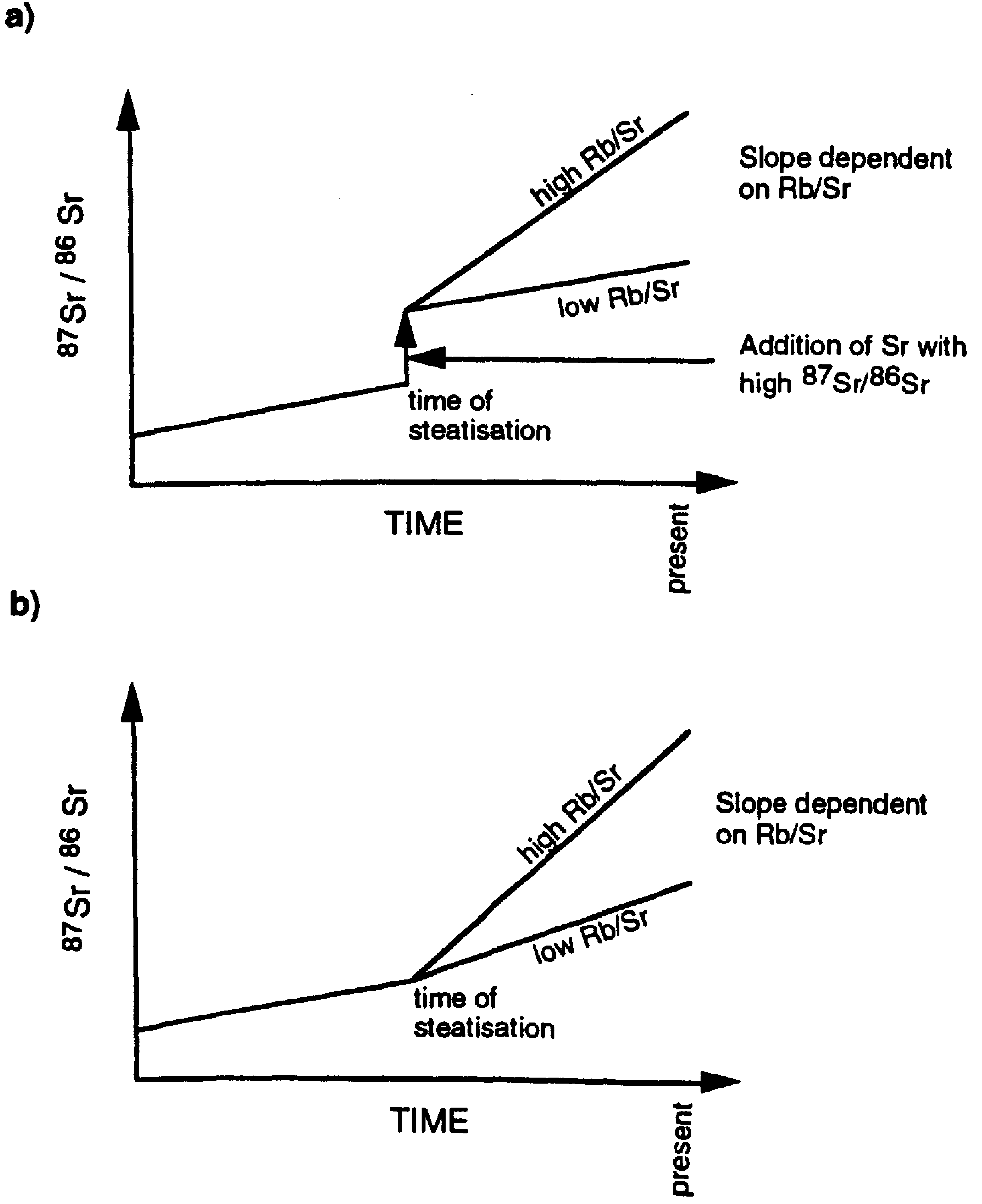
5.4.1 Variation in strontium isotopes within ultramafics

Reisberg *et al* (1989) demonstrated that isotopic variation within peridotites from the Ronda ultramafic complex occurred over very small distances (few metres) (0.7031 to 0.7039) and significant variation occurred across the mass as a whole (0.70205 to 0.70391. Furthermore they suggested that these variations resulted from the mixing of a depleted and as enriched component. However these internal variations are small when compared to the variations seen within comparatively small steatite bodies. Therefore it can be concluded that internal variation within the parental ultramafic was likely to have been small and probably had an insignificant effect on variations within steatites.

5.5 The Effect of Steatisation on Strontium Isotopic Composition

The measured $^{87}Sr/^{86}Sr$ ratios of the steatites represent the initial $^{87}Sr/^{86}Sr$ ratio of the steatite plus any addition of strontium with a different isotopic composition subsequent to the steatite's formation and/or the in situ decay of ^{87}Rb to ^{87}Sr over the time since steatite formation.

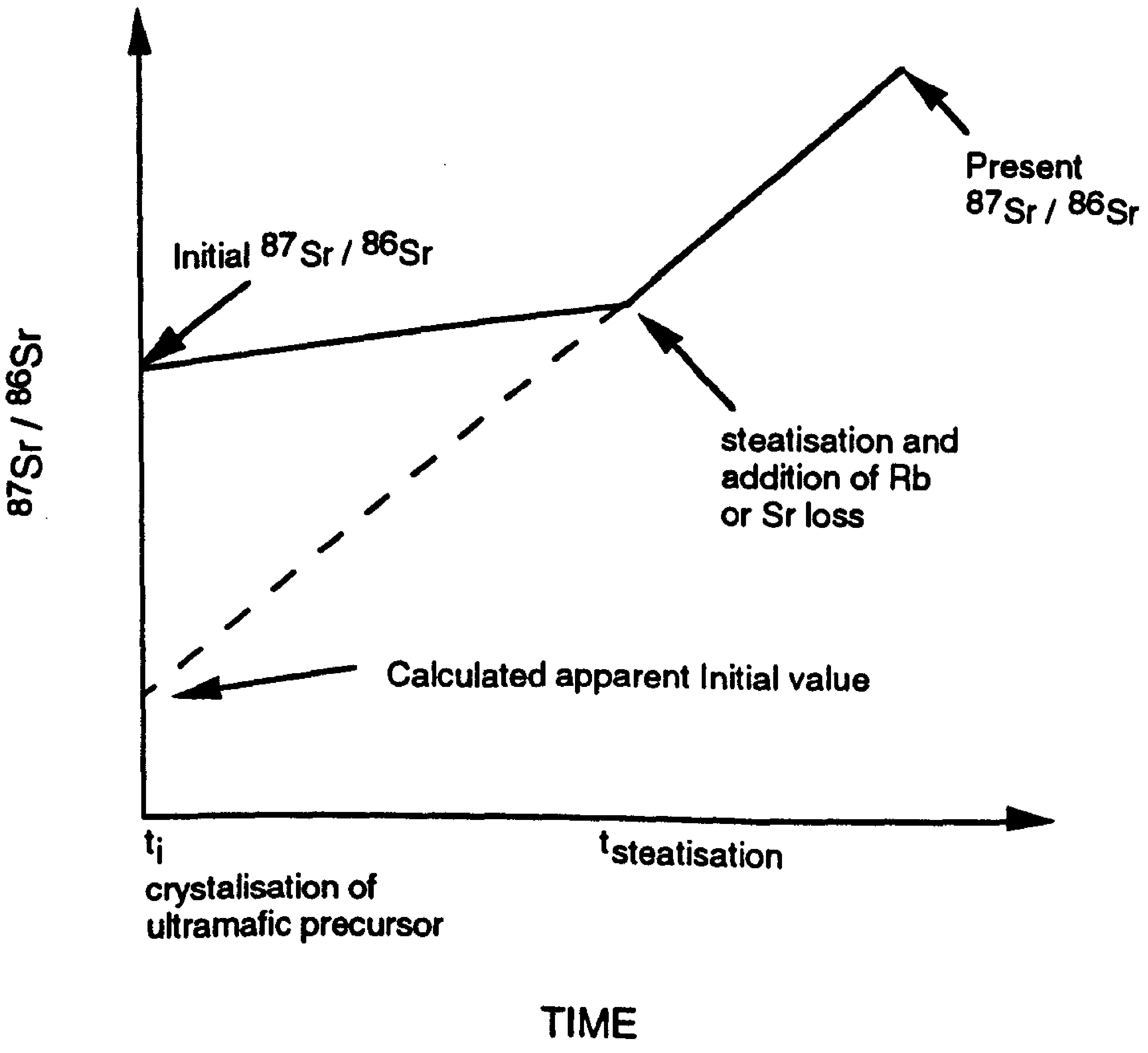
Figure 5.1 A diagrammatic representation of the evolution of $^{87}Sr/^{86}Sr$ ratios with time. a) demonstrates the effect of the addition of Sr with higher $^{87}Sr/^{86}Sr$ ratio. b) demonstrates the effect of changes in the Rb/Sr ratio on the $^{87}Sr/^{86}Sr$ ratio.



In geology variations in the initial $^{87}Sr/^{86}Sr$ ratio may be used to assess petrogenetic processes. Initial $^{87}Sr/^{86}Sr$ ratios could also potentially be used in source and artifact characterisation, however this would be impractical, as it would require the establishment of the age of steatisation of all artifacts of unknown provenance. Uncertainties in the timing of the steatisation process in each body, as well as any Rb/Sr fractionation or change in the $^{87}Sr/^{86}Sr$ during the process may preclude the use of initial $^{87}Sr/^{86}Sr$ ratios (i.e. the ratio the steatites would have had at the time of formation of the ultramafic precursor) as a diagnostic tool.

Steatisation may have a major effect on the $^{87}Sr/^{86}Sr$ ratio of the original parent body. As ultramafic rocks typically have low strontium contents, their Sr isotopic composition is particularly susceptible to change during alteration caused by the passage of a fluid with a different Sr isotopic signature. Furthermore, if the metasomatic fluids have derived much of their Sr from the host country rocks which are likely to have a high $^{87}Sr/^{86}Sr$ then the resulting steatites will have a higher $^{87}Sr/^{86}Sr$ ratio than that of the parent ultramafic rocks. The degree of this increase will be dependant on the Sr isotopic composition of the ultramafic rock immediately prior to steatisation, its Sr content and the amount and $^{87}Sr/^{86}Sr$ ratio of crustal strontium added to the system during steatisation. The subsequent slope of the line describing the evolution of $^{87}Sr/^{86}Sr$ will depend on the Rb/Sr ratio of the steatite. Figure 5.1a show this diagramatically.

Figure 5.2 A diagrammatic representation of the effect on the apparent calculated initial $^{87}Sr/^{86}Sr$ value of changes in the Rb/Sr ratio subsequent to initial crystallisation during processes such as steatisation.



Rb/Sr fractionation during steatisation will also have an effect on the measured $^{87}Sr/^{86}Sr$ ratio, Figure 5.1b. This will result in a higher Rb/Sr ratio in the steatite than the ultramafic precursor and, with time, a higher $^{87}Sr/^{86}Sr$ ratio will develop due to ^{87}Rb decay. The degree to which the $^{87}Sr/^{86}Sr$ ratio will be increased is dependent on the Rb/Sr ratio a high Rb/Sr ratio, will result in a large increase in the $^{87}Sr/^{86}Sr$, whereas a low Rb/Sr ratio will have a proportionately smaller effect, over the same time interval. The result of this increase in the Rb/Sr ratio on the calculated initial $^{87}Sr/^{86}Sr$ ratio is a lower than expected value, figure 5.2.

Thus the effect of changes in the strontium isotopic composition during steatisation, Rb/Sr fractionation and the uncertainty of the age of steatisation precludes the use of the initial ratio of the precursor as a characterisation tool. Therefore characterisation must be made using the measured present day ratio.

5.6 Application to British Steatite Sources

There are number of reasons why Sr isotopic ratios may be of potential use in the provenancing of steatite. Principally, the fact that steatite sources in Britain, and in other localities in the world, are found in a number of tectonically different environments. In Britain steatites are found within a number of ophiolite fragments, the Dalradian and Moine metasediments and the Lewisian complex, see chapter 2. These different lithostratigraphic units have a considerable variation in age; Lewisian 2 700 - 2 900 Ma (Park 1991), Moine 800 - 1 000 Ma, Dalradian 600 - 800 Ma, the Unst ophiolite 490 Ma (Spray & Dunning 1991) and the Lizard complex 375 Ma (Davis 1984).

If these different tectonic environments result in different $^{87}Sr/^{86}Sr$ isotopic ratios in the steatite, Sr isotopes would prove useful in provenancing studies. The ophiolitic material, both Shetland and the Lizard, is surrounded by typical ophiolitic units; ultrabasics, serpentinites and basic rocks, with only small fragments of metasediments. Since this material has relatively low strontium concentrations, low Rb/Sr ratio and a low $^{87}Sr/^{86}Sr$ isotopic composition, it was thought that the hydrothermal alteration fluids that resulted in the formation of the steatite would have these $^{87}Sr/^{86}Sr$ characteristics. Thus steatisation of an ultramafic body in part of an ophiolite may only result in a small change the $^{87}Sr/^{86}Sr$ isotopic ratios, if any, as is discussed in section 5.5.

Conversely, the steatite bodies within the Dalradian are largely surrounded by metasediments. These generally have high Sr concentrations, high Rb/Sr ratios and high $^{87}Sr/^{86}Sr$ ratios, relative to ultrabasics. Therefore if the steatisation fluid derived much of their Sr from within the Dalradian metasediments then the $^{87}Sr/^{86}Sr$ isotopic ratio of the parental ultrabasics would be significantly changed in this process.

The Lewisian in general has higher than average concentration of strontium and low Rb resulting in low Rb/Sr ratios. If no change in the $^{87}Sr/^{86}Sr$ occurred during steatisation this low Rb/Sr would result in a low $^{87}Sr/^{86}Sr$. However, the Lewisian is considerably older than the other geological regions, therefore it was thought that the Lewisian sources might have characteristic $^{87}Sr/^{86}Sr$ ratios.

Therefore if the metasomatic fluid is largely derived from the surrounding rocks, variations might be expected in the $^{87}Sr/^{86}Sr$ ratio of these different lithostratigraphical units due to the factors outlined above.

This method has the advantage that the measurement of a single parameter may allow sources to be characterised and provenance of artifacts made. Another factor that made strontium isotopic analysis potential useful is the relatively small sample size that is needed. This is particularly important when using a destructive technique that will be applied to artifacts.

5.7 Samples

In total 24 samples were selected to represent the different tectonic and geological environments. In order to characterise the variation in $^{87}Sr/^{86}Sr$ ratio within a single steatite body and quarry site, four samples were analysed from each of two separate quarries and three samples from a third quarry, from both the ophiolitic and Dalradian sources.

5.8 Analytical Procedure

The samples were cleaned of all weathered material with a diamond saw to obtain clean blocks of approximately 100g. These were then crushed and milled to less than 150μm. Samples were that were used in the analysis were further ground to 53μm using an agate mortar and pestle. The sample dissolution was identical to the method used for the multi-element analysis and REE analysis using PFA teflon screw-top beakers (Savillex) described in section 3.4.

Sr was separated using standard cation exchange chromatography techniques. The dissolved samples were transferred to centrifuge tubes and any residues were removed. This was not a problem with any of the samples. The solution was loaded onto a preconditioned cation exchange column containing 10 mls Bio-Rad AG50W x 8, 200-400 mesh resin. The sample was washed in with 2 X 1 ml 2.5M HCl and eluted with 46 mls 2.5 M HCl. The Sr fraction was collected with 10 ml 2.5M HCl and evaporated to dryness. In a number of cases the separation did not achieve the separation of Ca and Sr. The presence of Ca results in problems when loading the samples onto the filament and so in these cases the sample was run though the column again. Strontium blanks were less than 5 ng.

All the Sr isotope ratio samples were determined using a VG 54E thermal ionisation mass spectrometer. Sr samples were dissolved in 1 ml 1M H_3PO_4 and were loaded onto a single outgassed tantalum filament. A small current was passed through the filament to dry the sample that was then increased slowly until the H_3PO_4 fumed off and the filament glowed dull red. Sr beams were managed to give an intensity of 1.5 pA ^{86}Sr. Peak intensities are corrected for zero, dynamic memory and Rb interferences, if necessary. The ^{87}Sr/^{86}Sr ratio was corrected for mass fractionation using ^{86}Sr/^{88}Sr = 0.1194. Repeat analysis of NBS 987 Sr standard gave ^{87}Sr/^{86}Sr 0.71028±3 (2σ); all data given here are reported relative to NBS standard value of ^{87}Sr/^{86}Sr = 0.71022. Sr and Rb concentrations were determined by ICP-MS, for discussion of the technique see section 6.4.1.

5.9 Results

The measured ^{87}Sr/^{86}Sr isotopic ratios for all the samples analysed are given in Table 5.1, along with Rb and Sr concentrations determined by ICP-MS and the Rb/Sr ratio.

Table 5.1 Measured Sr, Rb concentrations and ^{87}Sr/^{86}Sr isotopic ratios for steatite samples analysed.

Sample	Location	Rb (ppm)	Sr (ppm)	^{87}Rb / ^{86}Sr	^{87}Sr / ^{86}Sr	2σ
Lewisian						
ge-1	Glenelg	0.27	1.32	0.5920	0.70809	3
eg-12	Eilean Glas	0.06	0.48	0.3621	0.71636	6
lno-1	Loch na'Oidche	0.08	1.08	0.2145	0.71081	4
Dalradian						
zmf-1	Fethaland	0.15	4.98	0.0874	0.73542	4
zmh-1	Hillswick Ness	0.15	190.4	0.0023	0.71208	3
zmh-2	Hillswick Ness	0.16	191.2	0.0024	0.71780	3
zmh-3	Hillswick Ness	0.15	184.4	0.0024	0.72234	4
zmh-4	Hillswick Ness	0.15	199	0.0022	0.71651	11
zc-2	Cunningsburgh	0.14	3.65	0.1111	0.71207	2
zmc-5	Cunningsburgh	0.15	2.56	0.1697	0.71340	5
zmc-1	Cunningsburgh	0.13	2.65	0.1421	0.71308	3
zmo-1	Orra Wick	0.16	140.9	0.0033	0.71341	4
zul-1	Gorsendi Geo	0.05	3.3	0.0439	0.71013	4
mps-2	Portsoy	0.11	50.55	0.0066	1.12152	12
msc-2	Corrycharmaig	0.08	5.34	0.0434	0.71666	3
Ophiolite						
zfd-4	Dammins	0.03	125.4	0.0007	0.70919	4
zfd-2	Dammins	0.04	130.4	0.0009	0.70899	4
zfd-5	Dammins	0.03	121	0.0007	0.70904	3
zfd-6	Dammins	0.03	127	0.0007	0.70991	3
zfc-2	Clemmil Geo	0.04	65.54	0.0018	0.70797	2
zub-1	Belmont	0.25	16.45	0.0440	0.70770	4
zuc-4	Clibberswick	0.12	12.52	0.0277	0.70849	5
liz-1	Gew-graze	0.55	6.53	0.2438	0.70727	3
mst-1	Toward	0.14	23.16	0.0175	0.71154	3

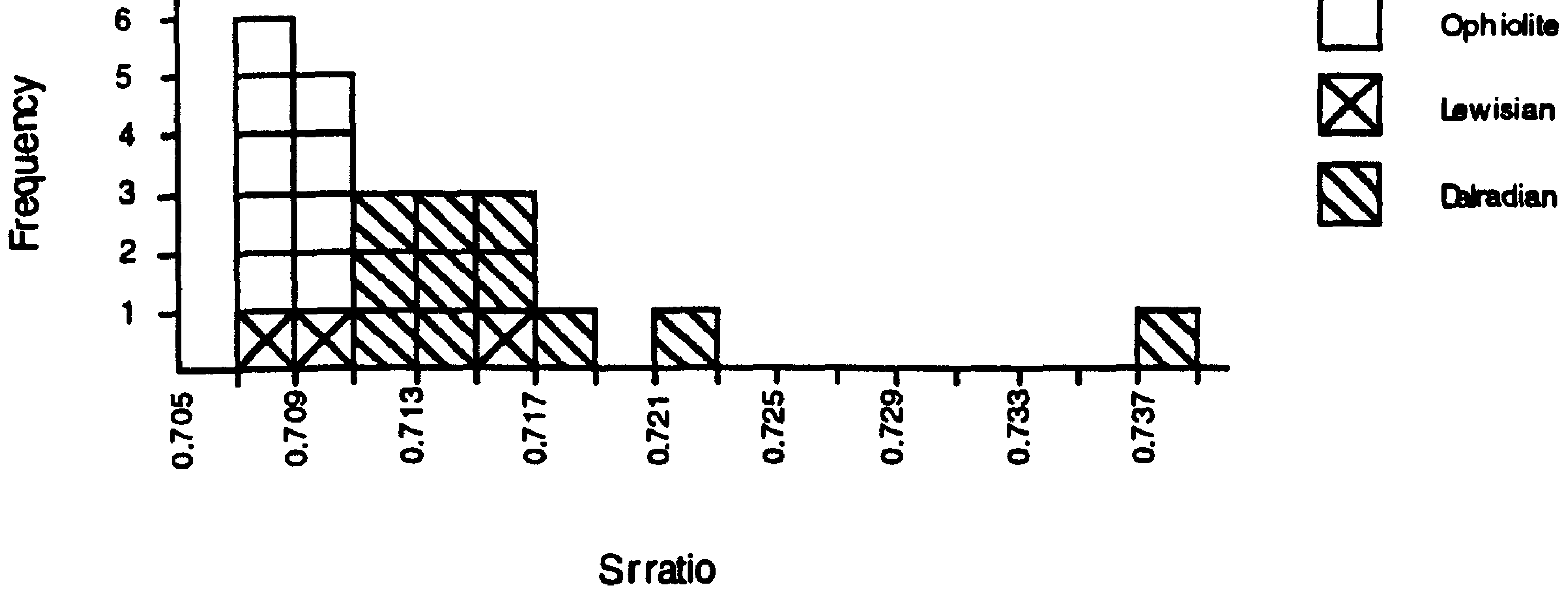
In order for this technique to be useful for characterisation and thus provenance studies differences must be apparent in the $^{87}Sr/^{86}Sr$ ratio between the different source groups. The Lewisian hosted samples have a range of $^{87}Sr/^{86}Sr$ ratios from 0.70809 to 0.71636. These samples have higher Rb/Sr ratios than samples from the other lithostratigraphical groups.

Dalradian hosted samples have a range of $^{87}Sr/^{86}Sr$ ratios which from 0.71013 to 1.12152 with an average of 0.71718 (standard deviation 0.00366). The Rb/Sr ratios are lower than those of the Lewisian group, but higher than ophiolite samples. In contrast the ophiolite hosted steatite samples have the lowest $^{87}Sr/^{86}Sr$ ratios, all samples have $^{87}Sr/^{86}Sr$ ratios of less than 0.70991 and range from 0.70727 to 0.70991 (average 0.70878, standard deviation 0.00075). All these samples have low Rb/Sr ratios.

Sample mst-1 which is from the serpentinites of the Highland Border Complex, is considered to be ophiolitic in nature (Ikin & Harmon 1983, Robertson & Henderson 1984). However the sample has a relatively high $^{87}Sr/^{86}Sr$ ratio of 0.71166. One explanation of this may be that as the serpentinites are surrounded by metasediments of the Highland Border Group and any metasomatic fluid that interacted with these would most likely have a high $^{87}Sr/^{86}Sr$ ratio. Therefore if steatisation took place prior to the emplacement of the Highland Border Complex on to the Dalradian a high $^{87}Sr/^{86}Sr$ ratio may have resulted due to the surrounding metasediments. Ikin & Harmon (1983) argued that serpentinisation resulted from the interaction with low temperature meteoric waters during cooling, post emplacement. Therefore a higher $^{87}Sr/^{86}Sr$ ratio is also likely if steatisation occurred post emplacement. Thus it can be concluded that the Toward/Inellan (Highland Border Complex) sample does not represent "typical ophiolite" $^{87}Sr/^{86}Sr$ ratio values for a number of possible reasons. It seems reasonable to place this sample along with other the samples surrounded by metasediments, the Dalradian. These results are shown diagrammatically in figure 5.3.

In order to characterise the intra-site variability a number of samples were analysed from a single ultramafic body or quarry. If the range of values from within a single site is relatively restricted, then it may be possible to use this method to determine individual quarry sources. Four samples were analysed from Hillswick Ness, Dammins/Hubie and three from the Cunningsburgh quarry. These represent both Dalradian and ophiolite sources, Hillswick Ness and Cunningsburgh are from within the Dalradian and Dammins/Hubie is part of the Unst/Fetlar ophiolite. The results show that $^{87}Sr/^{86}Sr$ ratios display some variation from within a single source, Hillswick 0.71208 to 0.72234, Dammins 0.70899 to 0.70991 and Cunningsburgh 0.71207 to 0.71340. However, this variation is smaller than that seen within the tectonic region as a whole.

Figure 5.3 $^{87}Sr/^{86}Sr$ ratio plotted for the different lithostratigraphical groups used in this study, showing the differences between these different groups.



5.10 Discussion

In order to assess whether or not $^{87}Sr/^{86}Sr$ ratios may be useful in characterisation of steatite sources, the differences between the $^{87}Sr/^{86}Sr$ ratios from the different regions were examined. The results show that the differences in $^{87}Sr/^{86}Sr$ ratios that were expected to exist between sources from different tectonic regions can be seen in the analysed samples. The samples from the Unst/Fetlar and Lizard ophiolites all have $^{87}Sr/^{86}Sr$ ratios of less than 0.7099, whereas samples from Dalradian hosted steatites have $^{87}Sr/^{86}Sr$ ratios greater than 0.71013. However, samples from Lewisian hosted source have a range of $^{87}Sr/^{86}Sr$ ratios that overlap both of the above groups. These Lewisian hosted sample results indicate that all the groups cannot be resolved from one another, however the Dalradian hosted steatite may be separated from ophiolite hosted sources.

$^{87}Sr/^{86}Sr$ ratios apparently are able to separate Dalradian and ophiolite hosted steatites, however the margin that discriminates between these sources is relatively small. Examination of the distribution of results from each group suggests that both populations are far from a normal distribution. However the evolution of $^{87}Sr/^{86}Sr$ ratios that preclude any value below 0.69897 may result in non-normal distributions. With further analysis of samples from these groups, if the populations are normally distributed, then overlap may occur. Nevertheless, it is still possible that the groups will remain discrete populations. In order to enable a more numerical artifact-source comparison Discriminant Analysis may be used to predict the probability of an unknown sample belonging to particular group. This may still produce useful artifact comparison information even if further sampling reveals overlap between the Dalradian and ophiolite groups.

If the intra-site variability in the $^{87}Sr/^{86}Sr$ ratios is relatively small, it may be possible to resolve the $^{87}Sr/^{86}Sr$ ratios on a site specific basis. However the $^{87}Sr/^{86}Sr$ ratios from individual quarry sites demonstrate that some variation also exists within a single site. These differences are large enough to preclude the identification of individual quarry sites by this method alone.

These results have important implications if this method is to utilised for archaeological provenancing. The intra-site variability is of a magnitude that precludes an individual quarry site from being identified from other sources. Thus by the use of this technique alone an artifact cannot be provenanced on a site specific basis. However, the results from the different tectonic groups may contain information that is useful for archaeological provenance studies. These results demonstrate that there are differences between the Dalradian hosted and ophiolite hosted steatite sources. However, the Lewisian hosted sources overlap with both the Dalradian and ophiolite sources. Therefore this technique may be utilised in order to resolve the ophiolite and Dalradian sources, two of the major steatite source groups, while the Lewisian samples can be resolved by the use of different techniques, for example through the elements identified from multi-elemental ICP-MS analysis (chapter 6). This is particularly important in Britain as both of these steatite types represent the majority of sources. Ophiolites and isolated masses are also the common tectonic environments in which steatites are found in Scandinavia. Thus strontium isotopic ratios may prove very useful in any future large scale provenancing of artifacts in the North Atlantic region, especially in a Viking context.

The steatite samples from the Dalradian hosted rocks are thought to have higher $^{87}Sr/^{86}Sr$ ratios than their ultrabasic precursors due to the higher $^{87}Sr/^{86}Sr$ ratios of the surrounding metasediments. The $^{87}Sr/^{86}Sr$ both measured and values calculated at 540 Ma, the peak of metamorphism and likely age of steatisation, can be compared with typical Dalradian metasediments, Table 5.2. This comparison shows that although the measured $^{87}Sr/^{86}Sr$ ratios in Dalradian hosted steatites are substantially different from those of Dalradian metasediments, due the higher Rb/Sr ratio of the metasediments, the initial ratios are similar. This similarity in values is consistent with the theory that the Dalradian steatite sources have $^{87}Sr/^{86}Sr$ ratios similar to the surrounding metasediments. It would be expected that steatites would have slightly lower values as some component of the original ultramafic will probably be present.

Table 5.2. Comparison of Sr isotope ratios measured ($^{87}Sr/^{86}Sr_M$) and calculated ($^{87}Sr/^{86}Sr_I$) from steatites and Dalradian metasediments for an age of 490 Ma. Dalradian metasediment data from Dempster (1985).

Dalradian	Mean $^{87}Sr/^{86}Sr_M$	Mean $^{87}Sr/^{86}Sr_I$	Range$_M$	Range$_I$
Metasediments	0.74840	0.71898	0.71682 - 0.81106	0.71240 - 0.74201
Steatite	0.71666	0.71622	0.71047 - 0.73543	0.71013 - 0.73479

The ophiolite hosted samples all have low $^{87}Sr/^{86}Sr$ ratios that suggest that the metasomatic fluids are largely intra-ophiolite derived with only a minor input, if any, from external sources.

Further evidence to support the theory that the $^{87}Sr/^{86}Sr$ ratio of the metasomatic fluid is controlled by the surrounding host lithologies comes from sample zul-1. This sample gave the lowest $^{87}Sr/^{86}Sr$ ratio (0.71013) of all the Dalradian samples. This sample came from Gorsendi Geo, Unst which is only 2000 m from the Saxa Vord Block of the Unst/Fetlar ophiolite, the closest to the ophiolite Dalradian hosted steatite sample analysed. If steatisation occurred after the emplacement of the ophiolite onto the continental margin the metasomatic fluid may have a lower $^{87}Sr/^{86}Sr$ ratio due to the presence of the low $^{87}Sr/^{86}Sr$ ratio units of the ophiolite.

The absence of no distinct characteristic to the samples from the Lewisian complex is problematic, although a number of possibilities can be suggested. Firstly, the Lewisian is considerably older than the Caledonian ophiolites and Dalradian metasediments and has had a complex tectonic history. Much of the Lewisian has been existence from 2.7 to 2.9 Ga, and has undergone multiple episodes of metamorphism/deformation. The various bodies within the Lewisian may have been generated in a number of different tectonic environments at different times in the past and thus display a wide variation in $^{87}Sr/^{86}Sr$ isotopic ratios.

The Lewisian hosted samples analysed are all from amphibolite facies Lewisian. Within the Lewisian granulite facies units have had low Rb/Sr for much of their history and so have only generated low $^{87}Sr/^{86}Sr$ ratios, compared to the amphibolites which have had higher time integrated Rb/Sr and thus much higher $^{87}Sr/^{86}Sr$ ratios at the present day.

In a number of cases the Rb/Sr ratio is likely to have increased some time after the ultrabasic formed. This can be illustrated by sample ge-1, which has a calculated initial $^{87}Sr/^{86}Sr$ ratio using an age of 2.7 Ga of 0.68494, a value that is less than Basic Achondrite Best Initial values and therefore impossible to achieve without an increase in the Rb/Sr value, see figure 5.2. It is interesting that if a correction is made to the other samples, lno-1 and eg-12, to an initial value of 0.702 ages of 2 740 Ma and 2 835 Ma are obtained. These are entirely plausible Lewisian ages. This suggests that steatisation may have occurred during the early evolution of the Lewisian and that subsequent events have not significantly disturbed the Sr isotopes.

These results from the different tectonic areas agree quite well with the hypothesis that the characteristic of the metasomatic fluid is controlled by the surrounding lithologies. A low $^{87}Sr/^{86}Sr$ ratio is expected if the steatite is hosted by unit with low $^{87}Sr/^{86}Sr$ ratios and conversely a higher $^{87}Sr/^{86}Sr$ ratio occurs where fluid is derived from lithologies with higher $^{87}Sr/^{86}Sr$ ratios.

The variation within a single quarry site may be a result of variations in the steatisation across an ultramafic body. In the case of Hillswick Ness, the uniformity of the Rb/Sr ratios means that the samples would have differences in the $^{87}Sr/^{86}Sr$ ratio no matter what age they were all corrected to. This variation in the $^{87}Sr/^{86}Sr$ ratio may be attributed to variable mixing of components during steatisation, assuming the initial ultramafic sources had a uniform Sr isotopic composition at the time of steatisation. This is a reasonable assumption given the modern range of $^{87}Sr/^{86}Sr$ ratios in ultramafics. In contrast the site at Dammins/Hubie has a uniform present day $^{87}Sr/^{86}Sr$ ratio coupled with a very low and uniform Rb/Sr ratio. These results suggest that the steatisation process produced a much more homogeneous body in this case. For Cunningsburgh the Sr evolution curves do not intersect at any common age, which is consistent with there being heterogeneity within the initial steatite, as in the case for Hillswick Ness.

5.11 Other Techniques that may Provenance Steatite

Several techniques and a range of trace element and isotopes have been evaluated in this study. However, there are a number of other techniques that may enable sources of steatite to be characterised and subsequently artifacts provenanced. This section will discuss some of these methods and their relative attributes in relation to provenancing.

5.11.1 Argon Isotopes

In chapter 5 the use of Sr isotopes was established as a method of provenancing steatite. K-Ar and $^{40}Ar/^{39}Ar$ dating may also provide a means of source characterisation that will enable artifact provenancing. The conventional method of K - Ar dating depends on the assumption that no argon is present within the sample at the time of its formation and that subsequently all radiogenic argon produced within it was quantitatively retained. Because argon may be lost by diffusion even at temperatures well below the melting point, K -Ar dates represent the time elapsed since the sample cooled to temperatures at which diffusion loss of argon is insignificant. The $^{40}Ar/^{39}Ar$ method of dating, first described by Merrihue and Turner (1966) overcomes some of the limitations of the conventional K - Ar method. It has the advantage that potassium and argon are determined on the same sample and only measurements of the isotope ratios of argon are required. The problem of inhomogeneity of samples and the need to measure the absolute concentrations of potassium and argon are thus eliminated. The method is therefore well suited to the dating of very small or valuable samples. A more detailed discussion K-Ar and $^{40}Ar/^{39}Ar$ dating methods is given by Faure (1986).

Potassium - argon techniques have previously been applied to several lithic provenance studies. Ellis (1969) performed a major systematic petrological study of English hone stone which included three K-Ar determination. Kars (1983) reports isotopic ages for four metamorphic hone stones, two sandstone hones and one possible source rock in his petrological study of Dorestad material. These initial studies were followed up by Mitchell *et al* (1983) and Crosby & Mitchell (1987) who examined large numbers of Viking and medieval metamorphic hone stones from Scandinavia, Germany, Poland and Britain. Clearly this technique is useful when sources are located in geological regions that exhibit different K - Ar ages.

The $^{40}Ar/^{39}Ar$ method has not as yet been applied to provenancing studies despite its obvious advantage, over the conventional K - Ar method, of requiring a much smaller sample for analysis, laser ablation requiring only a few 100 μm grains. However the $^{40}Ar/^{39}Ar$ technique has recently been used to test whether or not suspect hearths and cooking pits from archaeological sites were utilised (Gillespie *et al* 1989). This study was also able to estimate the intensity and age of the utilisation of these hearths in some cases, which is particularly relevant to sites with dates older than ^{14}C.

Clearly, if the $^{40}Ar/^{39}Ar$ or K-Ar methods are to be useful for steatite provenancing then sources must display a range of $^{40}Ar/^{39}Ar$ dates that enable differentiation. In chapter 2 the geological province of British and Scandinavian steatite sources was discussed. Within these regions there are large differences in the ages of the provinces. In Britain these range from the 2.7 - 2.9 Ga Lewisian, to the ca 1000 Ma Moine, 600 - 800 Ma Dalradian, 490 Ma Unst ophiolite and 375 Ma Lizard complex. A similar wide range of formation ages and subsequent histories is apparent from the provinces of Scandinavian steatite sources. These are crystallisation ages whereas the ages that may be obtained by $^{40}Ar/^{39}Ar$ represent the time at which the sample cooled to temperatures at which diffusion loss of argon is insignificant (clearly these may be younger than the formation age). Therefore, this wide range and the varied subsequent history of these provinces will probably result in a range of $^{40}Ar/^{39}Ar$ ages. If differences in the $^{40}Ar/^{39}Ar$ ages could be established between steatite sources in the different geological provinces then this technique might be potentially very useful for steatite provenancing.

An initial feasibility study was carried out in order to test whether these differences could be demonstrated. Four whole rock samples were analysed, using the laser ablation and subsequent ratio measurement described by Burgess *et al* (1992), two from Lewisian sources and two from the Unst/ Fetlar ophiolite. These provinces have a considerable variation in formation age and have different cooling ages. ^{36}Ar, ^{39}Ar and ^{40}Ar were measured, ^{36}Ar is used to correct ^{40}Ar for atmospheric contamination ($^{40}Ar/^{36}Ar = 295.5$).

These results, despite the lack of precision, appear to demonstrate distinct populations between the two regions. A Student's t-test conducted on the ages gave a value of 5.249. This value at a significance level of 5% is greater than the critical t value at 2 degrees of freedom, Therefore the null hypothesis that the two groups represent the same population may be rejected. This strongly suggests that with increased precision of analysis much useful information may be obtained from Ar isotopes.

Table 5.3 Average argon ratios obtained from whole rock steatite samples.

Sample	**Province**	$^{39}Ar/^{40}Ar$	$^{40}Ar^{*}/^{40}Ar$	$^{40}Ar^{*}/^{39}Ar$	**Age Ma (2σ)**
zfd-4	Unst ophiolite	0.00059	0.1186	285.27	1547 ± 1070
zuc-4	Unst ophiolite	0.00033	0.0942	249.70	1412 ± 763
lno-1	Lewisian	0.00011	0.0289	1104.62	3309 ± 1378
eg-15	Lewisian	0.00046	0.2978	828.70	2883 ± 307

The lack of precision is due to the combination of a number of factors. The samples analysed were whole rock (not single mineral) which as a result of the different closure temperatures of different constituent minerals results in mixed ages. The samples have low potassium concentration, in common with most steatites (average value 0.05% weight), this low potassium results in little radiogenic ^{40}Ar in the samples. Perhaps the most serious problem is the high percentage of excess Ar. Excess Ar is Ar that is incorporated into rocks and minerals by processes other than by in-situ decay of ^{40}K. In some cases this excess argon can be attributed to air presumably dissolved in hydrothermal fluids associated with steatite formation. Figure 5.4 shows Ar in sample zuc-4 to be a two component mixture of air ($^{40}Ar/^{36}Ar = 295.5$, $Ar^{*} = 0$) and radiogenic Ar ($^{36}Ar = 0$). This is not particularly surprising as hydrothermal fluids often contain large quantities of excess Ar. Figure 5.5 demonstrates Ar in sample zfd-4 is consistent with a model that has more than two components. In these cases non-atmospheric excess Ar is involved in the system, therefore an accurate date cannot be produced.

The poor precision problem may be reduced by several techniques thus enabling the different sources to be compared. Firstly, in order to alleviate the mixed age problem of whole rock samples, single phase mono-mineralic grain can be analysed. This would require slightly larger samples as mineral separates would be required. Little is known about the behaviour of Ar in talc and the closure temperature at which diffusion becomes insignificant is not known. However, steatite contains several phases, magnetite and chlorite, that may contain sufficient K to allow a $^{40}Ar/^{39}Ar$ ratio to be analysed with the required precision. Secondly, the samples analysed in the initial feasibility study used spot fusion by laser to release the Ar. Step heating of the sample may release the excess Ar at a lower temperature than Ar derived from the in-situ decay of K. Thus by using a step-wise heating procedure separate measurements may be made of both the excess and radiogenic Ar. Recently, Ozdemir *et al* (1991) have determined the $^{40}Ar/^{39}Ar$ age from a single grain (400 µm) of magnetite from the alteration of mafic minerals to chlorite and magnetite. This suggests that obtaining age information from magnetites from steatite should be possible.

Figure 5.4 Argon ratio diagram from the analysis of sample zuc-4 demonstrating mixing between trapped presumably atmospheric component (air) and radiogenic component (^{36}Ar = 0). Intercept corresponds to model age of 1412 Ma. that is considerably older than the formation of the Unst ophiolite.

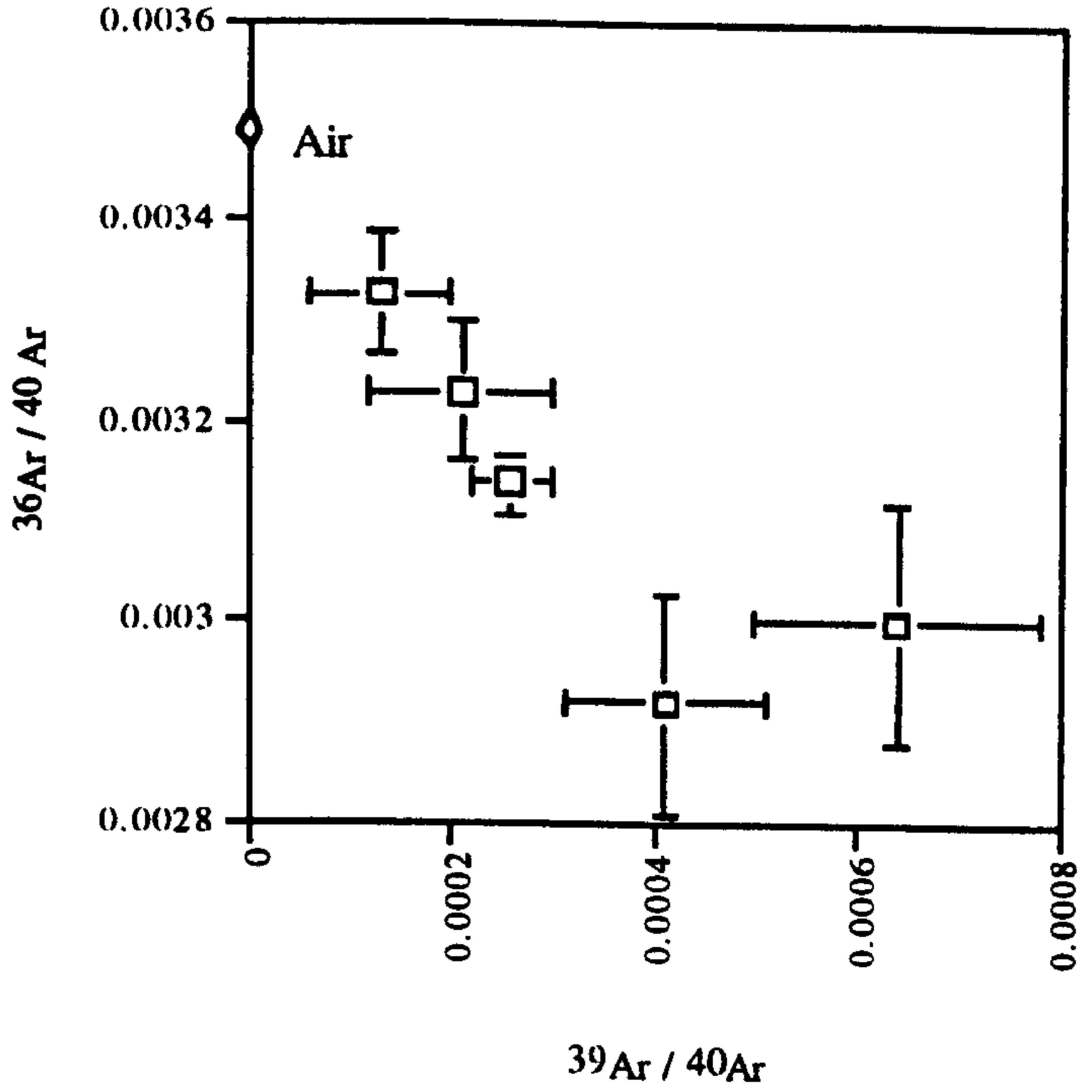
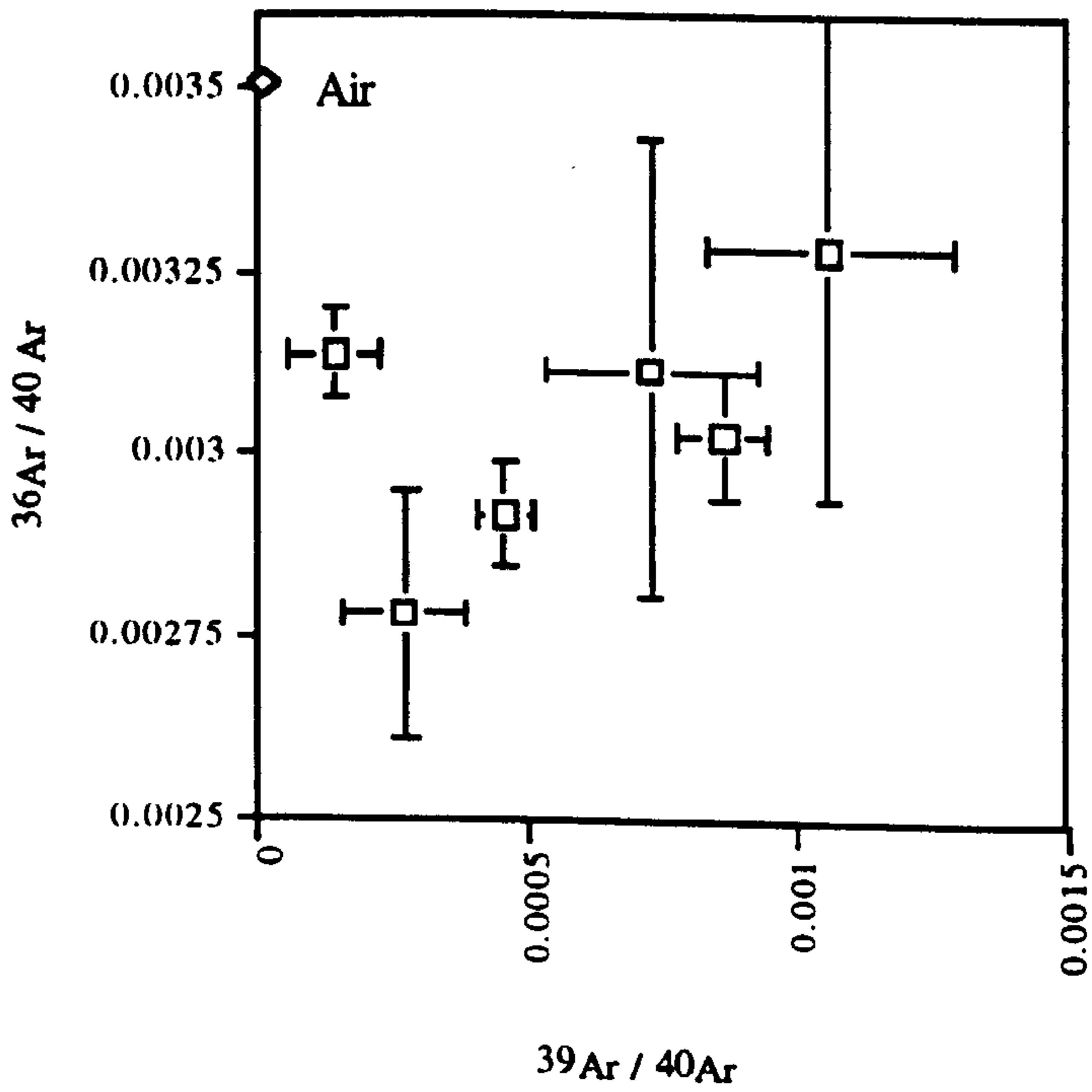


Figure 5.5 Argon ratio diagram from the analysis of sample zfd-4 demonstrating a three or greater component system. Clearly non-atmospheric argon is involved.



If by the analysis of magnetite or chlorite from steatite the problems of mixed ages and the high proportion of excess argon can be overcome, then steatite sources may be compared. If suitable precision can be obtained it is probable that the different geological provinces will display different Ar isotope dates thus enabling useful artifact comparison.

5.11.2 Lead Isotopes

Lead isotopes long have been utilised to characterise sources of metal used in prehistory (Goucher *et al* 1978, Gale 1989, Sayre *et al* 1992). However, the only lithic material that Pb isotopes have as yet been applied to is Egyptian galena (PbS) (Hassan & Hassan 1981).

Lead isotopic composition is a record of the chemical environment in which the Pb resides. Pb has four naturally ocurring isotopes ^{208}Pb, ^{207}Pb, ^{206}Pb and ^{204}Pb. The first three are decay products of U and Th, ^{238}U - ^{206}Pb (half-life $4.468X10^9$), ^{235}U - ^{207}Pb(half-life $0.7038X10^9$), ^{232}Th - ^{208}Pb(half-life $14.010X10^9$), whereas ^{204}Pb is non-radiogenic Different geological environments have different U/Pb and Th/Pb ratios that affect the isotopic composition of Pb. The U/Pb and Th/Pb ratios are changed by magmatic generation and fractionation, hydrothermal and metamorphic processes, and by weathering and other low-temperature processes. The isotopic composition of a particular sample of Pb may be modified both by the decay of U and Th, and by the mixing with Pb having different isotopic composition. Therefore as a result, isotopic composition of Pb displays complex patterns of variation that reflect their particular geological history.

Lead isotopes may provide a means of characterising steatite sources that will enable these sources to be differentiated. Thirlwall (1986) has shown that the Lewisian complex (amphibolites and granulites), Dalradian metasediments and the Carboniferous lavas have different Pb isotope compositions. If these differences are also apparent within steatite sources, sources from the different geological provinces may have Pb isotope composition that enables their separation.

An initial feasibility study was undertaken in order to assess whether Pb isotopes are useful for steatite source characterisation. The Pb ratios; $^{206}Pb/^{207}Pb$, $^{206}Pb/^{208}Pb$ and $^{207}Pb/^{208}Pb$ were analysed after pre-concentration by ICP-MS. The results are given in Table 5.4.

If these results are displayed graphically, figures 5.6-5.8, the different geological provinces can be compared. These graphs demonstrate that there are differences between the different geological provinces. The Lewisian samples have low Pb isotopic ratios, along with the Shetland basement samples, whereas the Unst ophiolite and Lizard samples have much higher

Table 5.4 Pb isotope ratios from British steatite sources.

Sample	Province	^{206}Pb/ ^{207}Pb	error (1σ)	^{206}Pb/ ^{208}Pb	error (1σ)	^{207}Pb/ ^{208}Pb	error (1σ)
eco-1	Lizard	1.155	0.008	0.476	0.004	0.410	0.003
zuc-2	Unst ophiolite	1.115	0.002	0.473	0.001	0.409	0.001
zfd-1	Unst ophiolite	1.187	0.016	0.485	0.005	0.410	0.005
zfc-2	Unst ophiolite	1.166	0.005	0.470	0.005	0.404	0.005
zfs-2	Unst ophiolite	1.157	0.036	0.466	0.007	0.410	0.012
zuq-1	Unst ophiolite	1.171	0.041	0.480	0.009	0.408	0.016
zub-1	Unst ophiolite	1.152	0.036	0.475	0.006	0.411	0.013
zuu-1	Unst ophiolite	1.141	0.025	0.469	0.004	0.412	0.008
zul-2	Dalradian	1.131	0.026	0.467	0.003	0.411	0.008
zmc-2	Dalradian	1.157	0.004	0.467	0.002	0.404	0.002
zmc-1	Dalradian	1.158	0.013	0.473	0.007	0.408	0.008
zmo-1	Dalradian	1.118	0.022	0.480	0.006	0.408	0.004
mps-2	Dalradian	1.191	0.016	0.482	0.001	0.407	0.004
msc-1	Dalradian	1.139	0.062	0.473	0.017	0.415	0.010
zmb-1	Basement	1.132	0.052	0.467	0.011	0.413	0.021
zmb-2	Basement	1.163	0.009	0.478	0.006	0.412	0.005
zmh-2	Basement	1.131	0.036	0.467	0.009	0.412	0.008
zmh-1	Basement	1.137	0.018	0.471	0.012	0.412	0.005
zmf-1	Basement	1.101	0.044	0.465	0.009	0.432	0.009
mge-1	Lewisian	1.123	0.036	0.458	0.021	0.404	0.021
mlo-1	Lewisian	1.152	0.051	0.478	0.018	0.413	0.009
heg-2	Lewisian	1.119	0.029	0.466	0.018	0.416	0.013

Figure 5.6 ^{206}Pb/^{207}Pb and ^{206}Pb/^{208}Pb compositions in steatite sources from a range of British geological provinces.

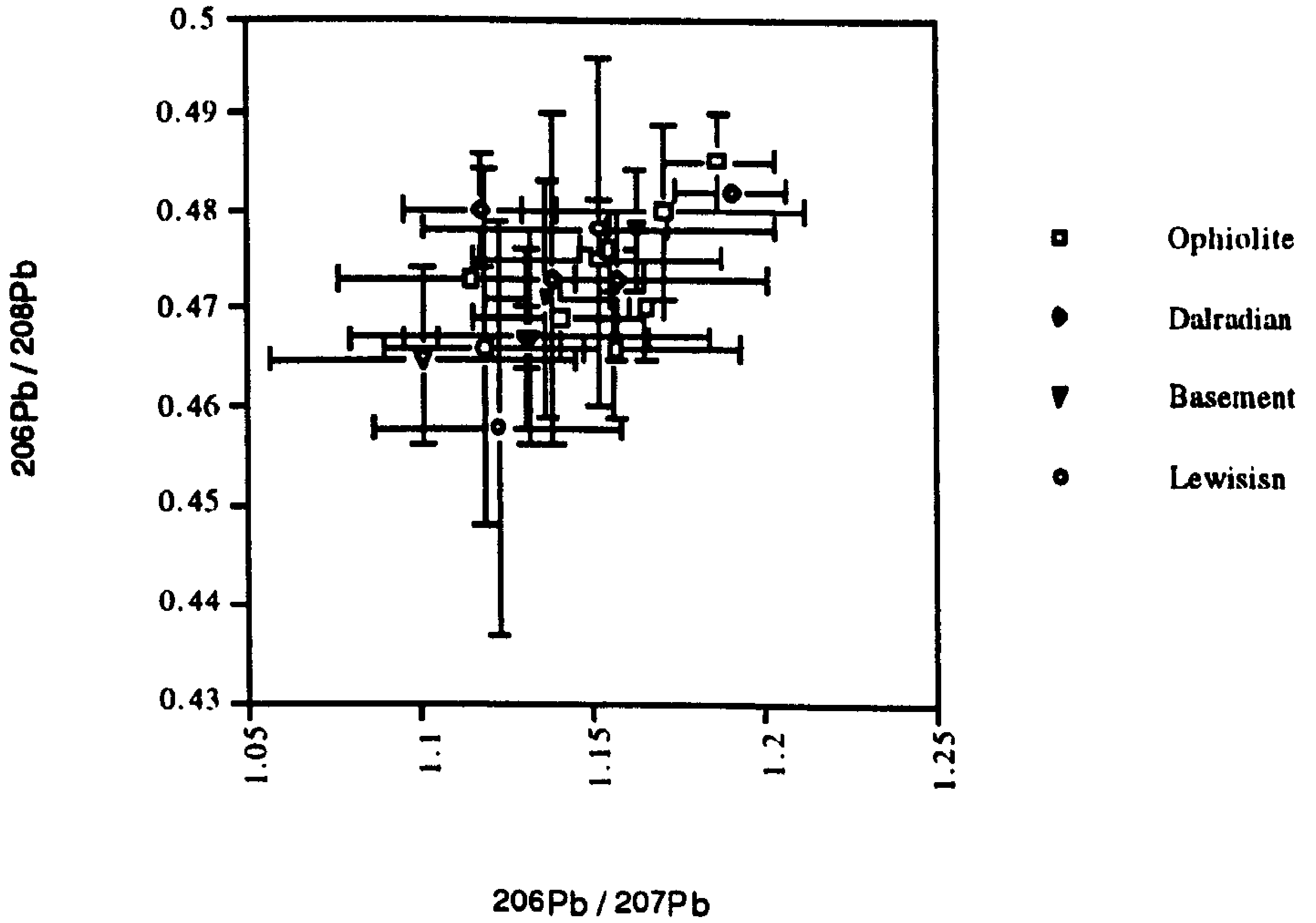


Figure 5.7 ^{206}Pb/^{207}Pb and ^{207}Pb/^{208}Pb compositions in steatite sources from a range of British geological provinces.

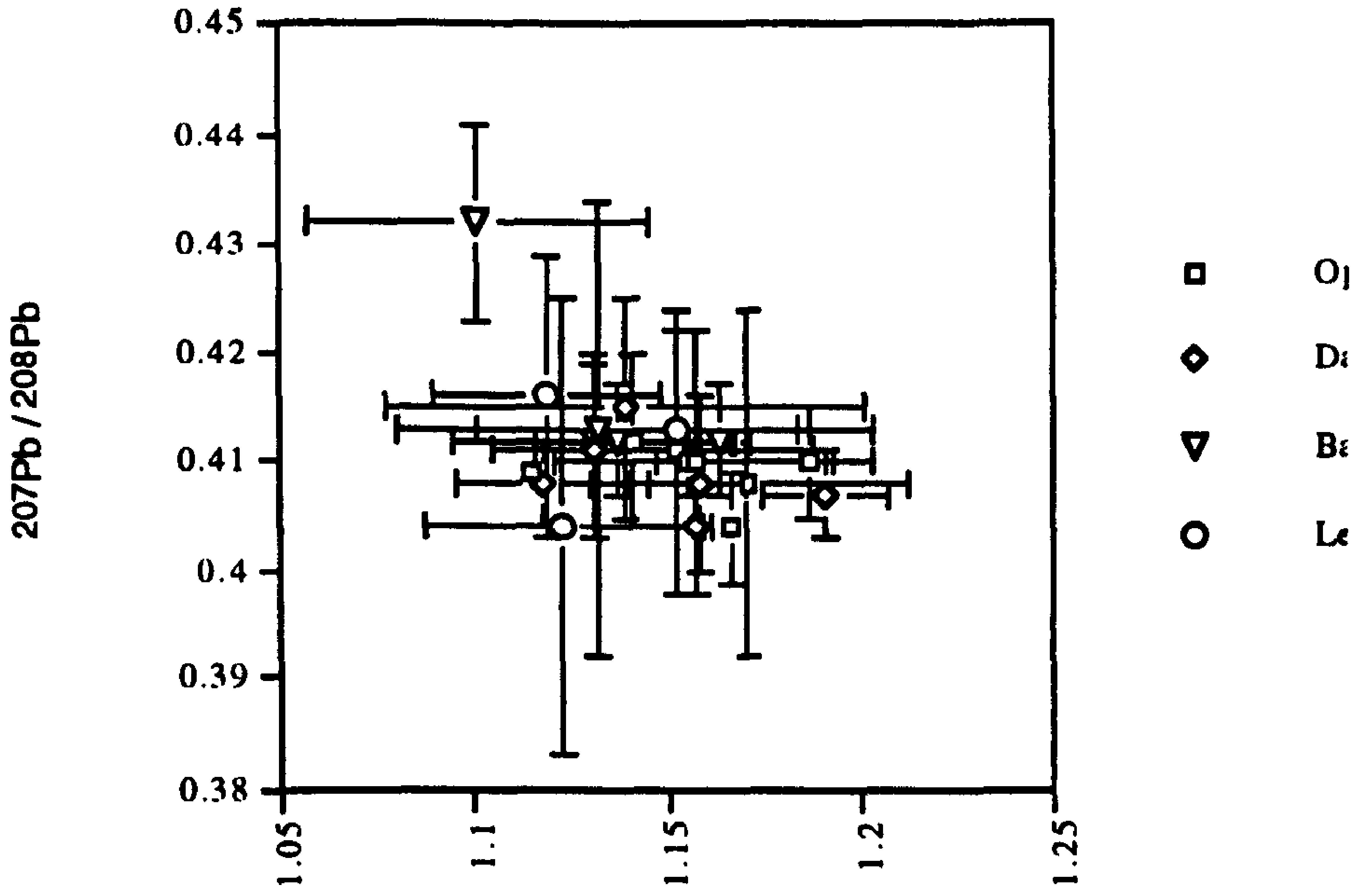
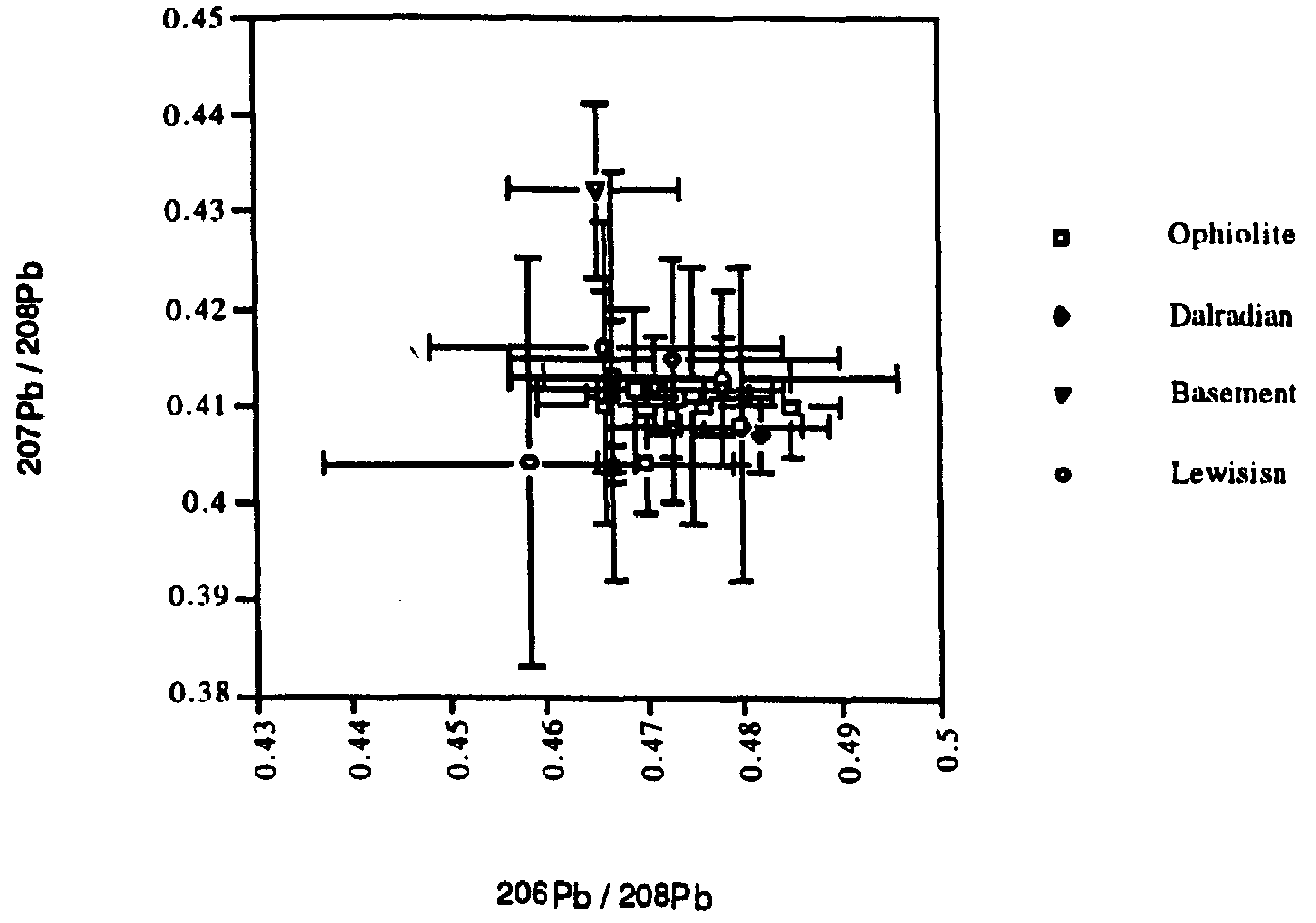


Figure 5.8 ^{206}Pb/^{208}Pb and ^{207}Pb/^{208}Pb compositions in steatite sources from a range of British geological provinces.



isotopic ratios. However the fields of these provinces overlap and the large errors probable cause the overlap limit the useful information that can be gained for such plots. Interpretation of these differences is difficult, with additional information, due to the complex relationship that reflects different U/Pb and Th/Pb ratios of the precursor ultrabasic rocks, these ratios after steatisation, and the Pb isotopic composition of the metasomatic fluid. With greater analytical precision the fields may be further resolved. Concentrations in the samples range from 100 ppb to 2 ppm and are generally in the order of 500 ppb. Greater precision, and precise and accurate measurement of ^{204}Pb, may be obtained from more modern ICP-MS or from thermal ionisation mass spectrometry. TIMS may obtain precision of 1-2% at these Pb concentrations. If the samples can be analysed with greater precision it may be possible to resolve the group structure in the Pb data.

5.11.3 Platinum Group Elements

The Principal Components Analysis in chapter 3 identified some of the platinum group elements (PGE - Ru, Rh, Pd, Os, Ir and Pt) as expressing a large proportion of the variance in the trace element data. The PGE are known to be fractionated by processes during ultrabasic rock formation, the initial melt having a characteristic positive chondrite normalised pattern whereas the residue a negative pattern. The different sources of steatite are known to have different types of precursor ultrabasic rock. Thus the PGE may display differences in the chondrite normalised patterns between different steatite sources, differences that may not be seen within individual sources. Most of the PGE are thought to be immobile at the P-T and fluid conditions of steatisation, except for Pd (and Au if this is determined with the PGE) (pers comm Macdonald). Determination may be made on either whole rock samples, which will probably reflect the pattern with the original olivine, or residual chromites. Chromites will probably retain most of the PGE in these samples, their individual analysis perhaps exhibiting differences between sources due to differences in precursor formation.

PGE are present in low concentrations in most in most rocks, < 25 ppb in most ultrabasics and are thought to be in the order of 1 - 10 ppb in most steatites. Therefore even with the low detection limits offered by ICP-MS, 0.4 - 0.05 ng ml^{-1} (Denoyer *et al* 1989) in order to enable analysis with sufficient precision, pre-concentration will be required. Jackson *et al* (1990) details both nickel sulphide fire-assay collection and tellurium co-precipitation methods. These pre-concentrations and analytical methods should enable PGE determination in steatite samples.

Analysis of steatite, either whole rock or individual phases, would confirm if differences in precursor formation are apparent as differences in chondrite normalised PGE pattern between different quarries. It seems probable that these patterns will remain unchanged within a single site. If results are favourable this technique, similar to REE characterisation, may prove to be extremely powerful as it may enable site specific provenance to be established.

5.11.4 Stable Isotopes

Stable isotope ratios have been utilised for source characterisation and source-artifact comparison for material important in prehistory (Herz 1987). The general homogeneous nature of all marbles, a problem also relevant to steatite provenancing, has resulted in marble being difficult to characterise by many other methods, such as hand specimens, petrology, and major and trace elements. However, Herz (1987, 1991) in a study of the principal marble sources of Classical Greece and Rome has demonstrated that in a number of cases source regions can be identified by $\delta^{13}C$ and $\delta^{18}O$ ratios, thus by artifact comparison the origin of some of these Classical marbles.

Oxygen and hydrogen isotope ratios may provide another means of discriminating between different steatite sources. Steatite is a product of the hydrothermal alteration of an ultramafic body. It is probable that a number of different types of metasomatic fluids are involved in this hydrothermal alteration. Antigorite serpentinisation and related alteration products may involve both meteoric and metamorphic fluids. Park (1983) has speculated that mantle derived fluid may also be involved in some steatisation processes. Since the δD and $\delta^{18}O$ of meteoric waters is a strong function of latitude these ratios may differ between steatite sources (Sheppard 1986). Clearly, the δD and $\delta^{18}O$ ratios of steatite will be dependent on the values of the fluid, that is a function of both type and location, and any mixing between fluids, so there is a strong probability that different sources will display significantly different ratios.

Because each phase has differing isotopic fractionation behaviour whole rock samples would probably result in a mixed value dependent on the relative proportions of individual mineral phases within a particular sample, in a similar manner to the Ar whole rock data. Single mineral values would therefore give the most consistent results. Within steatites there are a number of mineral phases that might be used for stable isotope analysis. Little is known about the behaviour of oxygen and hydrogen in talc, the major component of steatites. It may behave in a similar manner to other sheet silicates such as micas and exchange isotopes after formation (Graham 1981 Fortier & Giletti 1991), if there is a fluid for them to exchange with. The fine grained texture of many steatites would also increase the potential for post formation isotope exchange. Thus talc may give results that do not reflect the values produced by the initial fluids hence increasing the range of values from a source or source region and thereby decreasing the potential for source separation. However, there are number of mineral phases within steatites that are more robust. Chlorite and magnetite are relatively common within most steatite samples. These phases are less likely to exhibit any post formational exchange, Mathews *et al* (1983) demonstrated that oxygen isotope exchange between chlorite and water is relatively slow in chlorite> Graham *et al* (1986) showed similar findings for hydrogen.

The sparse data available on serpentinites from ophiolites (Ikin & Harmon 1983) indicate that they have interacted with fluid from several different sources during the time interval between oceanic crust formation and ophiolite emplacement and subsequent sub-aerial exposure (Highland Border Serpentinite gave an average value of for antigorite serpentinite δD -62 $\delta^{18}O$ +8 ‰).

Wenner & Taylor (1974) and Barnes *et al* (1978) analysed serpentinites and their related metasomatic alteration products, talc and "blackwall" minerals, from a range of ultramafics across the North American continent. They have shown that the δD of the lizardite and chrysotile serpentinites from all the ultrabasics exhibits a total range of -59 to -209 ‰, and most show a good correlation with geographical position and latitude of the sample locality. They show a progressive change in δD that parallels the present day variation in δD of meteoritic fluids across North America.

The $\delta^{18}O$ values of the lizardite and chrysolite range from +8.7 to -5.0 per mil and correlate more with the $\delta^{18}O$ values of the country rock than the latitude. These relationships combine with model estimates of the isotope composition of the fluid involved in such serpentinisation, suggesting that much of the lizardite-chrysolite serpentinites formed by fluids of meteoric-hydrothermal origin at relatively shallow levels in the earth's crust.

In contrast to the lizardite and chrysotile the pure antigorites have a more restricted range of δD (-39 to -66) and $\delta^{18}O$ values (+4.7 to +8.7). These values are similar to those of metamorphic chlorite, suggesting that the antigorites and other metasomatic products formed during regional metamorphism in the presence of non-meteoric fluids.

If these differences in δD and $\delta^{18}O$ values from serpentinites, an intermediate stage in the formation of steatite and its alteration products, can be seen in analysis of steatite samples from different quarries, and single quarry sites show little internal variation in values, then oxygen and hydrogen isotopes may prove be an important tool in provenancing steatite. Clearly, rock samples and analysis of talc will probably result in larger range of values,from a single source than may be obtained from a single phase such as chlorite and magnetite. Analysis of a range of steatite sources would confirm if differences in the stable isotope values may allow suitable source characterisation to enabling useful information to be obtained from artifact comparison.

5.12 Conclusion

This current work has demonstrated that isotope techniques and PGE have great potential for source characaterisation, if methodological difficulties can be overcome.

The study has shown that steatite sources in Britain have a wide range of strontium isotopic ratios. If significant differences could be established between steatites hosted within different tectonic regions then Sr isotopic techniques could be utilised for provenancing of artifacts. The results of this study have demonstrated that two of the major tectonic environments in which steatite is found, ophiolites hosted and Dalradian metasediments hosted steatites, have different $^{87}Sr/^{86}Sr$ isotopic ratios. However, steatites from Lewisian hosted sources display values that overlap with both of the ophiolite and Dalradian fields. Thus by the use of Sr isotopes the Dalradian hosted and ophiolite hosted sources may be separated from one another, while another technique is used to resolve the Lewisian source steatites.

Internal variation has been documented for a number of quarries, from the different tectonic environments. If the $^{87}Sr/^{86}Sr$ ratio intra-site was relatively small then site specific provenancing might be possible. However, intra-site results demonstrate that $^{87}Sr/^{86}Sr$ ratios vary by significant amounts which would obscure any differences between individual quarries.

Thus although steatite artifacts of unknown provenance may not be assigned using Sr isotopes to an individual quarry, strontium isotopes may prove useful in future provenancing programmes as they are able separate two of the major tectonic regions. The Dalradian and the ophiolite sources can be separated, and these two regions dominate the British steatite sources. In Shetland, the largest area of steatite production in Britain, these are the major tectonic regions of steatite production.

In the broader Northern Atlantic region steatite sources in Scandinavia also can be divided into ophiolitic and sources similar to the Dalradian surrounded by metasediments. Thus strontium isotopes may well become an important part of any multi-technique steatite provenancing programme.

The variations in the $^{87}Sr/^{86}Sr$ ratios between different tectonic environments have been explained in terms of the alteration of ultramafic rocks that typically have low Sr contents, thus their Sr isotopic composition is particularly susceptible to change during steatisation by the passage of a fluid with a different Sr isotopic signature. Furthermore, if the steatising fluids have derived much of their Sr from the host rocks that are likely to have a higher $^{87}Sr/^{86}Sr$ ratio then the resulting steatite will have a higher $^{87}Sr/^{86}Sr$ ratio. Conversely, if the surrounding rocks have a lower $^{87}Sr/^{86}Sr$ ratio then the steatite will have a low $^{87}Sr/^{86}Sr$ ratio.

Several intra-site analyses indicate that the steatisation process may result in uniform present day $^{87}Sr/^{86}Sr$ ratios across a body and in other cases a much more heterogeneous Sr isotopic composition in the initial steatite.

The results of an initial $^{40}Ar/^{39}Ar$ feasibility study have demonstrated that differences exist between separate geological provinces. However, large errors on these analyses make useful source characterisation difficult. These errors were probably a consequence of mixed ages from whole rock samples, and the high proportion of excess Ar often associated with metasomatic systems. These problems may be overcome in future studies by single phase analysis and step heating thus alleviating problem of non-radiogenic Ar.

The results of the Pb isotope study demonstrate that some differences exist between sources, however the different geological provinces apparently cannot be totally separated as poor analytical precision precludes their full appraisal. These differences may be further investigated, and extended to ^{204}Pb, with more precise analysis utilising new generation ICP-MS or TIMS.

PGE, δD and $\delta^{18}O$ have been suggested as possible effective methods of source characterisation. Future analysis may prove these techniques to be valuable provenancing methods,

Clearly, isotope techniques have much to contribute to steatite source characterisation. With further analysis these techniques may prove important elements in any characterisation study.

CHAPTER 6 : PROVENANCING OF IRON AGE SCOTTISH ARTIFACTS BY USING TRACE ELEMENTS AND RARE EARTH ELEMENTS

6.1 Introduction

Having demonstrated that muti-element analysis and statistical treatment are able to resolve the Lewisian sources with confidence and discriminate a high proportion of the other groups, and furthermore that REE patterns may enable a source specific provenance to be established, this chapter presents an initial archaeological demonstration of the application of geochemical approaches. The abilities of several approaches for distinguishing between British steatite sources were assessed. In chapter 3, 60 major and trace elements were evaluated as to their discriminating potential between the different source regions. Although not all the source groups could be totally separated from one another, the Lewisian sources could be resolved from all other groups. This could be demonstrated from the analysis of Sr, Nb, As, Ga and Ba, and from multivariate statistics, PCA and Discriminant Analysis of several groups of elements. This enabled a reasonable degree of confidence to be attached to the premise that these sources were different from all other sources. Further quantitative ICP-MS analysis of 16 trace elements, that previously displayed potential at discriminating between sources, in this chapter has consolidated the findings of the multi-elemental semi--quantitative work.

The pre-concentration and ICP-MS REE analysis results , in chapter 4, demonstrate that individual quarries display a characteristic chondrite normalised REE pattern and this may be utilised to distinguish between individual sources. However, due to similarities between the REE patterns from different quarries a unique provenance is not always possible. However, if trace elemental data is able to restrict the potential sources, REE can be utilised to enable a more precise provenance to be established.

In this chapter, results from 21 samples of artifact material of unknown origin were compared with the same British sources analysed in the previous chapters. Artifacts that are thought to come from pre-Viking contexts were mainly selected from the Scottish mainland , since the source characterisation conducted so far has only dealt with British sources. Thus it was hoped to exclude any material which may have originated from Scandinavian sources, that have not been characterised as yet. A small set of samples from Shetland was included for completeness, although in these cases the possibility of Scandinavian link could not be excluded at the outset. This comparison of concentration data from source and artifact samples, by the use of both univariate/bivariate and multivariate techniques and REE, enabled the probable provenance of the artifact samples to be established.

Successful provenancing of these artifacts may provide important evidence for cultural contacts, especially in the Iron Age, a period in Scotland when little is known about the contacts different peoples had.

In this chapter the artifacts and their contexts have been discussed, in order to establish the potential and limitation of provenance information. The sampling of artifacts and sources, and their analysis by ICP-MS has been commented upon. The following sections on the analysis of the data have been subdivided into i) univariate/bivariate, ii) multivariate analysis and iii) REE analysis. The trace element data from the sources has been analysed, both univariate and multivariate, in the light of the higher precision analysis, and has enabled the consolidation and enhancement of the classification that was established using multi-element semi-quantitative results. The REE classification was based on the classification devised in chapter 4. In each section, following a re-definement of the source classification, artifact samples have been compared to sources. The results from each section of this source-artifact comparison have been synthesised and the probable sources established, where possible. The archaeological implications of these probable provenances have then been discussed.

6.2 Artifact Material and their Contexts

Twenty one samples of artifact material were made available from the National Museum of Scotland's collection, table 6.1. Locations of all the sites from which artifact samples were analysed are shown in figure 6.1. These artifacts were the only objects that were available for sampling from the National Museums collection.

It was thought that the steatite artifacts from Britain, found within a context prior to the Viking invasion, have a higher probability of originating in Britain than later material, since evidence for contact, if any, with Scandinavia, from these periods is much more limited. During the Viking colonisation of much of northern Britain the settlers brought with them their preference for steatite and presumably at least in the initial stages of colonisation much of the steatite. From this point onwards Scandinavia must be considered as a possible source of steatite in Northern Britain. The artifacts sampled in this study from the Scottish mainland are all considered to be from pre-Viking contexts and therefore presumably of British origin. Prior to the arrival of the Vikings the use of steatite was limited, (see section 1.3.1). However, a marked cluster of artifacts can be observed around Glenelg, Lochalsh and southern Skye. This, it is proposed, probably reflects the utilisation of a local resource, the steatite sources in Glenelg. Many of the pre-Viking British artifacts are stone cups. About 60% of all stone cups found in Scotland are from steatite (Steer 1956). Most of these have been found north of the Clyde/Forth

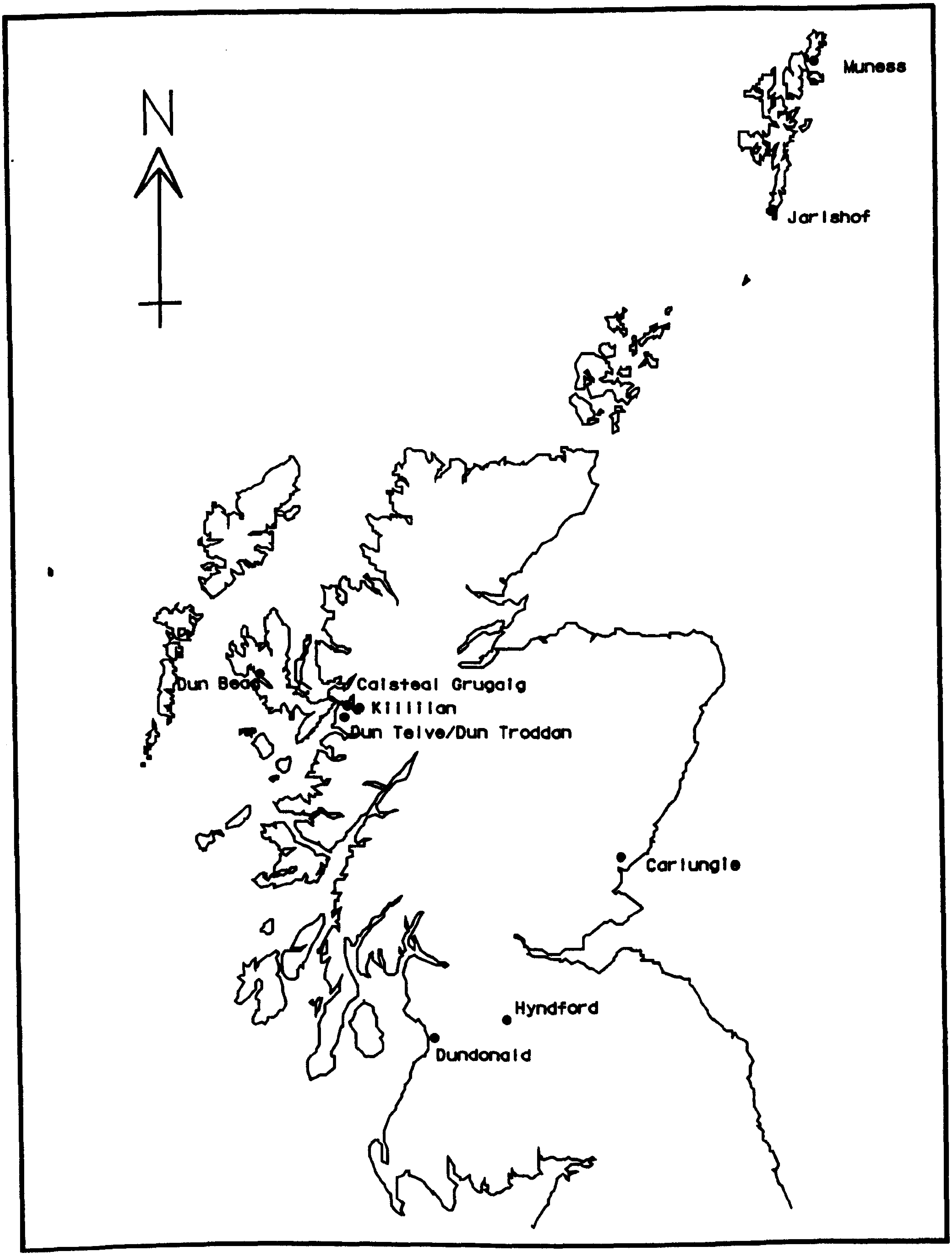


Figure 6.1 Map of the Scotland showing locations of archaeological sites from which artifacts were analysed.

isthmus. These artifacts provide direct evidence that handled stone cups were being fashioned in Scotland from the pre-Roman iron age until the 2^{nd} - 3^{rd} centuries AD. Childe (1935) suggested that these objects originated in the Bronze Age, however Steer (1956) observed that although the style and ornamentation are considered by some to be in the Bronze Age tradition there is no evidence of their association with Bronze Age sites, most having Iron Age contexts.

Table 6.1 Classification (National Museum of Scotland reference number), description and site localities of artifact sampled

Classified (NMS)	Object and physical description	Site location
GA 979	Small, handled cup	Dun Telve, Glenelg, Inverness-shire
GA 984	Whorl, lenticular, with incised line around	Dun Telve, Glenelg, Inverness-shire
GA 985	Whorls, discoid	Dun Telve, Glenelg, Inverness-shire
GA 986	Whorl	Dun Telve, Glenelg, Inverness-shire
GA 989	Vessel, bowl shaped / portion, with half round moulding below rim	Dun Telve, Glenelg, Inverness-shire
GA 1132	Whorl, globular	Dun Troddan, Glenelg, Inverness-shire
GA 1133	Whorl, round edge	Dun Troddan, Glenelg, Inverness-shire
GA 1134	Whorl, flat edge	Dun Troddan, Glenelg, Inverness-shire
GA 1136	Whorl, flat edge	Dun Troddan, Glenelg, Inverness-shire
AQ 14	Circular Cup, with handles	Killilan, Lochalsh, Ross & Cromarty
AQ 116	Cup-shaped, moulding notched to form short billets	Caisteal Grugaig, Lochalsh, Ross & Cromarty
GA 1047	Cup, with handle	Dun Beag, Struan, Skye, Inverness-shire
HD 1748	Lamp /cup portion, cup-shaped, burnt black except outside of base	Carlungie I, Angus
HTA 71	Lamp /cup fragment, with projecting square handles	Hyndford, Lanarkshire
AQ 114	Lamp / portion rectangular perforated handle	Dundonald, Ayrshire
BD 35	Pieces of an oval steatite vessel, base much worn	Muness, Unst, Shetland
HSA 672	Vessel / rim, rounded rim, slight bevel outside rim, chiselling slanting below, remains of vertical chiselling	Jarlshof, Sumburgh, Shetland
HSA 681	Vessel / bowl / fragment, blackened, square rim, straight everted walls	Jarlshof, Sumburgh, Shetland
HSA 688	Bowl / rim, rounded rim, fine slanting chisel marks inside	Jarlshof, Sumburgh, Shetland
HSA 722	Vessel / fragment, from round vessel	Jarlshof, Sumburgh, Shetland
HSA 726	Vessel / fragment	Jarlshof, Sumburgh, Shetland

Samples from brochs at Dun Troddan (Curle 1921) and Dun Telve (Curle 1916) in Glenelg, Dun Beag, Skye (Callander 1921) and Caisteal Grugaig, Lochalsh (Wallace 1897) are all considered to be part of the "iron age". All these sites were excavated in the later part of the last century or early this century and unfortunately these excavations did not record the context of the material to modern standards. Hence an "iron age" date in the broadest sense is not unreasonable for these artifacts. However, caution must be used in interpretation of results of artifacts from these sites as many brochs have extensive periods of use associated with them. Many were later re-used by Viking and later settlers, who may have introduced steatite onto the site.

Samples were also taken from steatite material from Hyndford crannog (Munro 1899); Carlungie, Angus (Wainwright 1963) and Dundonald, Ayrshire. The cup fragment from Hyndford was discovered during the excavation by Munro (1899) (cup illustrated Munro fig. 8). The Roman iron age dates suggested for these sites are based on the presence of Roman goods on the sites. Although the date of manufacture of the Roman goods is known quite closely, this may bear little relationship to the date when they were finally dumped as rubbish on the native sites, particularly as steatite would be a rare material and thus may have been treated with great care.

There is a major dating problem with the Scottish iron age since it is impossible to date artifacts typologically and only a few, more recent, excavations have produced ^{14}C dates (Hunter, F. pers. comm.).

The quantity of Roman material on Hyndford does suggest a date span including the Roman period (Curle 1932, Robertson 1970). A range from 0 - 400 AD. is probably a conservative estimate. However, there is no Antonine period (2nd century AD.) Samian ware on the site, although there is much 1st century material. Robertson (1970) argued that this indicates that the site was abandoned before the mid-2nd century AD.

The same range, 0 - 400 AD., is likely for Carlungie, but here there are only a few amphora sherds to provide dating, that could have survived for a long time before being broken. The site itself does have several structural phases, although the steatite cup was found in levels of the same phase as the Roman pottery, in the paving of a hut associated with the souterrain. A relatively recent review of souterrains was made by Barclay (1980).

Six samples of material from Shetland were included. It is extremely unlikely that these samples came from the Scottish mainland, and they are used to compare with the mainland material. Five samples of vessel fragments were from the Norse levels at Jarlshof. Steatite was the most common find in these levels. A single sample of a vessel fragment from Muness, Unst was also included. The manufacture of vessels was not common until the Viking period.

6.2.1 Sampling of Artifact and Source Material

Roughly 100 mg samples were obtained from artifacts using an tungsten carbide 3 mm bit intended for glass/ceramic drilling. A new bit was used and it was ultrasonically cleaned in acetone prior to use. A similar cleaning and brushing was carried out between each sampling. No detectable carry-over from one sample to the next or contamination from the bit itself has been found with the sampling technique (Wilthew pers. comm.). The surface drillings were discarded in all cases. HD 1748 seemed to have internal cracks that may have resulted in a very small contamination. HTA 71 had to be sampled at two points, on joining pieces, the two samples were then combined.

The twenty-one source samples are previously detailed and dissolution methods described in section 3.2.

6.3 ICP-MS analysis

Sample introduction used the aspiration of liquid nebulisation of aqueous samples, described by Jarvis *et al* (1992). The instrument operating conditions of the selected trace elements are the same as those used for multi-element analysis. The isotopes used for the determination of the trace elements are shown in Table 6.2. In general the most abundant isotope is used where it is free from isobaric overlap.

Table 6.2 Isotopes used in ICP-MS determination of trace elements

Element	Isotope	Abundance (%)
B	11	80.22
Ga	69	60.4
Ar	75	100
Rb	85	72.15
Sr	88	82.56
Y	89	100
Zr	90	51.45
Nb	93	100
Sb	121	57.25
Cs	133	100
Ba	137	11.32
La	139	99.91
Ce	140	88.48
Sm	152	26.27
Hf	178	27.14
Ta	181	99.98
Pb	208	52.3

6.3.1 Assessment of Accuracy and Precision

During the period of the analysis standard reference materials were analysed in order to characterise the precision within sample runs and during the period of the analysis. Analysis of standard reference materials analysed throughout the program is given in Appendix E. The precision over the period of the analysis was generally better than 7% RSD.

An assessment of the analytical accuracy may be made by comparison of the measured values with the compilation of Govindaraja (1989) Appendix E, although many of the trace element values reported have a great deal of uncertainty due largely to the relatively small data sets used in the compilation. However, the ICP-MS data compares favourably with the limited number of values reported by Govindaraja (1989). These results are in broad agreement with granitic standards of Jarvis (1990), although different dissolution techniques were used. However, as Jarvis (1990) observes there are potential problems with the analysis of certain *incompatible elements*, these may only be fully understood with the analysis of more standard reference material.

6.4 Results

The results of the analysis of artifact material and the source samples are in Appendix E.

6.5 Univariate and Bivariate Analysis

6.5.1 Source Data

In chapter 3 several differences were noted from both univariate and multivariate analysis between the Lewisian sources and all other British sources. The Lewisian sources showed characteristic high Nb, Ba, and low Sr. As concentrations, figure 6.4. These differences were also apparent from the higher precision source data. Clearly these elements may be used to provenance artifacts. Other elements were also noted in chapter 3, which although unable to fully resolve the group structure, showed promise at discriminating between sources. Therefore this higher precision data was assessed for any other differences and similarities between source regions.
The major points noted were:

Lewisian:	relatively high concentrations:	Ba, Nb, Ta, Pb
	relatively low concentrations:	As
Dalradian/ Cunningsburgh	relatively high concentrations:	Rb, Sr, Zr
	relatively low concentrations:	La, Ce, Sm, Hf
Basement	relatively high concentrations:	Zr, Pb
	relatively low concentrations:	Cs
Ophiolites	relatively high concentrations:	Zr
	relatively low concentrations:	Ba, Pb

The relatively high concentration of Nb and Ba in the Lewisian samples was also observed in the multi-element analysis. However, the more precise measurements have also revealed a number of other differences between the source tectonic regions. It is also clear that a number of other differences are apparent between the other tectonic regions although these are not as large as those observed between the Lewisian and the other regions. These differences may enable further resolution of the non-Lewisian sources than was achieved previously using discriminant analysis. A graphical representation of the data also allows groups to be identified and characterised. Figures 6.2 - 6.4 show that the Lewisian samples may be separated from the other tectonic groups using combination of Ba, Cs, Nb and Sr, the range of the Lewisian semi-quantitative results being shown as a shaded region as this region was considered to be the probable provenance of the artifacts. The area is defined as the range of results that were recorded from the results in chapter 3. The other tectonic regions are less easily separated using one or two variables.

Figure 6.2 Bivariate scatter-plot Cs vs. Ba of the four major tectonic source regions and the single quarry of Cunningsburgh, part of the Dalradian group, shaded area semi-quantitative Lewisian range.

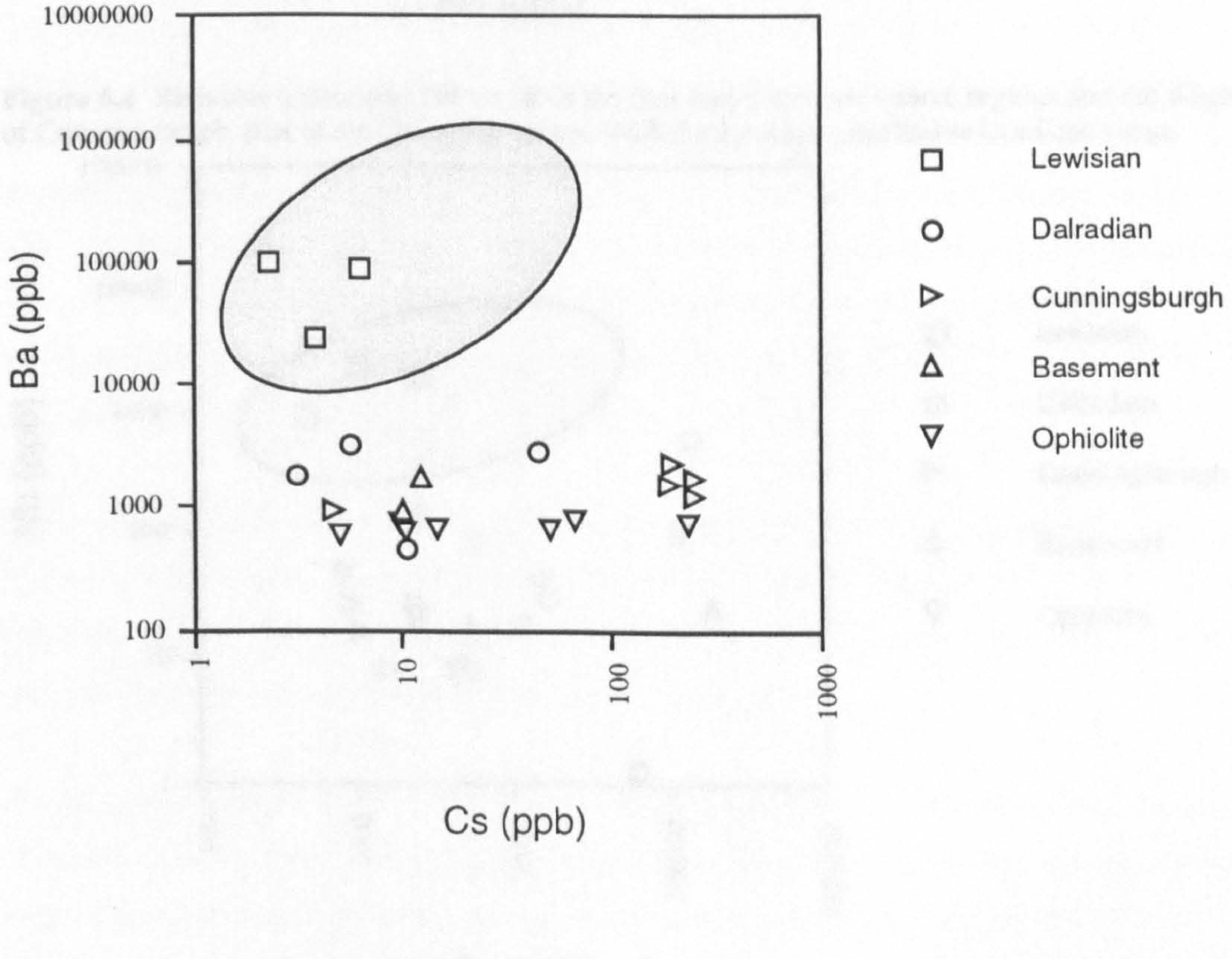


Figure 6.3 Bivariate scatter-plot Cs vs. Nb of the four major tectonic source regions and the single quarry of Cunningsburgh, part of the Dalradian group, shaded area semi-quantitative Lewisian range.

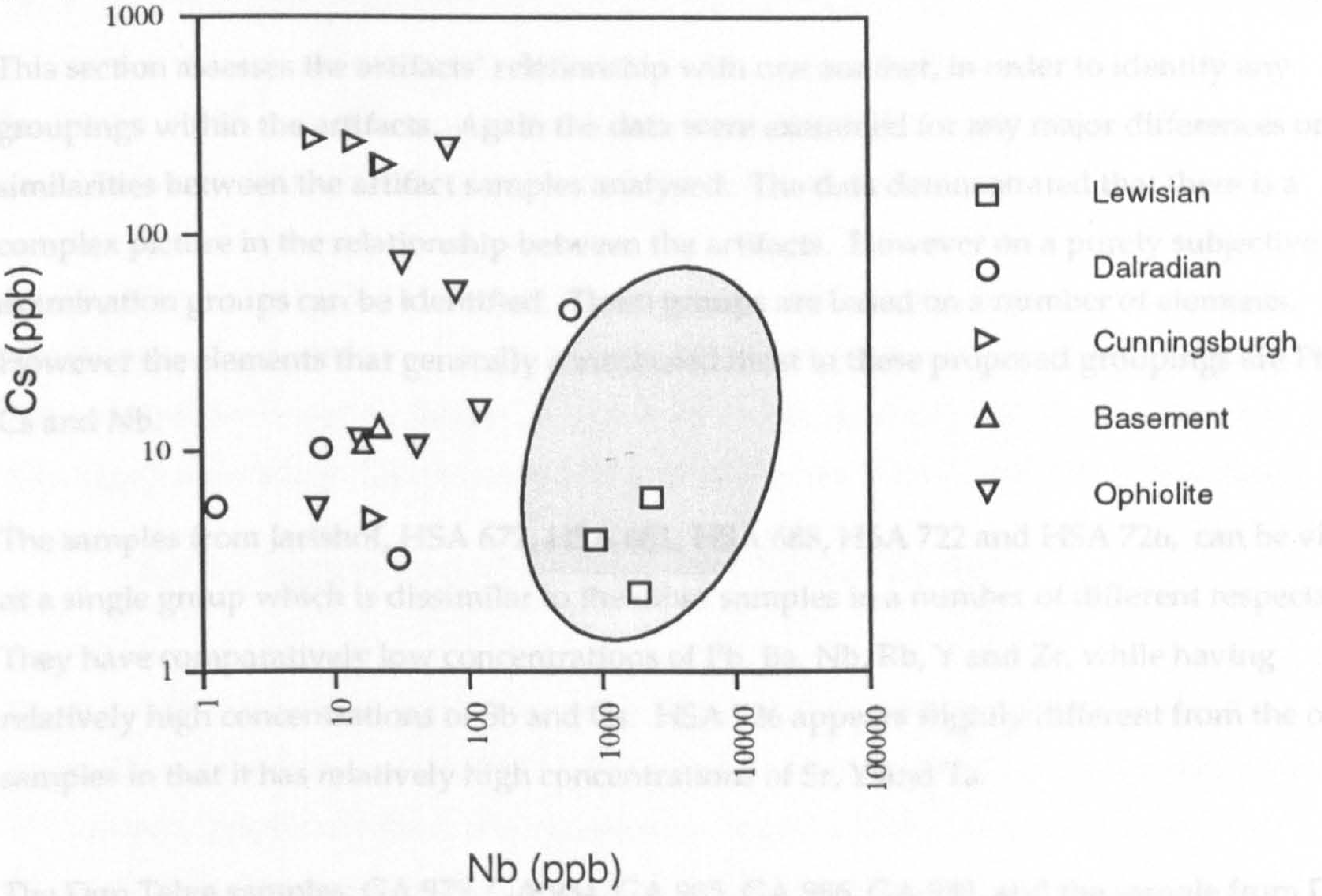
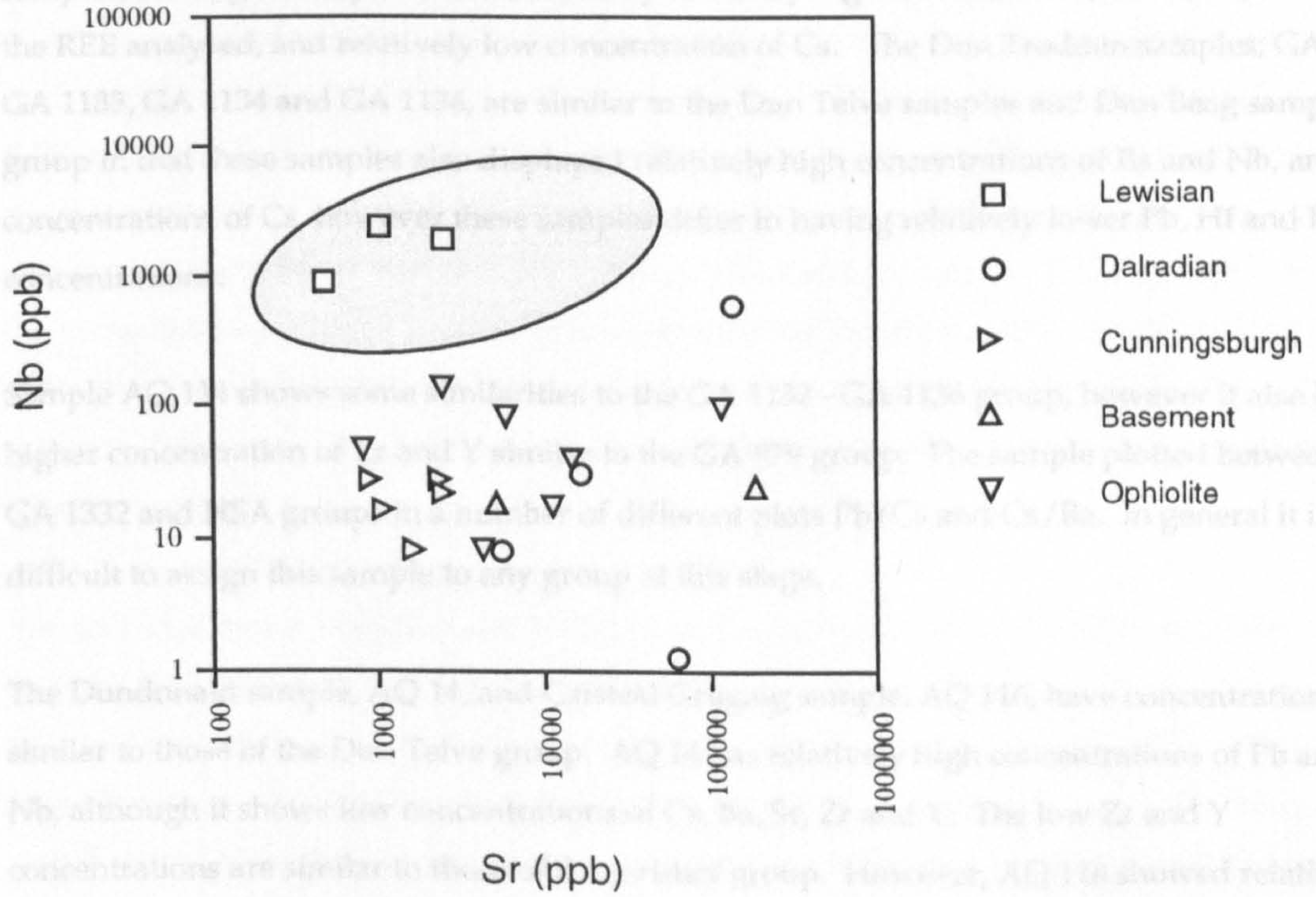


Figure 6.4 Bivariate scatter-plot Nb vs. Sr of the four major tectonic source regions and the single quarry of Cunningsburgh, part of the Dalradian group, shaded area semi-quantitative Lewisian range.



6.5.2 Artifact Data

This section assesses the artifacts' relationship with one another, in order to identify any groupings within the artifacts. Again the data were examined for any major differences or similarities between the artifact samples analysed. The data demonstrated that there is a complex picture in the relationship between the artifacts. However on a purely subjective examination groups can be identified. These groups are based on a number of elements. However the elements that generally contributed most to these proposed groupings are Pb, Ba, Cs and Nb.

The samples from Jarlshof, HSA 672, HSA 681, HSA 688, HSA 722 and HSA 726, can be viewed as a single group which is dissimilar to the other samples in a number of different respects. They have comparatively low concentrations of Pb, Ba, Nb, Rb, Y and Zr, while having relatively high concentrations of Sb and Cs. HSA 726 appears slightly different from the other samples in that it has relatively high concentrations of Sr, Y and Ta.

The Dun Telve samples; GA 979, GA 984, GA 985, GA 986, GA 989, and the sample from Dun Beag, GA 1047, form another group of samples. This group is less distinct than the HSA samples, although it may be characterised by relatively high concentrations of Ba, Pb, Nb and the REE analysed, and relatively low concentration of Cs. The Dun Trodden samples; GA 1132, GA 1133, GA 1134 and GA 1136, are similar to the Dun Telve samples and Dun Beag sample group in that these samples also displayed relatively high concentrations of Ba and Nb, and low concentrations of Cs, however these samples differ in having relatively lower Pb, Hf and REE concentrations.

Sample AQ 114 shows some similarities to the GA 1132 - GA 1136 group, however it also has higher concentration of Zr and Y similar to the GA 979 group. The sample plotted between the GA 1332 and HSA groups in a number of different plots Pb/Cs and Cs/Ba. In general it is difficult to assign this sample to any group at this stage.

The Dundonald sample, AQ 14, and Caisteal Grugaig sample, AQ 116, have concentrations similar to those of the Dun Telve group. AQ 14 has relatively high concentrations of Pb and Nb, although it shows low concentrations of Cs, Ba, Sr, Zr and Y. The low Zr and Y concentrations are similar to those of the Jarlshof group. However, AQ 116 showed relatively high concentrations of Pb, Ba, REE, and Y, which is very similar to the Dun Telve group.

The Hyndford sample, HTA 71, is probably the most similar to the Dun Telve group, with relatively high concentrations of Ba, Pb and the REE. However unlike the Dun Telve group HTA 71 has a much higher Nb concentration.

The sample from Carlungie, HD 1748, is also in some respects similar to the Dun Telve group. However it showed many characteristics that set it apart from the other samples; relatively high Ba, Nb, Sb, Sr, Rb and REE concentration, and especially high concentrations of Pb and Zr. On initial inspection this showed the greatest difference from the others.

The Mu Ness sample, BD 35 has trace element concentrations are similar to the Jarlshof group, relatively low concentration of Y, Zr, Nb and Hf, and high concentrations of Sb and Cs. However it differs from the Jarlshof group in that it has relatively high Pb and Ba concentration. Also BD 35 show a high Ga concentration only seen in the HTA 71 and HD 1748 samples.

6.5.3 Comparison of Artifact and Source Samples

The question of the provenance of the artifact samples has been initially tackled by the comparison of the source and artifact sample data in a simple bivariate scatter-plot. Figures 6.5 - 6.13 display graphically the artifact and source samples with respect to the good discriminating elements identified from the initial data analysis.

These plots demonstrated that in most cases the artifact material from Dun Telve, Dun Troddan and Dun Beag plotted within or close to the Lewisian fields, thus implying that the source of these artifacts occurs within the Lewisian tectonic region. The samples from Caisteal Grugaig, Killilan, Carlungie, Hyndford and Dundonald also displayed similar trends to the Lewisian sources, although in a number of cases the material plotted outwith the general Lewisian field and close to the fields of other tectonic regions. This perhaps indicates that a greater number of source samples are needed in order to fully characterise the source field. Alternatively it may reflect the complex relationship between the trace elements emphasised by this simple bivariate analysis. However, all these samples appeared to have most in common with the Lewisian sources.

The artifact samples from Shetland included for comparison with the Scottish mainland material revealed interesting trends. The Jarlshof material plotted outwith the Lewisian source field and appears to have most in common with the Dalradian/Cunningsburgh and Ophiolite tectonic regions. It is apparent that these samples are not of a Lewisian origin. The sample from Muness, Unst showed trends not seen in any source sample. In some cases it resembled the Lewisian samples while others showed Dalradian or Ophiolite trends. Thus the provenance of this sample is unclear at the present.

Figure 6.5 Bivariate scatter-plot Cs vs Ba of major tectonic regions (Lewisian semi-quantitative range shaded) and the single quarry site of Cunningsburgh (part of the Dalradian source) and artifact samples from Dun Telve (GA 979, GA 984, GA 985, GA 986, GA 989) Dun Beag (GA 1047) and Dun Troddan (GA 1132, GA 1133, GA 1134, GA 1136).

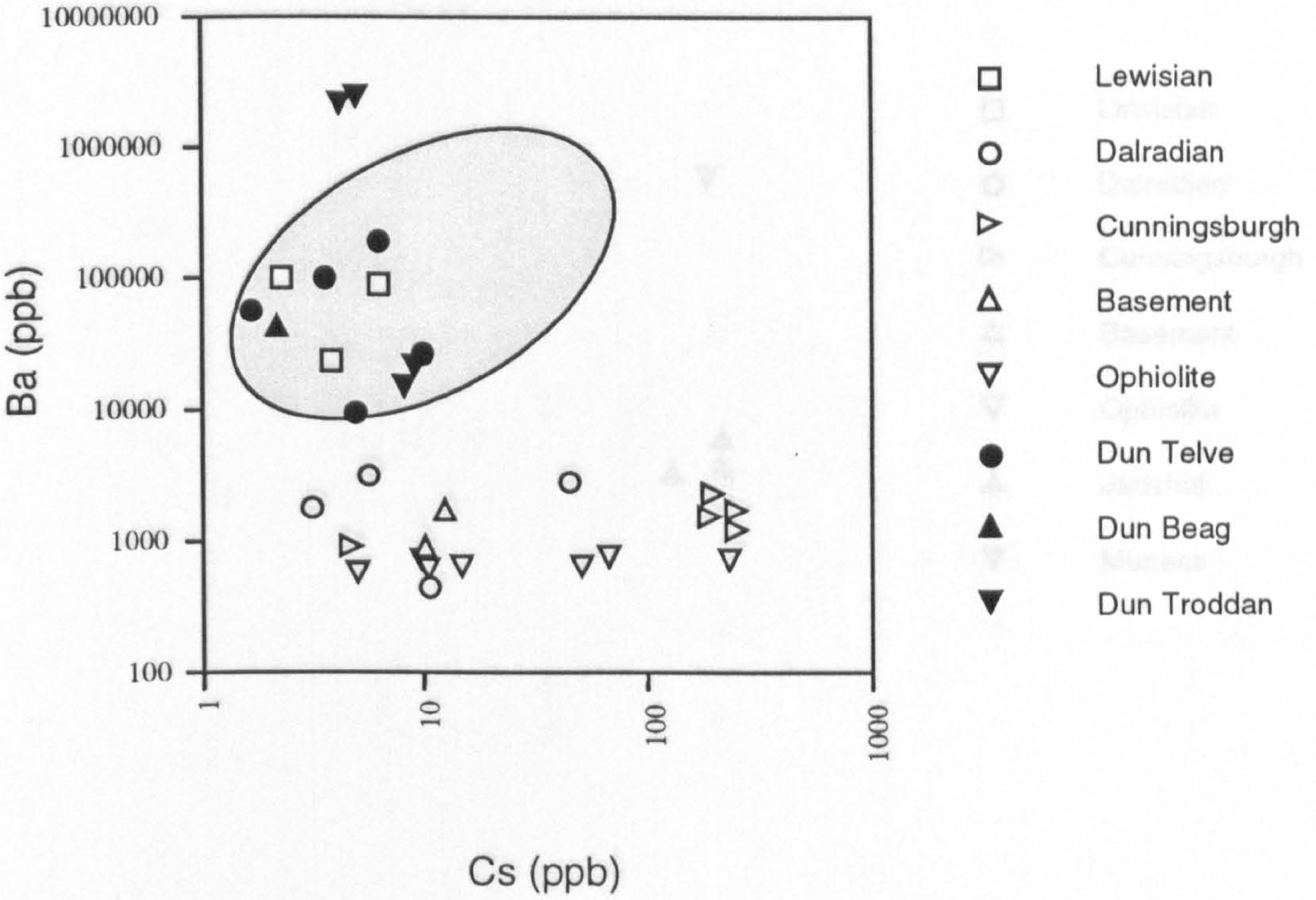


Figure 6.6 Bivariate scatter-plot Cs vs Ba of major tectonic regions (Lewisian semi-quantitative range shaded) and the single quarry site of Cunningsburgh (part of the Dalradian source) and artifact samples from Caisteal Grugaig, Lochalsh (AQ 116), Killilan, Lochalsh (AQ 14), Carlungie (HD 1748), Hyndford (HTA 71) and Dundonald (AQ 114).

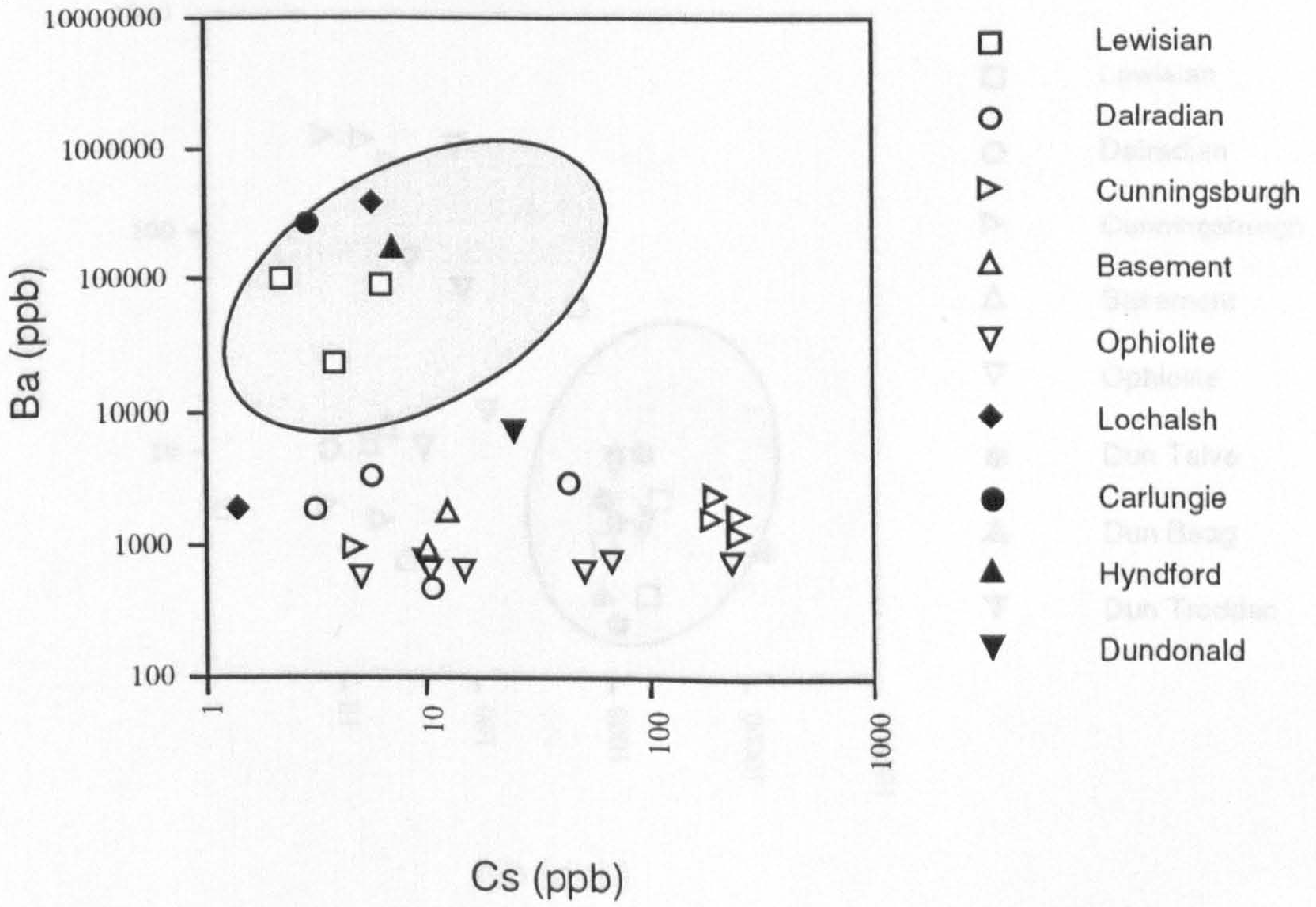


Figure 6.7 Bivariate scatter-plot Cs vs Ba of major tectonic regions (Lewisian semi-quantitative range shaded) and the single quarry site of Cunningsburgh (part of the Dalradian source) and artifact samples from Jarlshof, Shetland (HSA 672, HSA 681, HSA 688, HSA 722, HSA 726) and Muness, Unst, Shetland (BD 35).

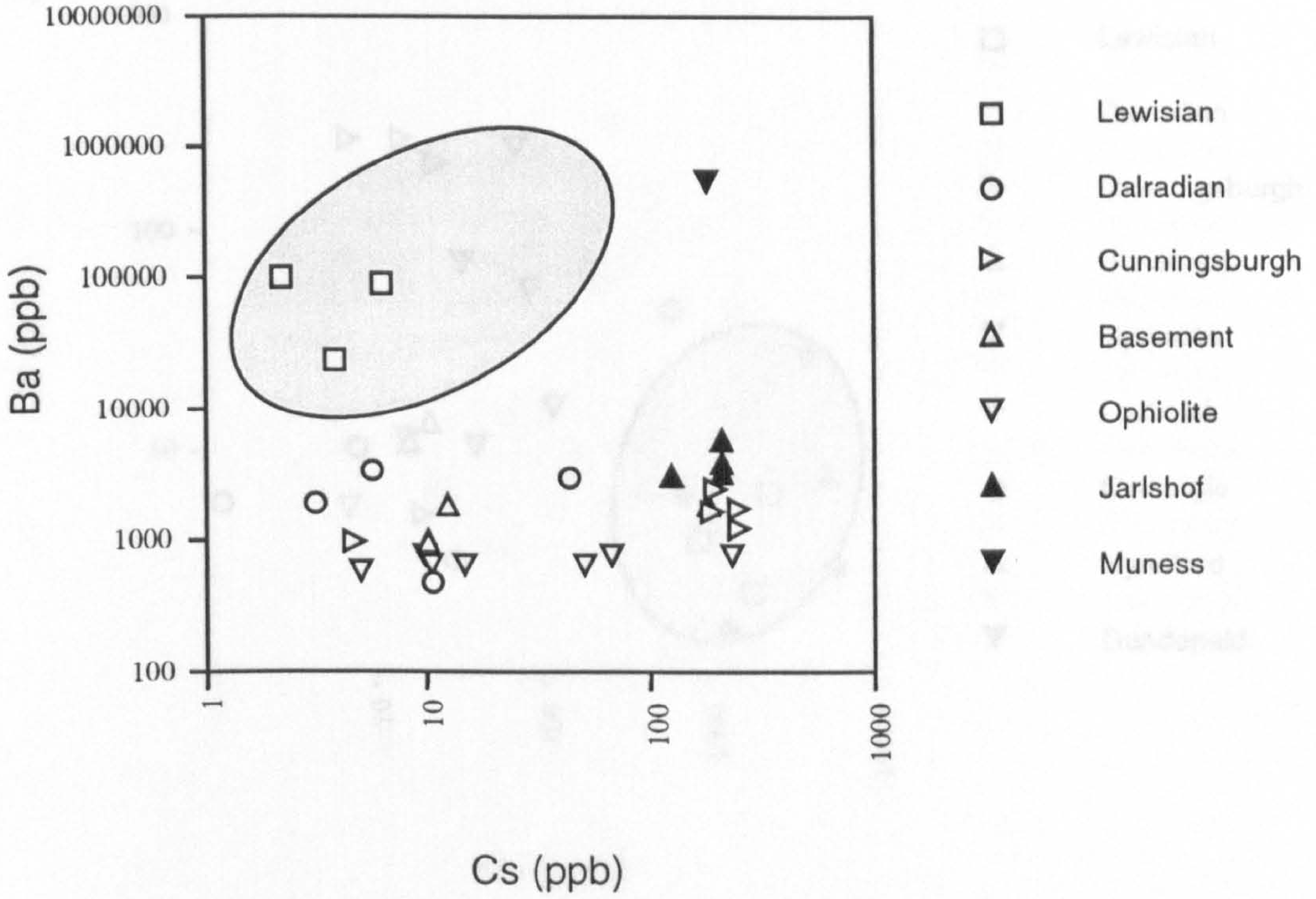


Figure 6.8 Bivariate scatter-plot Cs vs Nb of major tectonic regions (Lewisian semi-quantitative range shaded) and the single quarry site of Cunningsburgh (part of the Dalradian source) and artifact samples from Dun Telve (GA 979, GA 984, GA 985, GA 986, GA 989) Dun Beag (GA 1047) and Dun Troddan (GA 1132, GA 1133, GA 1134, GA 1136).

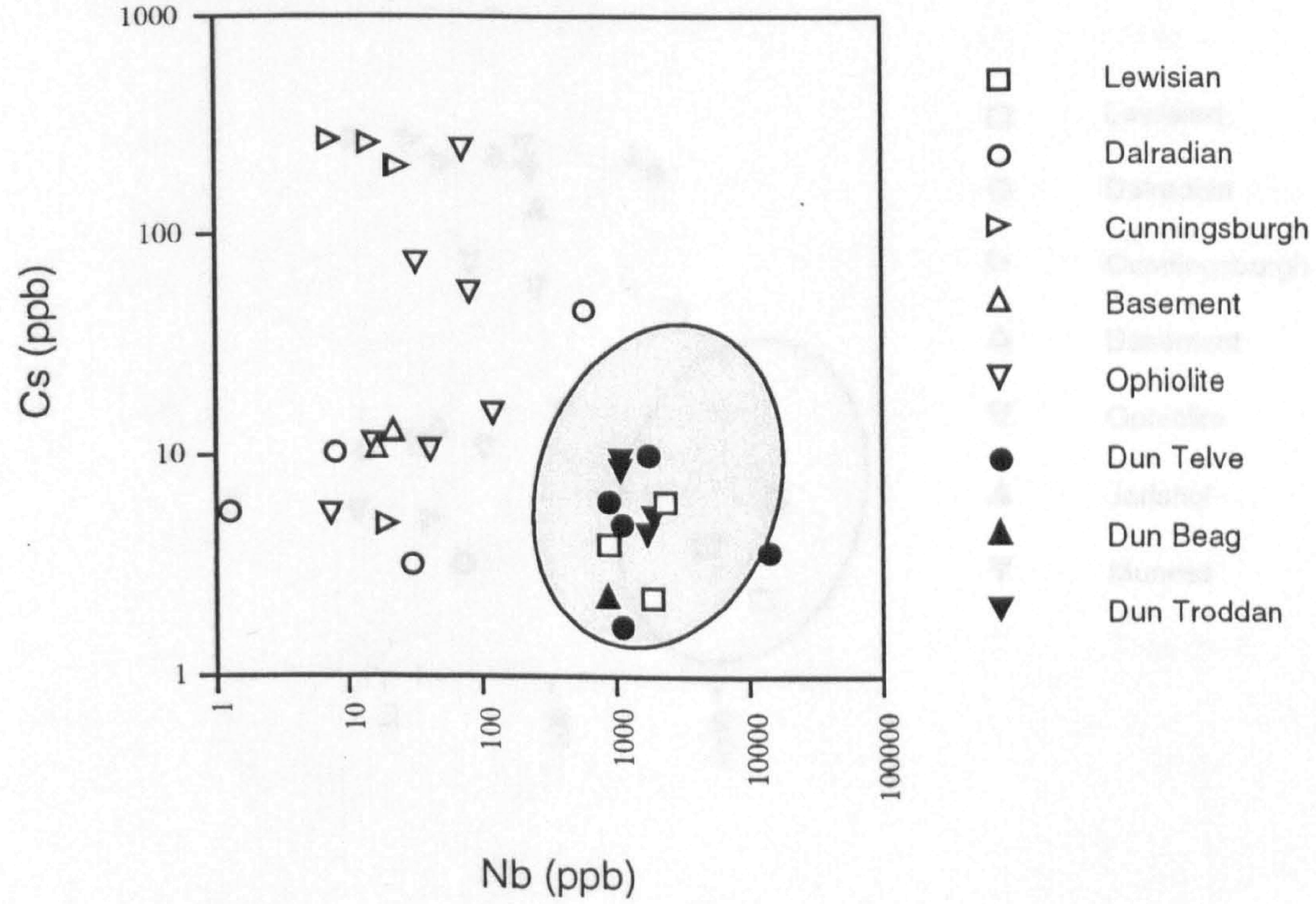


Figure 6.9 Bivariate scatter-plot Cs vs Nb of major tectonic regions (Lewisian semi-quantitative range shaded) and the single quarry site of Cunningsburgh (part of the Dalradian source) and artifact samples from Caisteal Grugaig, Lochalsh (AQ 116), Killilan, Lochalsh (AQ 14), Carlungie (HD 1748), Hyndford (HTA 71) and Dundonald (AQ 114).

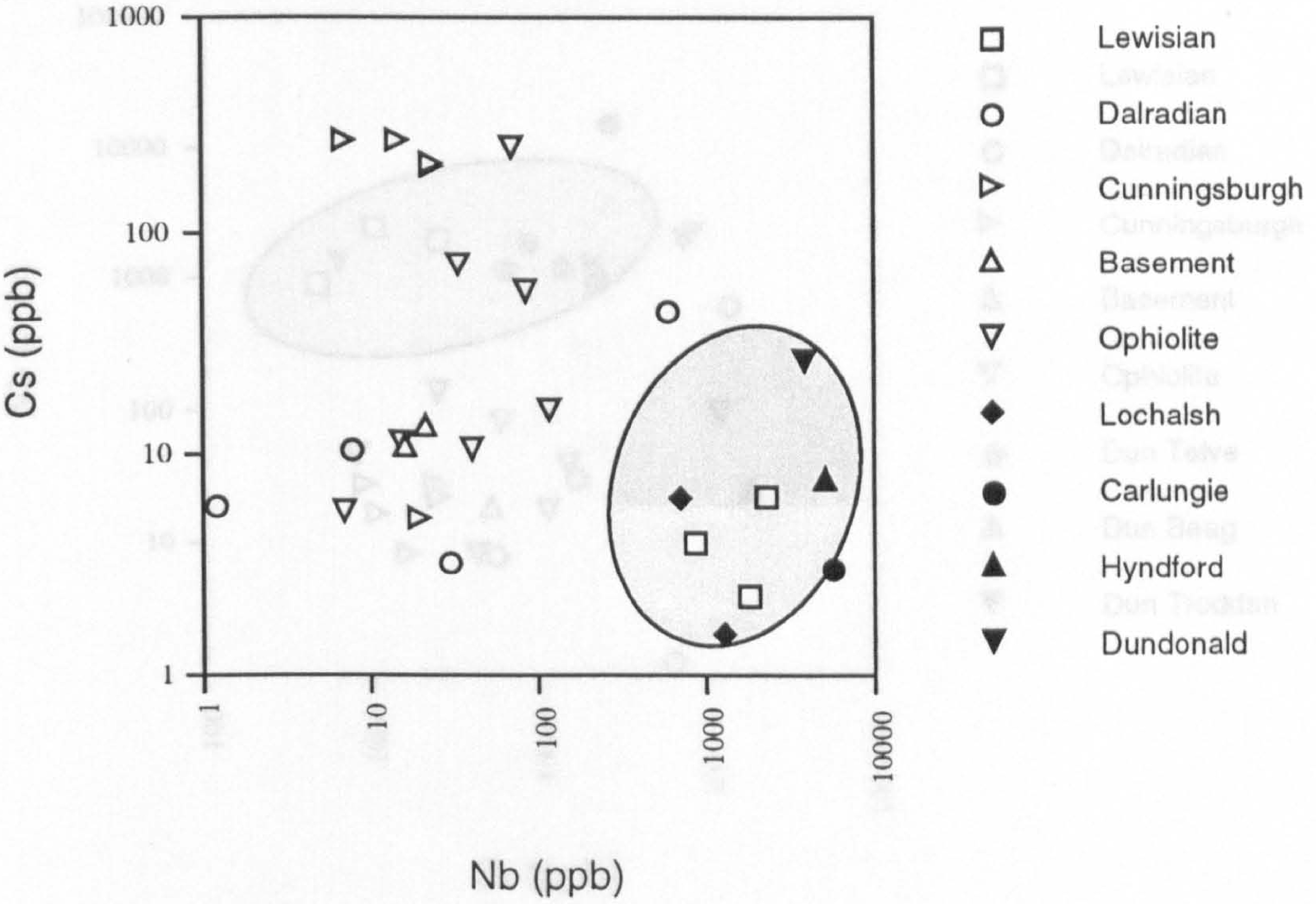


Figure 6.10 Bivariate scatter-plot Cs vs Nb of major tectonic regions (Lewisian semi-quantitative range shaded) and the single quarry site of Cunningsburgh (part of the Dalradian source) and artifact samples from Jarlshof, Shetland (HSA 672, HSA 681, HSA 688, HSA 722, HSA 726) and Muness, Unst, Shetland (BD 35).

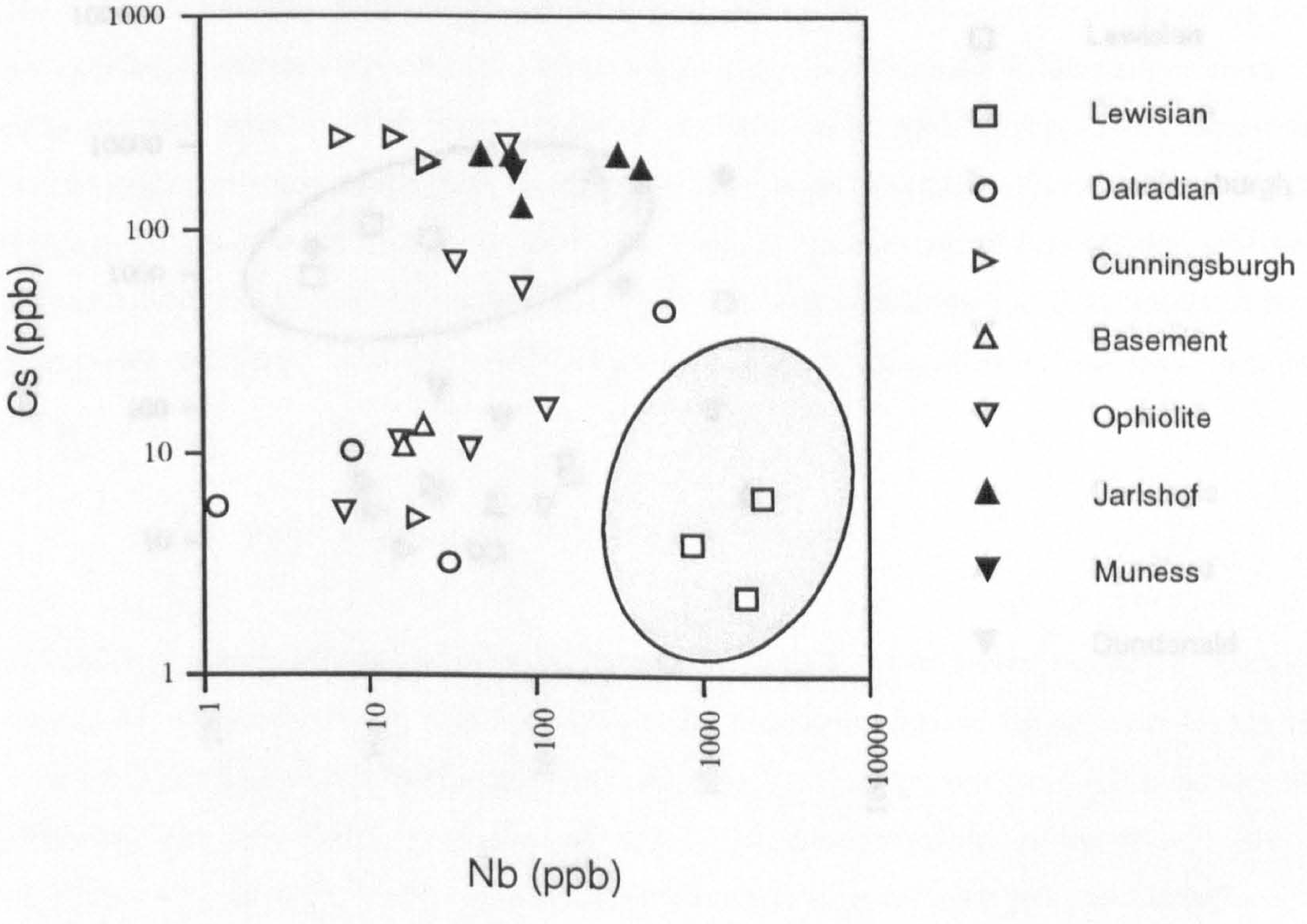


Figure 6.11 Bivariate scatter-plot Nb vs Sr of major tectonic regions (Lewisian semi-quantitative range shaded) and the single quarry site of Cunningsburgh (part of the Dalradian source) and artifact samples from Dun Telve (GA 979, GA 984, GA 985, GA 986, GA 989) Dun Beag (GA 1047) and Dun Troddan (GA 1132, GA 1133, GA 1134, GA 1136).

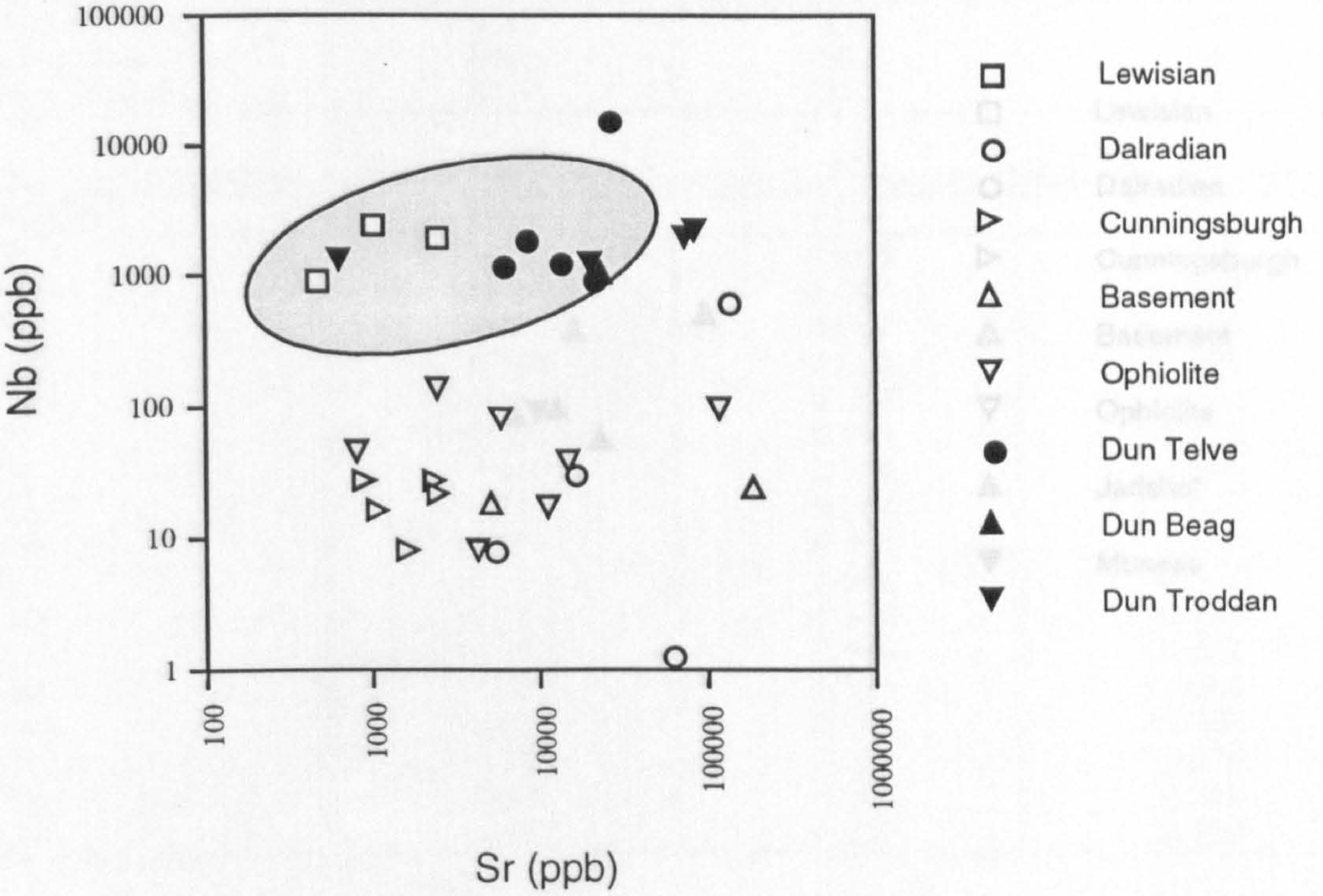


Figure 6.12 Bivariate scatter-plot Nb vs Sr of major tectonic regions (Lewisian semi-quantitative range shaded) and the single quarry site of Cunningsburgh (part of the Dalradian source) and artifact samples from Caisteal Grugaig, Lochalsh (AQ 116), Killilan, Lochalsh (AQ 14), Carlungie (HD 1748), Hyndford (HTA 71) and Dundonald (AQ 114).

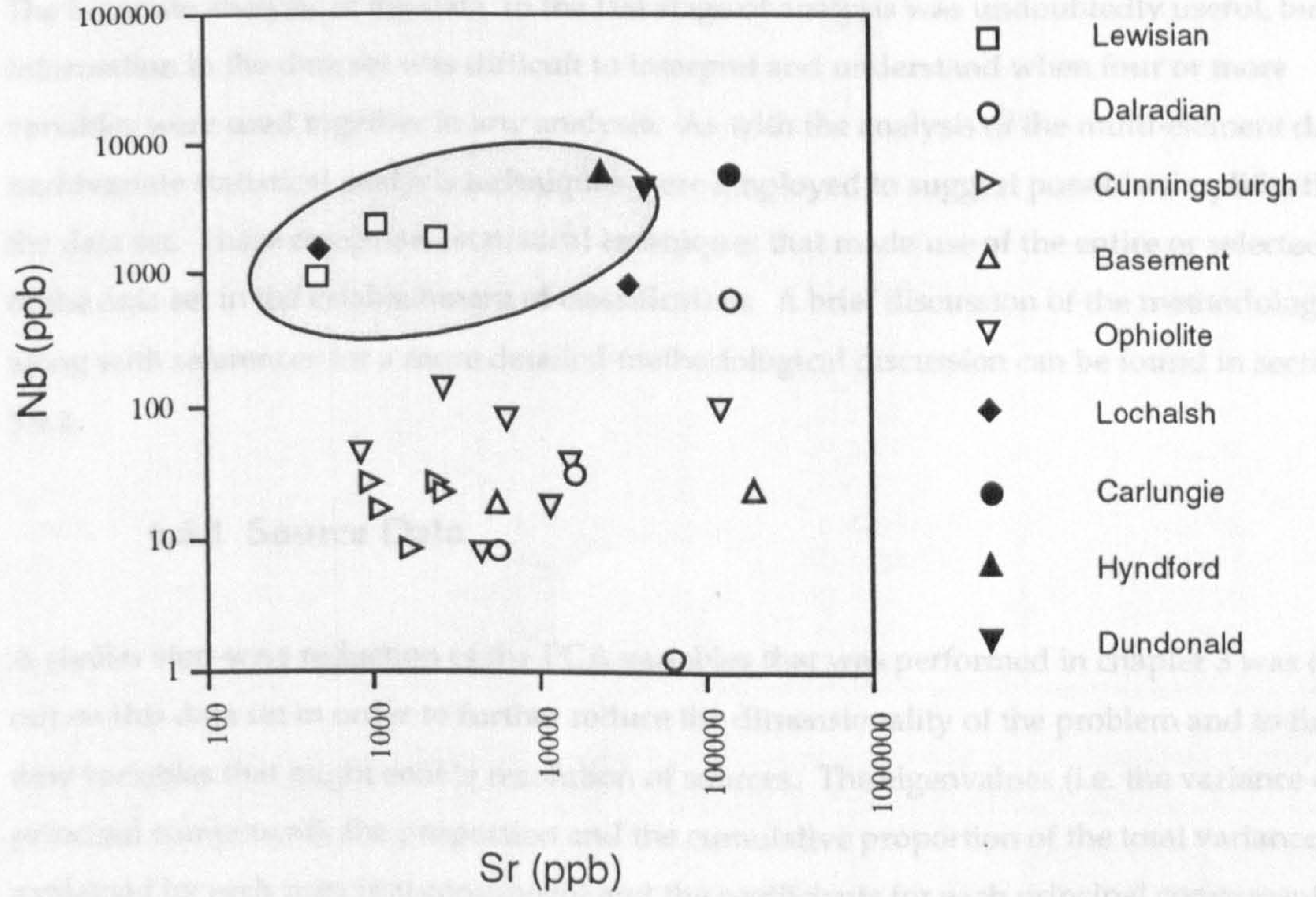
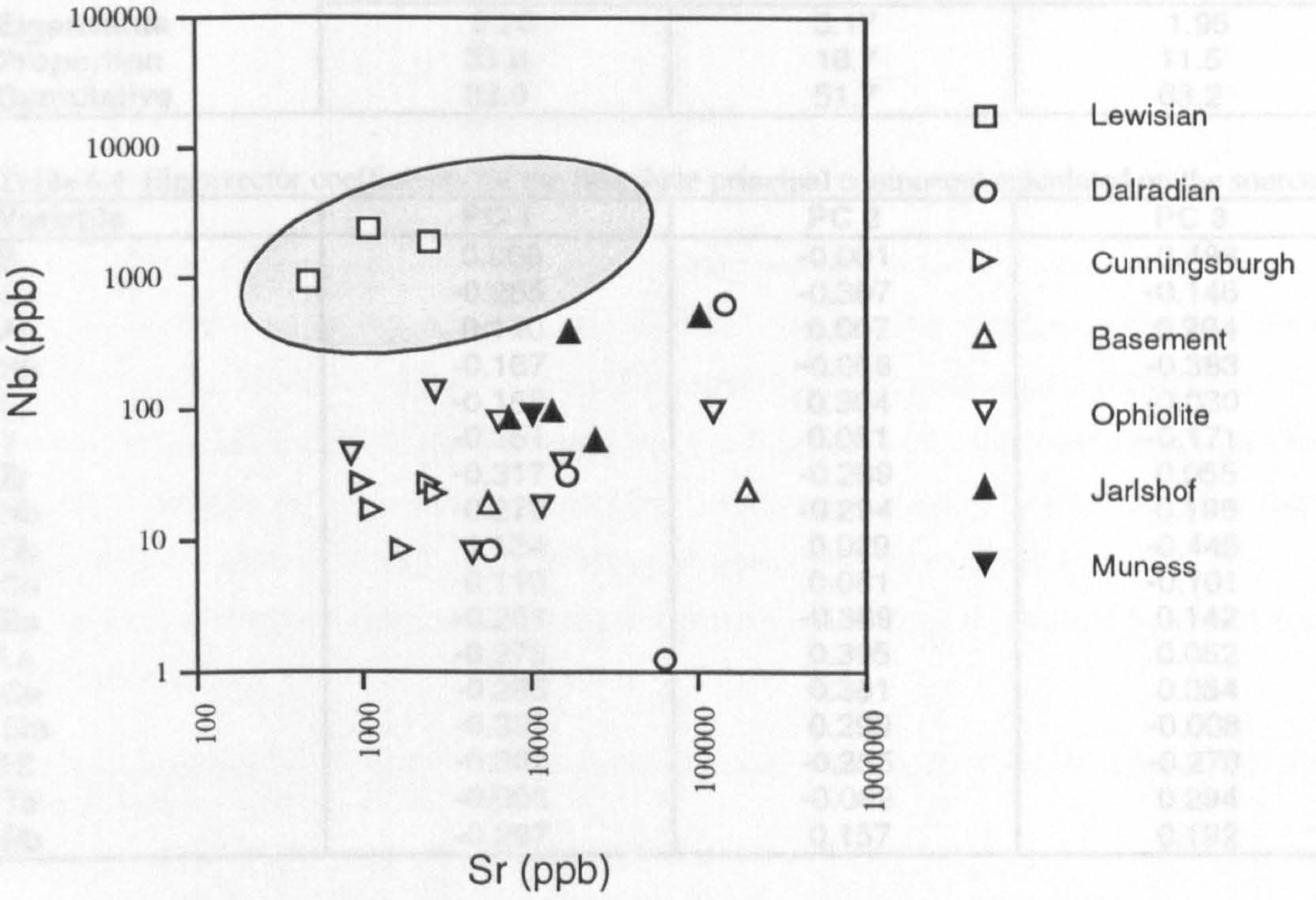


Figure 6.13 Bivariate scatter-plot Nb vs Sr of major tectonic regions (Lewisian semi-quantitative range shaded) and the single quarry site of Cunningsburgh (part of the Dalradian source) and artifact samples from Jarlshof, Shetland (HSA 672, HSA 681, HSA 688, HSA 722, HSA 726) and Muness, Unst, Shetland (BD 35).



6.6 Multivariate Analysis

The bivariate analysis of the data in the last stage of analysis was undoubtedly useful, but the information in the data set was difficult to interpret and understand when four or more variables were used together in any analysis. As with the analysis of the multi-element data multivariate statistical analysis techniques were employed to suggest possible simplification of the data set. These comprised statistical techniques that made use of the entire or selected parts of the data set in the establishment of classification. A brief discussion of the methodology along with references for a more detailed methodological discussion can be found in section 3.9.1.

6.6.1 Source Data

A similar step-wise reduction of the PCA variables that was performed in chapter 3 was carried out on this data set in order to further reduce the dimensionality of the problem and to find new variables that might enable resolution of sources. The eigenvalues (i.e. the variance of the principal component), the proportion and the cumulative proportion of the total variance explained by each principal component and the coefficients for each principal component for each stage in the analysis are given in tables 6.3-6.12.

Table 6.3 The eigenvalues, proportion and the cumulative proportion of the total variance explained by the first three principal component calculated on the source data.

	Eigenvector		
	1	2	3
Eigenvalue	5.26	3.17	1.95
Proportion	33.0	18.7	11.5
Cumulative	33.0	51.7	63.2

Table 6.4 Eigenvector coefficients for the first three principal component calculated on the source data.

Variable	PC 1	PC 2	PC 3
B	0.068	-0.001	-0.488
Ga	-0.265	-0.307	-0.146
As	0.140	0.007	0.294
Rb	-0.167	-0.058	-0.383
Sr	-0.168	0.304	-0.030
Y	-0.351	0.091	-0.171
Zr	-0.317	-0.289	0.055
Nb	-0.279	-0.294	0.196
Sb	0.124	0.029	-0.445
Cs	0.110	0.081	-0.101
Ba	-0.261	-0.389	0.142
La	-0.275	0.395	0.052
Ce	-0.285	0.381	0.054
Sm	-0.339	0.299	-0.008
Hf	-0.302	-0.255	-0.278
Ta	-0.006	-0.089	0.294
Pb	-0.297	0.157	0.192

Table 6.5 The eigenvalues, proportion and the cumulative proportion of the total variance explained by the first three principal component calculated on selected variable (As, Rb, Sr, Zr, Nb, Cs, Ba, La, Ce, Ta, Pb) using the source data.

	Eigenvector		
	1	2	3
Eigenvalue	3.46	2.48	1.54
Proportion	31.5	22.5	14.1
Cumulative	31.5	54.1	68.2

Table 6.6 Eigenvector coefficients for the first three principal component calculated on selected variable (As, Rb, Sr, Zr, Nb, Cs, Ba, La, Ce, Ta, Pb).

Variable	PC 1	PC 2	PC 3
As	0.178	0.032	0.630
Rb	-0.127	0.024	-0.441
Sr	-0.216	-0.381	-0.015
Zr	-0.398	0.310	-0.003
Nb	-0.397	0.376	0.029
Cs	0.140	-0.077	-0.335
Ba	-0.355	0.462	-0.018
La	-0.359	-0.429	0.135
Ce	-0.371	-0.414	0.139
Ta	-0.026	0.148	0.508
Pb	-0.420	-0.140	0.018

Table 6.7 The eigenvalues, proportion and the cumulative proportion of the total variance explained by the first three principal component calculated on selected variables (As, Nb, Cs, Ba, Pb).

	Eigenvector		
	1	2	3
Eigenvalue	2.37	1.22	0.77
Proportion	47.4	24.5	15.3
Cumulative	47.4	71.9	87.9

Table 6.8 Eigenvector coefficients for the first three principal component calculated on selected variables (As, Nb, Cs, Ba, Pb).

Variable	PC 1	PC 2	PC 3
As	0.213	0.594	0.771
Nb	-0.627	0.112	0.134
Cs	0.195	-0.677	0.515
Ba	-0.601	0.140	0.073
Pb	-0.404	-0.395	0.340

The first three PC scores were plotted against one another for the final analysis, Figures 6.14 - 6.16. These plots showed that the geological groups show some structure, especially the ability of PC 1 to separate the Lewisian sources. The ophiolite sources showed a wide spread of plotting positions and the Dalradian sample, zmo-1 plotted away from the other Dalradian sources. Thus by utilising these elements the Lewisian source may be discriminated from all other sources. Unfortunately no other source region could be resolved from the other. However, the Lewisian sources are probably the most important in terms of production on the Scottish mainland.

Figure 6.14 Principal component score plot of steatite sources using PC 1 and PC 2 from PCA using selected variable (As, Nb, Cs, Ba, Pb).

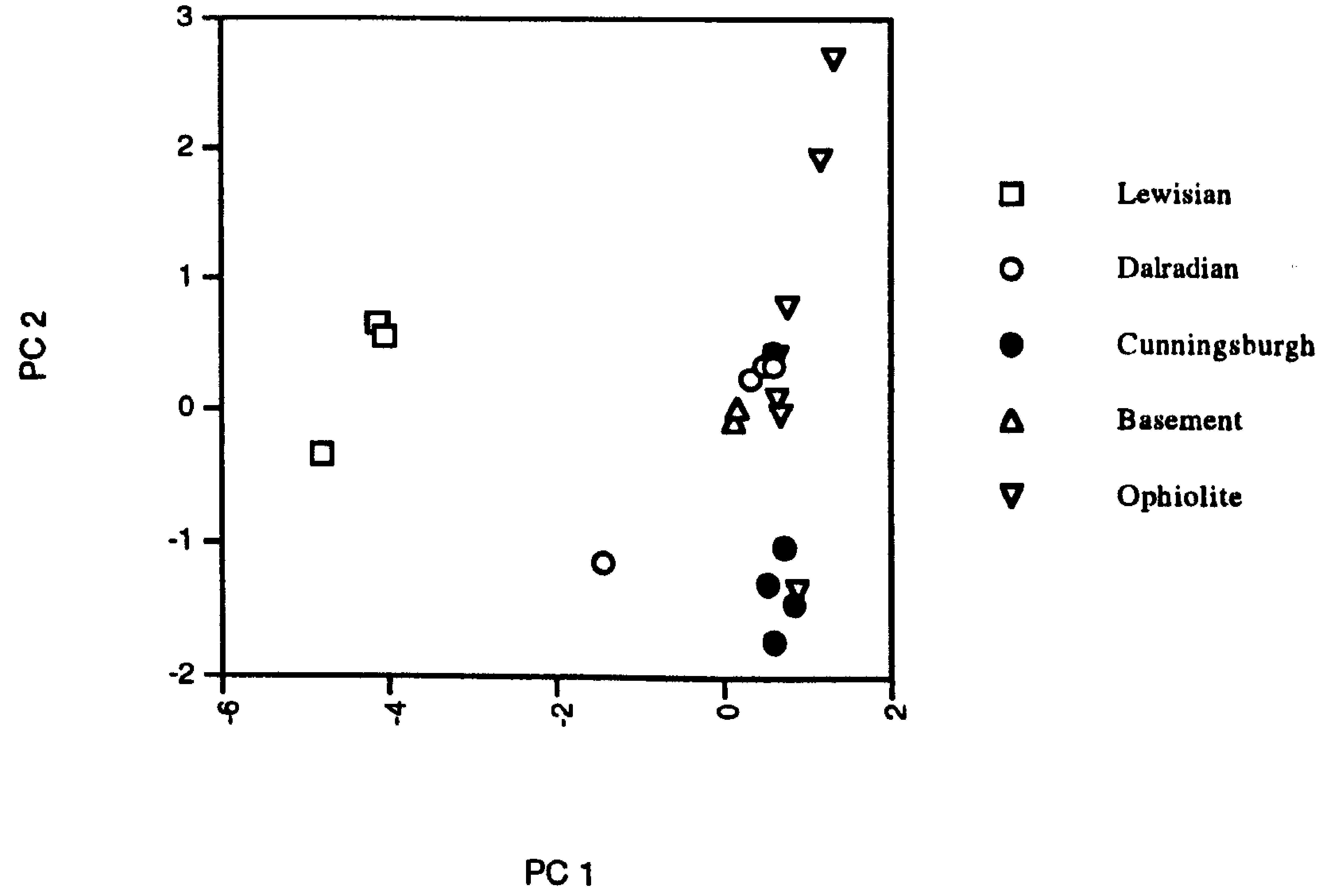


Figure 6.15 Principal component score plot of steatite sources using PC 1 and PC 3 from PCA using selected variable (As, Nb, Cs, Ba, Pb).

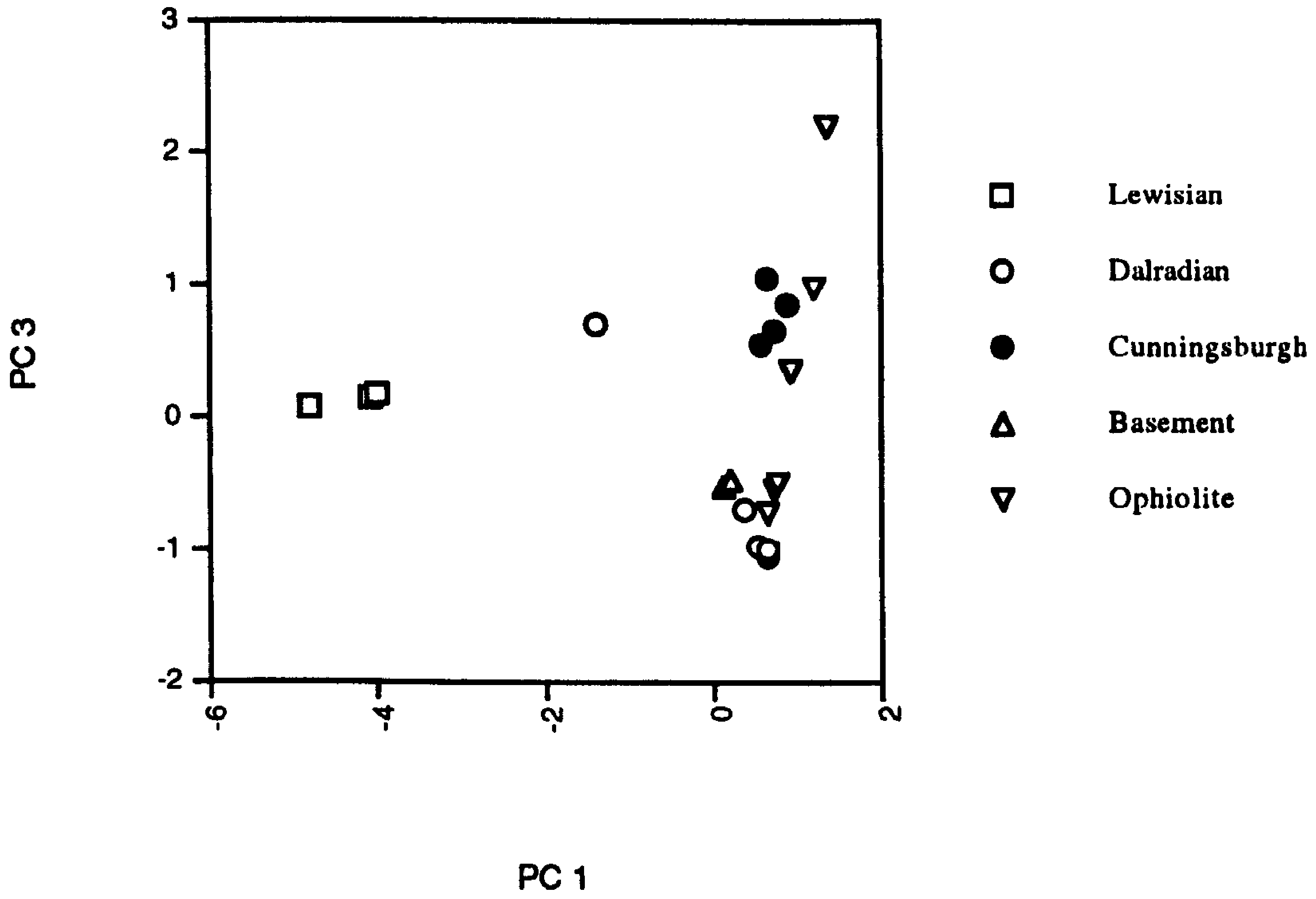
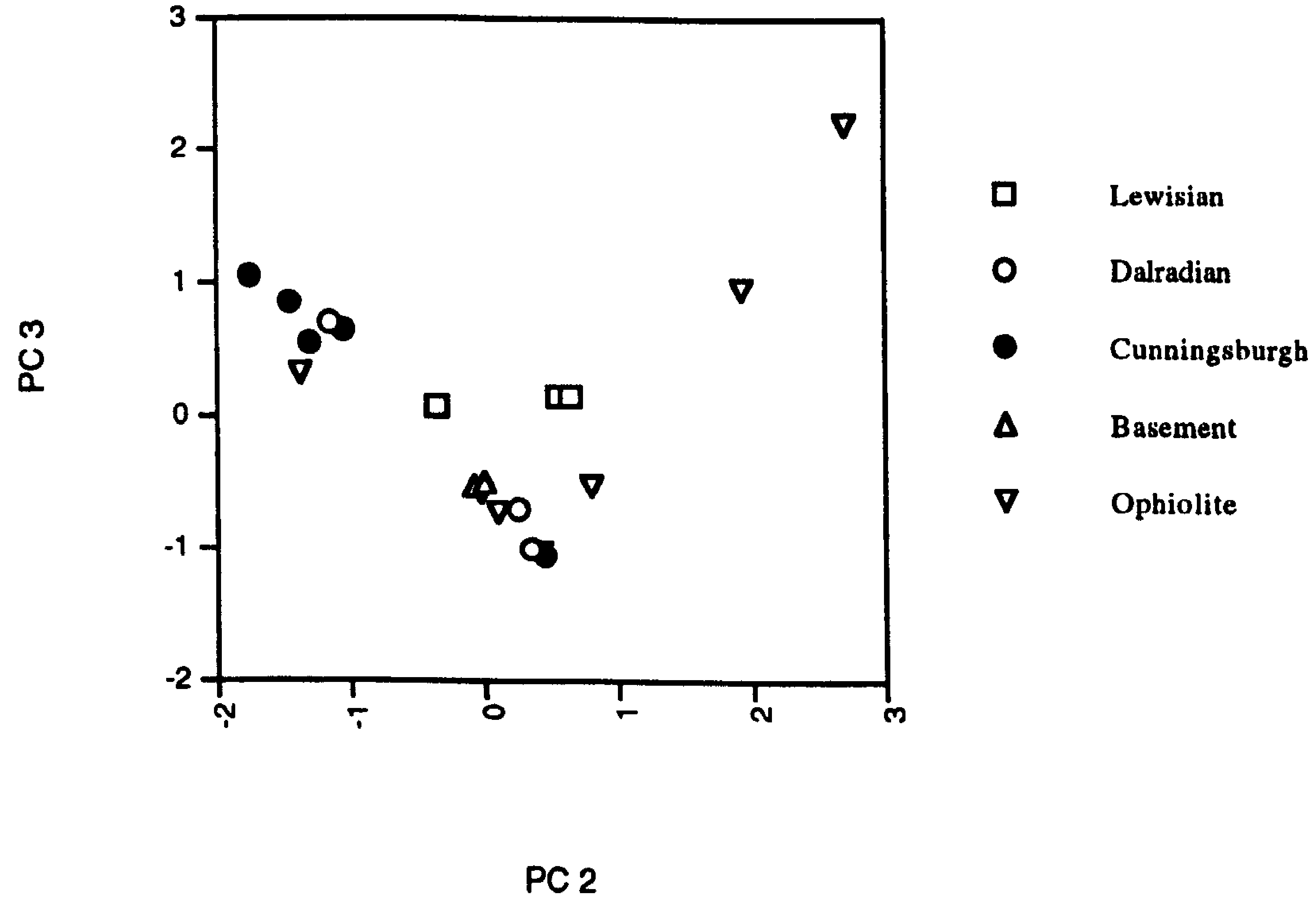


Figure 6.16 Principal component score plot of steatite sources using PC 2 and PC 3 from PCA using selected variable (As, Nb, Cs, Ba, Pb).



6.6.2 Comparison of Artifact Samples to Source Regions

Following the analysis of the source data which again demonstrated that the Lewisian source could be separated from the other potential steatite sources in Britain, the artifact samples were analysed with the source data in an attempt to establish any similarities and thus the provenance of the artifacts.

Principal components analyses were performed on the total data set, sources and artifacts. Again the initial analysis utilised all the variables, and the variables that had previously been identified as separating the Lewisian source. The eigenvalues, proportion and the cumulative proportion of the total variance explained by the principal components and the coefficients for the first three PCs are given in tables 6.9 - 6.12. The scorse are plotted in figures 6.17-6.19.

Table 6.9 The eigenvalues, proportion and the cumulative proportion of the total variance explained by the first three principal component using all available variables on the source and artifact data.

	Eigenvector		
	1	2	3
Eigenvalue	6.81	2.05	1.57
Proportion	40.0	12.1	9.2
Cumulative	40.0	52.1	61.4

Table 6.10 Eigenvector coefficients for the first three principal component using all available variables on the source and artifact data.

Variable	PC 1	PC 2	PC 3
B	0.081	-0.199	-0.451
Ga	-0.136	0.607	-0.173
As	-0.008	0.119	-0.165
Rb	-0.137	-0.023	0.208
Sr	-0.190	0.120	-0.315
Y	-0.335	0.044	0.049
Zr	-0.345	-0.119	0.023
Nb	-0.256	0.027	0.291
Sb	0.084	-0.205	-0.532
Cs	0.127	-0.188	-0.087
Ba	-0.065	0.635	-0.176
La	-0.270	-0.139	-0.308
Ce	-0.332	-0.137	-0.220
Sm	-0.357	-0.041	-0.036
Hf	-0.349	-0.086	0.080
Ta	-0.234	-0.102	0.179
Pb	-0.330	-0.094	-0.073

Table 6.11 The eigenvalues, proportion and the cumulative proportion of the total variance explained by the first three principal component calculated on selected variables (As, Nb, Cs, Ba, Pb).

	Eigenvector		
	1	2	3
Eigenvalue	1.67	1.06	0.95
Proportion	33.4	21.4	20.2
Cumulative	33.4	54.8	75.0

Table 6.12 Eigenvector coefficients for the first three principal component calculated on selected variables (As, Nb, Cs, Ba, Ce, Pb).

Variable	PC 1	PC 2	PC 3
As	-0.003	0.803	-0.526
Nb	0.606	-0.273	-0.029
Cs	-0.501	-0.213	-0.086
Ba	0.257	0.472	0.750
Pb	0.562	-0.108	-0.391

Figure 6.17 Principal component score plot of steatite sources and artifacts using PC 1 and PC 2 from PCA using selected variable (As, Nb, Cs, Ba, Pb).

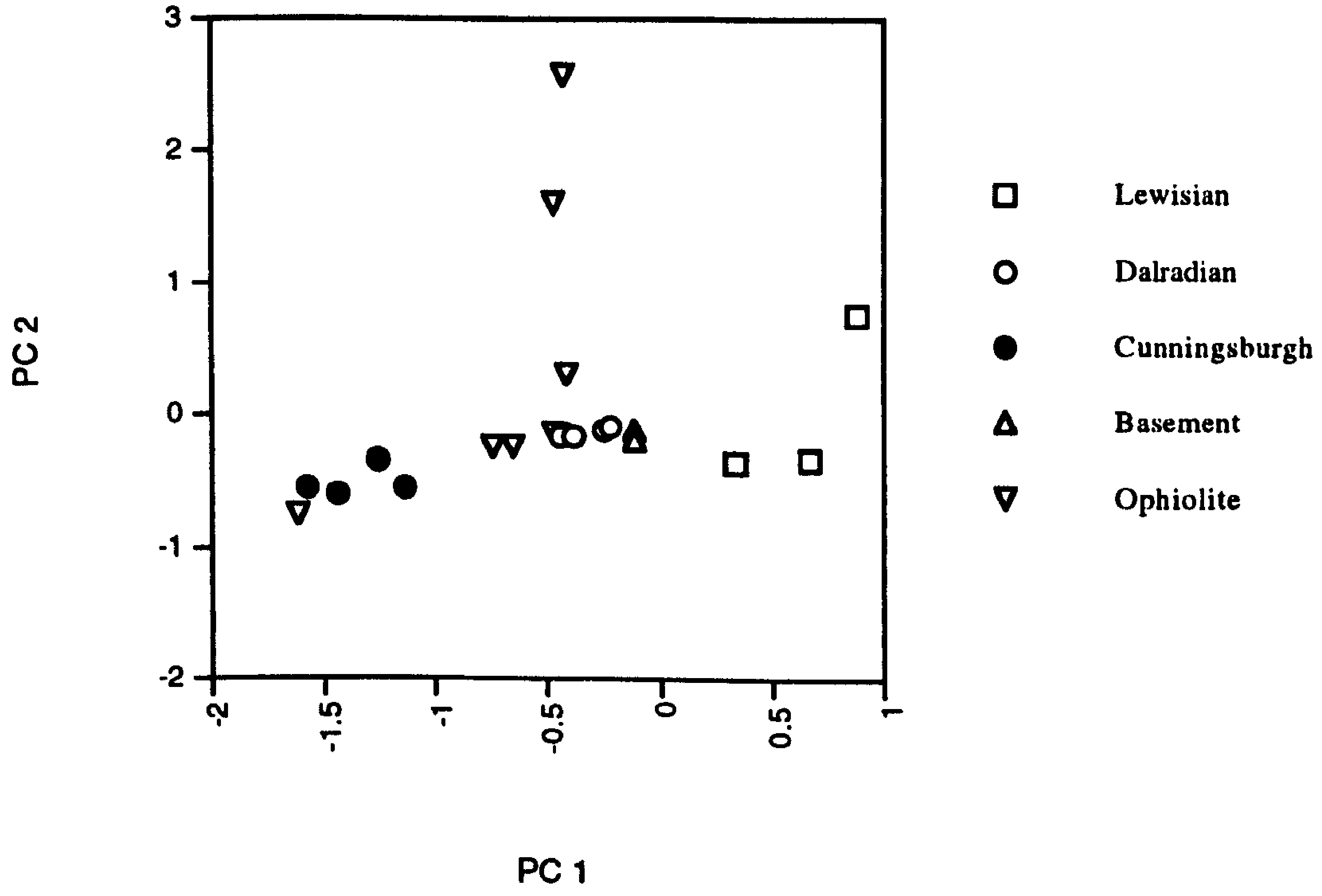


Figure 6.18 Principal component score plot of steatite sources and artifacts using PC 1 and PC 3 from PCA using selected variable (As, Nb, Cs, Ba, Pb).

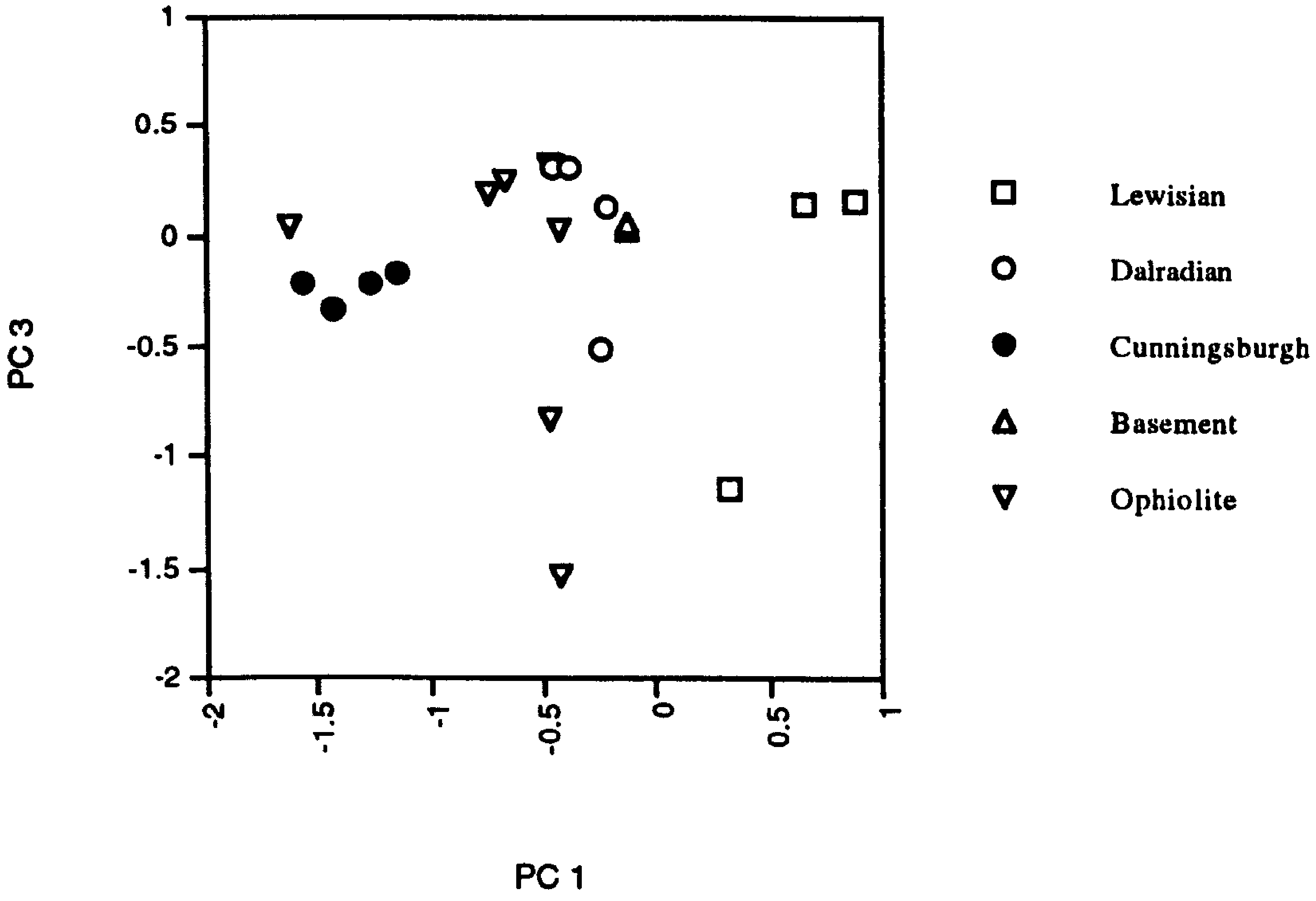
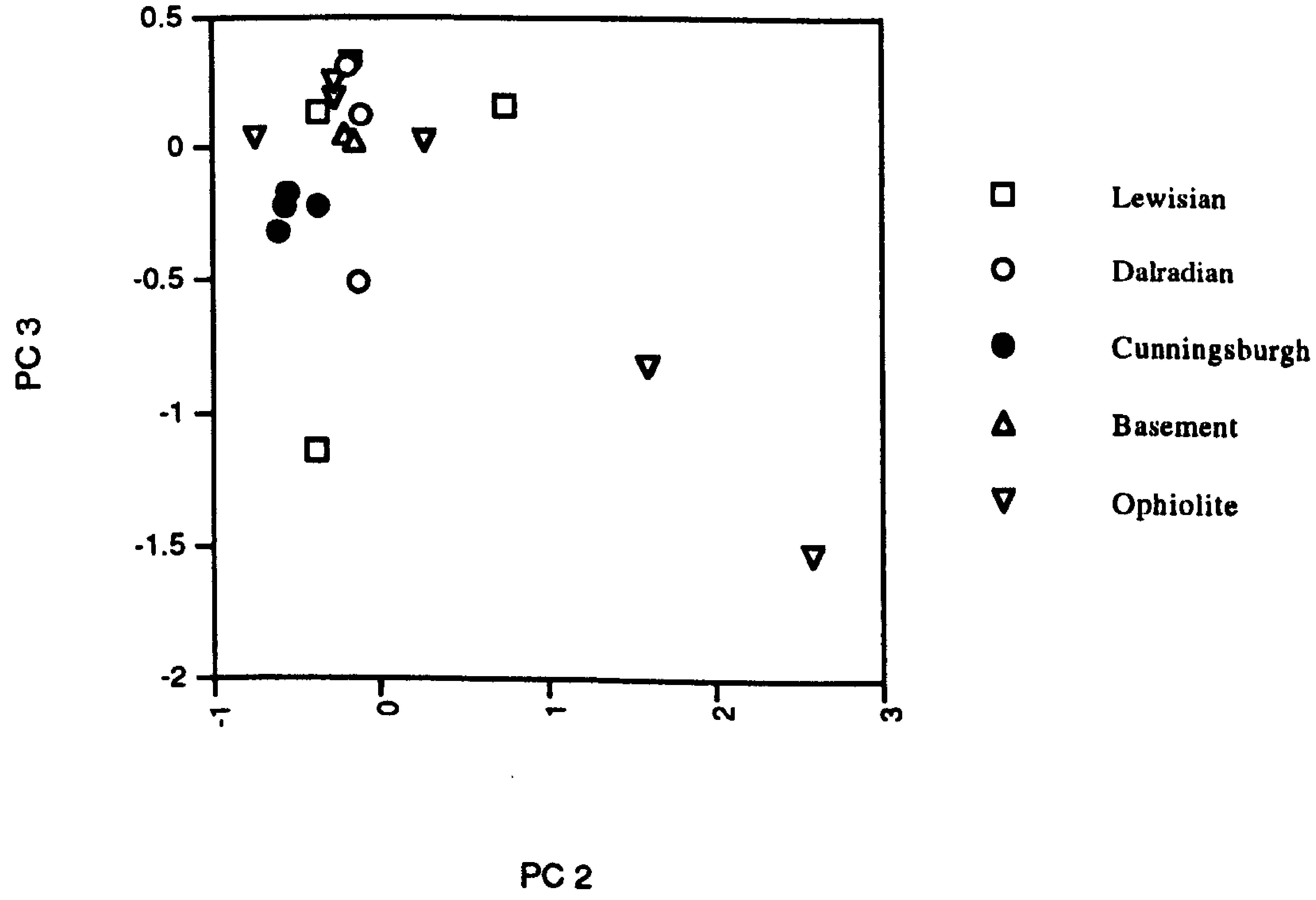


Figure 6.19 Principal component score plot of steatite sources and artifacts using PC 2 and PC 3 from PCA using selected variable (As, Nb, Cs, Ba, Pb).



The artifact data is plotted with the source data using the scores that had been able to separate the Lewisian sources from the other British sources. Figures 6.20 - 6.25 shows the PCs scores for the artifact samples plotted with sources using the limited number of variables in the analysis. Only the PC 1/PC 2 and PC 1/PC 3 plots are utilised as they show the best source discrimination. The artifact samples from Dun Telve (GA 979, GA 984, GA 985, GA 986, GA 989) are plotted with the samples from Dun Beag, Skye (GA 1047) and Dun Troddan (GA 1132, GA 1133, GA 1134, GA 1136). Figure 6.21 shows the samples from the rest of mainland Scotland; Lochalsh, Dundonald, Carlungie, Hyndford(AQ 14, AQ 116, AQ 114, HD 1748, HTA 71). The remaining samples from Jarlshof (HSA 672, HSA 681, HSA 688, HSA 722, HSA 726) and Muness, Shetland (BD 35) are plotted on a figure 6.22.

Figure 6.20 Principal component score plot of British steatite sources and artifact samples from Dun Telve, Glenelg (GA 979, GA 984, GA 985, GA 986, GA 989), Dun Beag, Skye (GA 1047) and Dun Troddan (GA 1132, GA 1133, GA 1134, GA 1136).

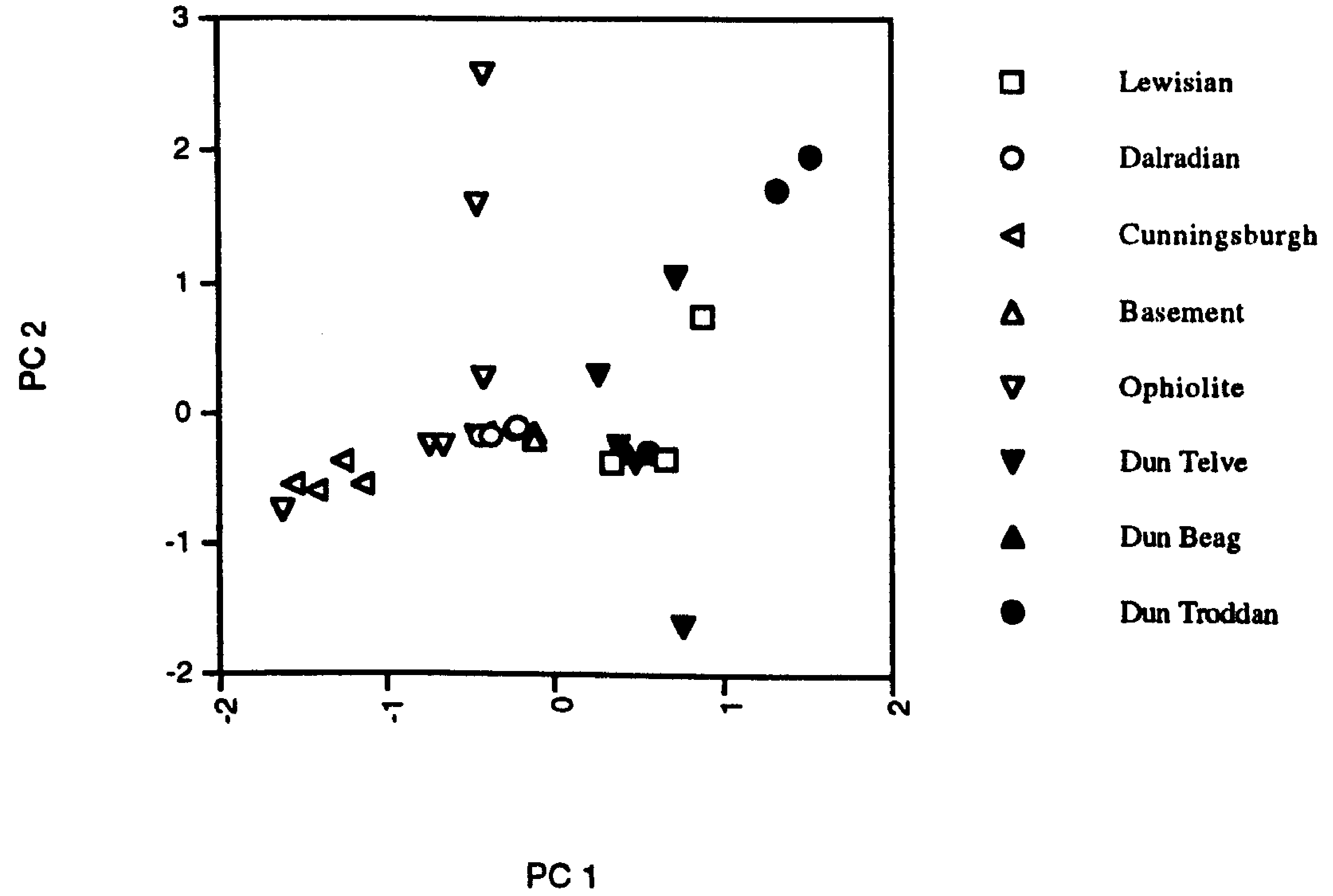


Figure 6.21 Principal component score plot of British steatite sources and artifact samples from the Scottish mainland, Lochalsh (AQ 14, AQ 116), Carlungie (HD 1748), Hyndford (HTA 71) and Dundonald (AQ 114).

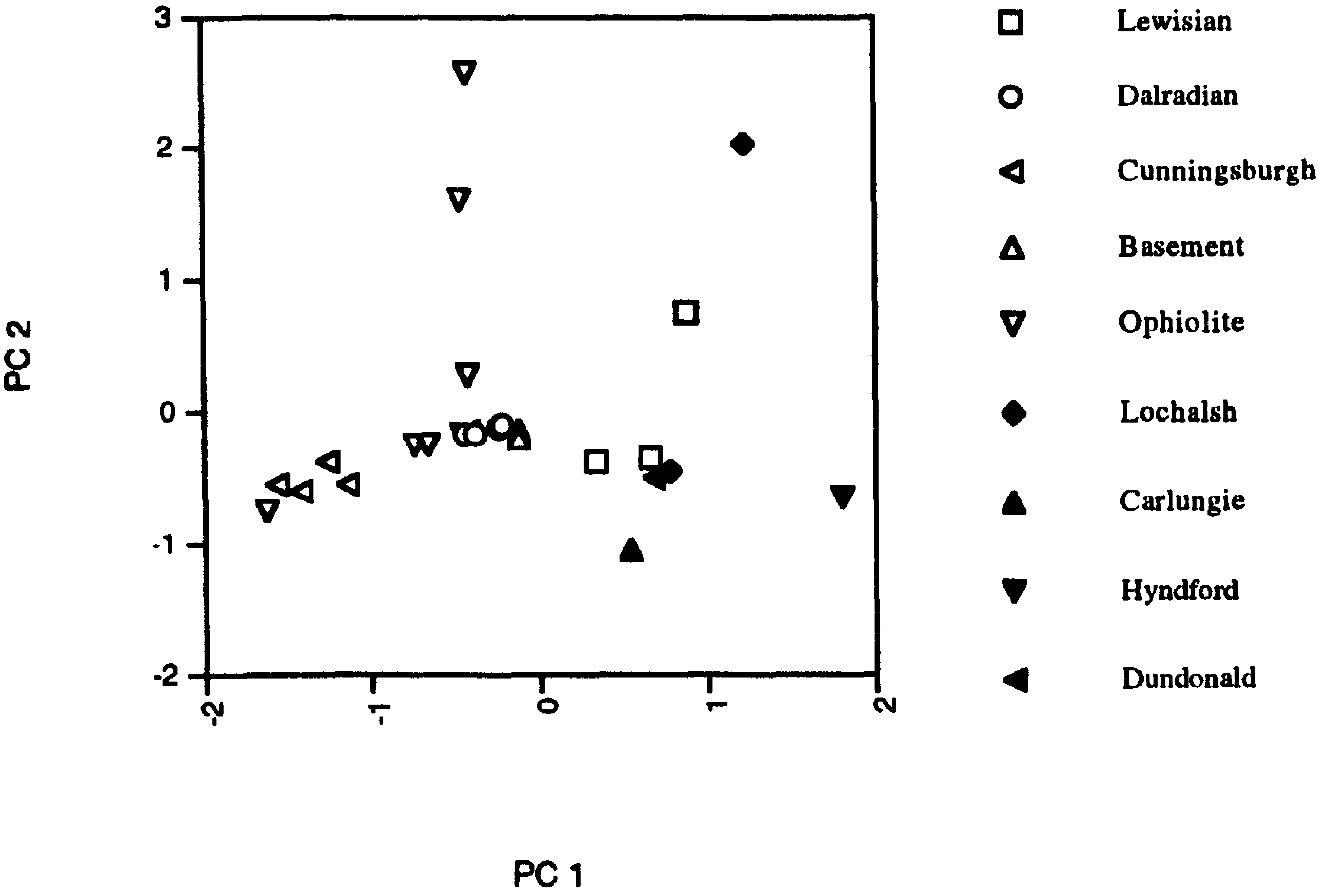


Figure 6.22 Principal component score plot of British steatite sources and artifact samples from Shetland, Jarlshof (HSA 672, HSA 681, HSA 688, HSA 722, HSA 726) and Muness, Unst (BD 35).

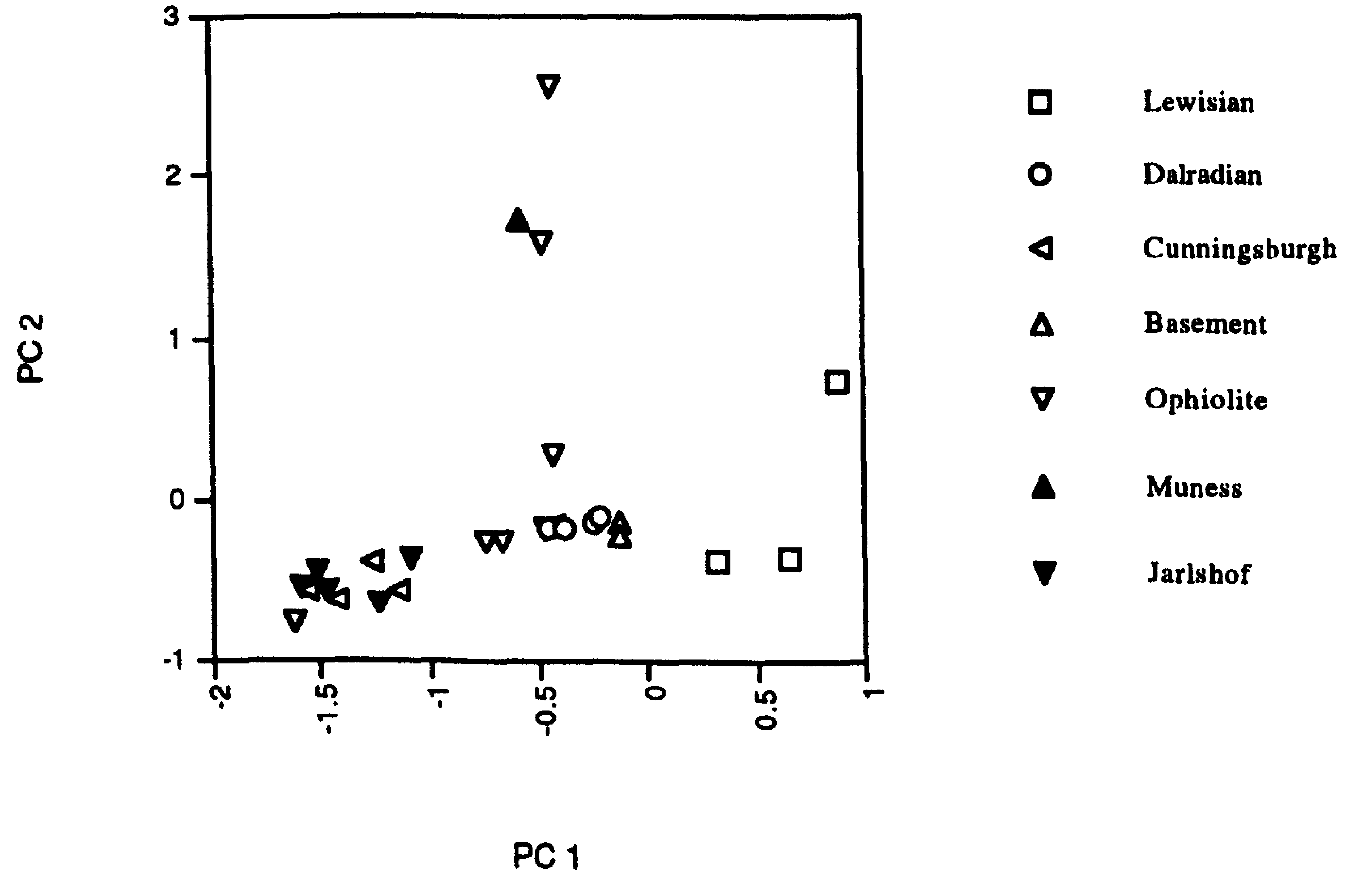


Figure 6.23 Principal component score plot of British steatite sources and artifact samples from Dun Telve, Glenelg (GA 979, GA 984, GA 985, GA 986, GA 989), Dun Beag, Skye (GA 1047) and Dun Troddan (GA 1132, GA 1133, GA 1134, GA 1136).

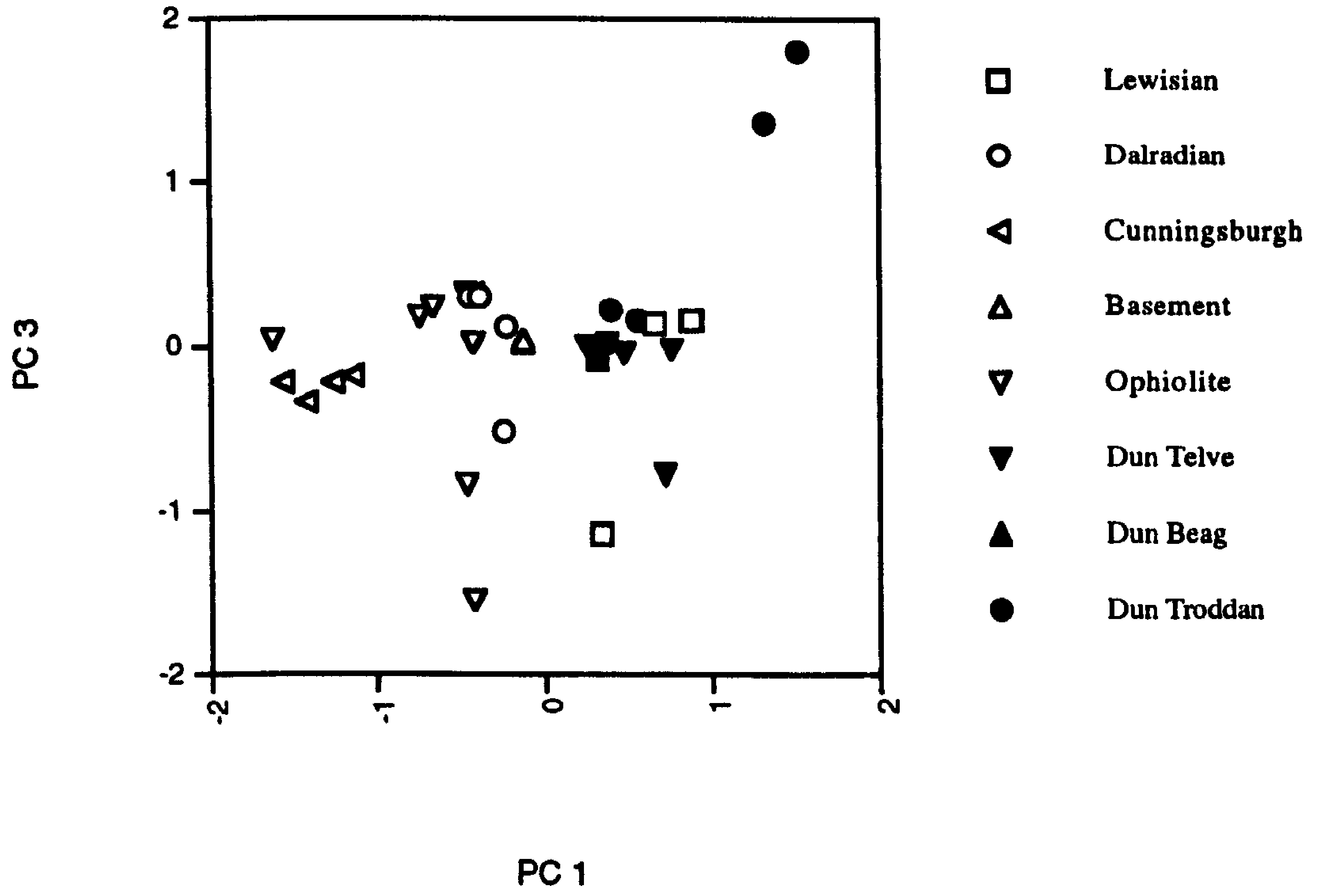


Figure 6.24 Principal component score plot of British steatite sources and artifact samples from the Scottish mainland, Lochalsh (AQ 14, AQ 116), Carlungie (HD 1748), Hyndford (HTA 71) and Dundonald (AQ 114).

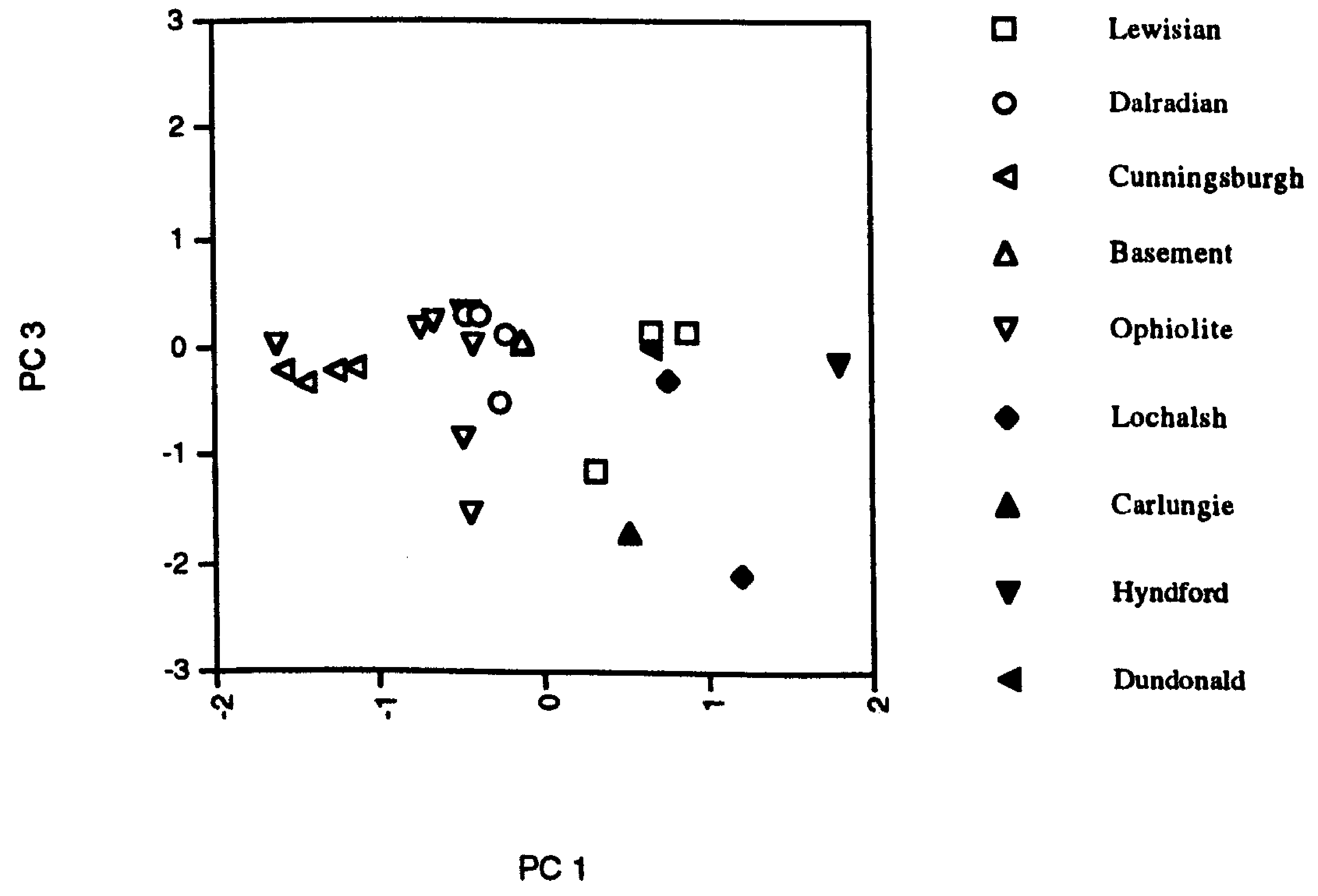
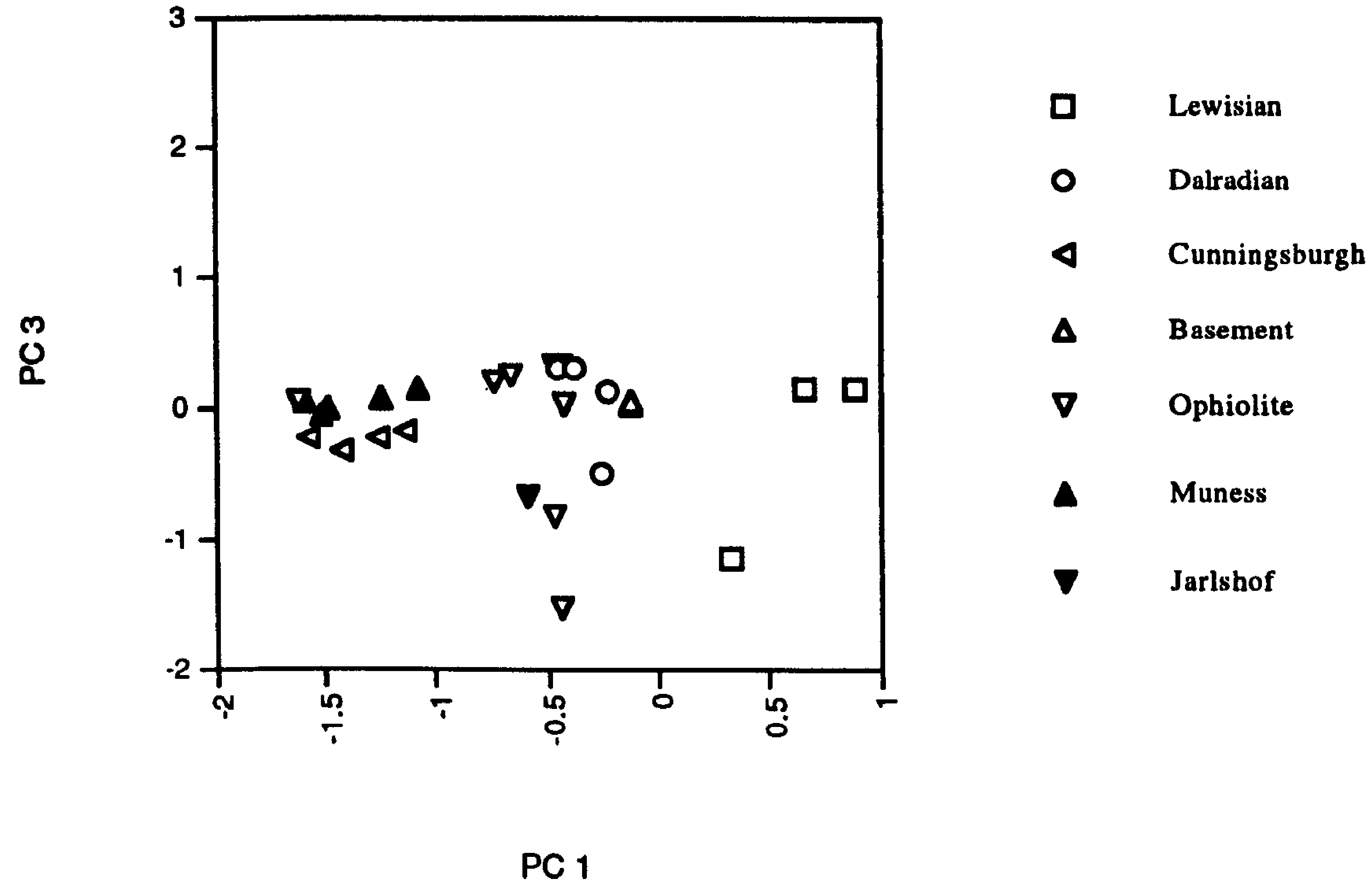


Figure 6.25 Principal component score plot of British steatite sources and artifact samples from Shetland, Jarlshof (HSA 672, HSA 681, HSA 688, HSA 722, HSA 726) and Muness, Unst (BD 35).



6.6.3 Provenance of Artifact based on Principal Component Analysis

Figures 6.20 - 6.25 indicate the probable provenance of the artifacts. The Dun Telve artifacts were similar to those of the Lewisian sources. The PC 1/PC 2 graphs showed that GA 985, GA 986 and GA 989 plotted within the Lewisian source field. GA 979 and GA 984 plotted relatively close to the Lewisian group. The PC 1/PC 3 graphs revealed that the artifact samples generally cluster close to the Lewisian group apart from GA 989, however this sample still plotted close to the general Lewisian field.

The artifact samples from the broch of Dun Troddan demonstrated that these samples were in general also similar to the Lewisian sources. The PC 1/PC 2 plots showed that GA 1132 and GA 1134 plotted within the Lewisian source field. Samples GA 1133 and GA 1136 plotted close to the Lewisian field, but have higher PC scores. These samples were similar to GA 989 from Dun Telve and suggested that the Lewisian field may extend in this direction with further source sampling. The PC 1/PC 3 plot showed similarities with the previous plot, GA 1132 and GA 1134 plotted within the Lewisian field and the other two samples, GA 1133 and GA 1136 plotted with higher PC scores. However all the samples appeared to have most in common with the Lewisian source.

The Dun Beag, Skye sample (GA 1047) also appeared to be similar to the Lewisian source. The PC 1/PC 2 plot showed the sample to plot within the Lewisian field. However, the PC 1/PC 3 graph showed the sample to plot outwith the general Lewisian field in the same area as GA 1133 and GA 1136.

The samples from Lochalsh (AQ 14, AQ 116) both demonstrated similar characteristics to the Lewisian sources. AQ 14 plotted within the Lewisian field in both plots. AQ 116 showed similarities with GA 1133 and GA 1136 on the PC 1/PC 2 plot, further suggested that the source region may include this area with further sampling. The PC 1/PC 3 plot showed that AQ 116 plots slightly outwith the Lewisian field, however the sample plots far from any other source region and therefore a Lewisian source must be considered probable.

The sample from Carlungie (HD 1748) was most similar to the Lewisian source. In both graphs the sample plotted slightly outwith the field defined by the Lewisian samples. However, the sample was relatively close to the Lewisian field in both plots.

The Hyndford crannog sample (HTA 71), was also similar to Lewisian sources. As with the Carlungie sample both plots showed the sample to lie slightly outside the Lewisian field, but in both cases it resembled no other source.

The sample from Dundonald (AQ 114) in both graphs plotted within the Lewisian field.

The material from the Jarlshof artifacts (HSA 672, HSA 681, HSA 688, HSA 722, HSA 726) proved to be entirely different in character from the previous samples when the PC scores are plotted. The PC 1/PC 2 graph demonstrated that these samples are not Lewisian in origin. All the samples plotted close to a group from the source at Cunningsburgh, but no positive statement could be made as the source regions cannot be resolved from one another using this analysis. The PC 1/PC 3 graph was similar and again the samples plot close to the Cunningsburgh source samples.

The single sample from Muness, Unst (BD 35) was also different in character from the samples from the Scottish mainland. In both plots the sample plotted away from the Lewisian source, close to the general trend of the ophiolite material.

6.6.4 Discriminant Analysis

From the PCA it was apparent that the Lewisian group is substantially different from the other sources. Although these other sources have proved difficult to resolve, for the purposes of this study it was important to discriminate between artifacts from Lewisian sources and those that are clearly not. Thus the next stage was to employ discriminant analysis in order to answer this question.

A brief discussion of the methodologies and references to more detailed discussion of this technique can be found in section 3.9.1.

Discriminant Analysis was not possible using all the variables, principally due to the existence of multi-colinearity, i.e. if one or more predictors is highly correlated with another. Similarly, if one or more predictor was essentially constant, discriminant calculations cannot be done. Therefore subsets of the predictor were used in the analysis in order to alleviate these problems. The source data was analysed in order to assess the classification the observations into the geological groups.

The first analysis made use of the optimum number of predictors, Ga, As, Rb, Y, Zr, Nb, Sb, Cs, Ba, La, Sm, Ta and Pb. The groups used in the analysis are; 1 - Lewisian, 2 - Dalradian, 3 - Basement, 4 - Ophiolite. A summary of the linear discrimination analysis is given in Table 6.13. The use of these predictors resulted in the successful placing of most observations.

Table 6.13 Summary of linear discrimination analysis, predictors; Ga, As, Rb, Y, Zr, Nb, Sb, Cs, Ba, La, Sm, Ta, Pb.

Put Into Group	True Group			
	1	2	3	4
1	3	0	0	0
2	0	8	1	0
3	0	1	1	0
4	0	0	0	7
n Total	3	9	2	7
n Correct	3	8	1	7
Proportion	1	0.889	1	1
	Square Distance Between Groups			
	1	2	3	4
1	0	572.059	465.227	660.322
2	572.059	0	116.290	42.558
3	465.227	116.290	0	73.636
4	660.332	42.558	73.636	0

The second selection of predictors was based upon the larger group of elements that has been identified from the initial univariate analysis to show some potential at differentiating between the groups. However a number of these elements showed the problems associated with multicolinearity, therefore two sub groups of elements were used to avoid this problem. The first sub-group included; As, Rb, Zr, Nb, Cs, Ba, La, Ce, Ta and Pb; whereas the second sub-group used; As, Rb, Sr, Zr, Nb, Ba, La and Pb. A summary of the linear discrimination analysis is given in Tables 6.14 and 6.15. These results demonstrated that the discrimination function was able to predict the correct group in nearly all the cases. The analysis only mis-classified one and two observations from the first and second sub-groups respectively, and these are placed from the second group (Dalradian) to the third (Basement) or vice versa. From the linear discrimination function it was apparent that these groups were relatively close together in multi-dimensional space, thus accounting for the mis-classification.

Table 6.14 Summary of linear discrimination analysis, predictors; As, Rb, Zr, Nb, Cs, Ba, La, Ce, Ta, Pb.

Put Into Group	True Group			
	1	2	3	4
1	3	0	0	0
2	0	8	0	0
3	0	1	2	0
4	0	0	0	7
n Total	3	9	2	7
n Correct	3	8	2	7
Proportion	1	0.889	1	1
	Square Distance Between Groups			
	1	2	3	4
1	0	244.517	220.974	331.327
2	244.517	0	28.226	18.715
3	220.974	28.226	0	35.279
4	331.327	18.715	35.279	0

Table 6.15 Summary of linear discrimination analysis, predictors; As, Rb, Sr, Zr, Nb, Ba, La and Pb

Put Into Group	True Group			
	1	2	3	4
1	3	0	0	0
2	0	9	1	0
3	0	0	1	0
4	0	0	0	7
n Total	3	9	2	7
n Correct	3	9	1	7
Proportion	1	0.889	0.5	1
	Square Distance Between Groups			
	1	2	3	4
1	0	156.580	174.968	200.195
2	156.580	0	9.536	7.454
3	174.968	9.536	0	11.458
4	200.195	7.454	11.458	0

The final analysis used the elements that were noted from the initial univariate analysis that showed the best discriminating potential. A summary of the discrimination function is given in Table 6.16. This analysis mis-classified three observations, again the differences between the Dalradian and the Basement sources was relatively small and may account for the mis-classification. This analysis also placed an ophiolite observation within the Dalradian sources. As the number of predictors have been reduced the squared distance between the groups has also been reduced, therefore mis-classifications are more likely.

From these analyses it was apparent that discrimination analysis was relatively successful at placing observation within the correct group. The mis-classifications of a number of observations can be accounted for by their relative closeness in multi-dimensional space. Of great importance to this study was the fact that the Lewisian source differed greatly from the other sources and this is reflected by the success at placing the Lewisian samples, 100% correct in all the analyses.

Table 6.16 Summary of linear discrimination analysis, predictors; As, Nb, Cs, Ba, Pb.

Put Into Group	True Group			
	1	2	3	4
1	3	0	0	0
2	0	7	0	1
3	0	2	2	0
4	0	0	0	6
n Total	3	9	2	7
n Correct	3	7	2	6
Proportion	1	0.714	1	0.857
	Square Distance Between Groups			
	1	2	3	4
1	0	34.168	34.958	40.273
2	34.168	0	2.255	2.802
3	34.958	2.255	0	6.732
4	40.273	2.802	6.732	0

6.6.5 Prediction of Artifact Provenance by Discriminant Analysis

The analysis of the source data confirmed that the Lewisian sources were substantially different from the other British sources. It was considered that these data sets would provide a suitable classification matrix for the prediction of the artifact sample data, even if the Dalradian, Basement and Ophiolite sources could not be resolved. Artifact samples were classified into the four groups using the four sets of predictors used above. The predicted group membership for the artifact samples is summarised in Table 6.17.

This analysis demonstrated that the same group membership is predicted using the different analysis for the majority of the artifact samples. The samples from the Scottish mainland were predicted to be part of the Lewisian group by the four separate analyses in all but four cases. These Scottish mainland samples that were predicted by the four separate analyses to a single source region can be assigned a Lewisian origin with some degree of confidence. The samples from Shetland were predicted to be part of a number of different groups and the different analysis results in different predicted groups. However the main point to note about these samples was that none were predicted to be part of the Lewisian group. The Scottish mainland samples that were not predicted by all analyses to be part of the Lewisian sources are GA 989, GA 1134, GA 1136 and AQ 116. In all these cases one analysis predicted that the samples were

Table 6.17 Summary of predicted group membership of artifact samples;
Analysis A used predictors Ga, As, Rb, Y, Zr, Nb, Sb, Cs, Ba, La, Sm, Ta, Pb.
Analysis B used predictors As, Rb, Zr, Nb, Cs, Ba, La, Ce, Ta, Pb.
Analysis C used predictors As, Rb, Sr, Zr, Nb, Ba, La and Pb
Analysis D used predictors As, Nb, Cs, Ba, Pb

Sample	Predicted Group Membership			
	Analysis A	**Analysis B**	**Analysis C**	**Analysis D**
GA 989	Lewisian	Dalradian	Lewisian	Lewisian
GA 986	Lewisian	Lewisian	Lewisian	Lewisian
GA 979	Lewisian	Lewisian	Lewisian	Lewisian
GA 984	Lewisian	Lewisian	Lewisian	Lewisian
GA 985	Lewisian	Lewisian	Lewisian	Lewisian
GA 1047	Lewisian	Lewisian	Lewisian	Lewisian
GA 1132	Lewisian	Lewisian	Lewisian	Lewisian
GA 1133	Lewisian	Lewisian	Dalradian	Lewisian
GA 1134	Lewisian	Lewisian	Lewisian	Lewisian
GA 1136	Lewisian	Dalradian	Lewisian	Lewisian
AQ 14	Lewisian	Lewisian	Lewisian	Lewisian
AQ 116	Lewisian	Lewisian	Dalradian	Lewisian
HD 1748	Lewisian	Lewisian	Lewisian	Lewisian
HTA 71	Lewisian	Lewisian	Lewisian	Lewisian
AQ 114	Lewisian	Lewisian	Lewisian	Lewisian
BD 35	Basement	Basement	Basement	Ophiolite
HSA 726	Dalradian	Dalradian	Dalradian	Ophiolite
HSA 182	Ophiolite	Ophiolite	Ophiolite	Dalradian
HSA 672	Dalradian	Dalradian	Dalradian	Ophiolite
HSA 722	Dalradian	Dalradian	Dalradian	Ophiolite
HSA 688	Dalradian	Ophiolite	Ophiolite	Dalradian

from the Dalradian group. Notable is the fact that these were the samples in the PCA that formed a small group with higher PC scores than the Lewisian group. This suggests that these samples were probably Lewisian in origin although they may reflect an as yet un-sampled part of the Lewisian source.

6.7 Rare Earth Element Analysis

Having established probable regional provenance for the artifact samples, a more detailed provenance may be determined if chondrite normalised REE patterns are utilised. In chapter 4 it was established that individual steatite sources have different REE patterns. Although the REE concentration varied across a single steatite outcrop the REE pattern remained essentially unchanged. Thus by comparing the REE patterns of known steatite sources to the REE pattern of artifacts of unknown provenance, some assessment of the origin of the artifact may be made.

A more detailed discussion of the REE and their use in artifact provenancing can be found in chapter 4. The sample preparation, dissolution and methods of analysis are also described in chapter 4.

6.7.1 Results

The REE results for the artifact samples are given in Appendix E. The results of the analysis and discussion of source samples are described in chapter 4.

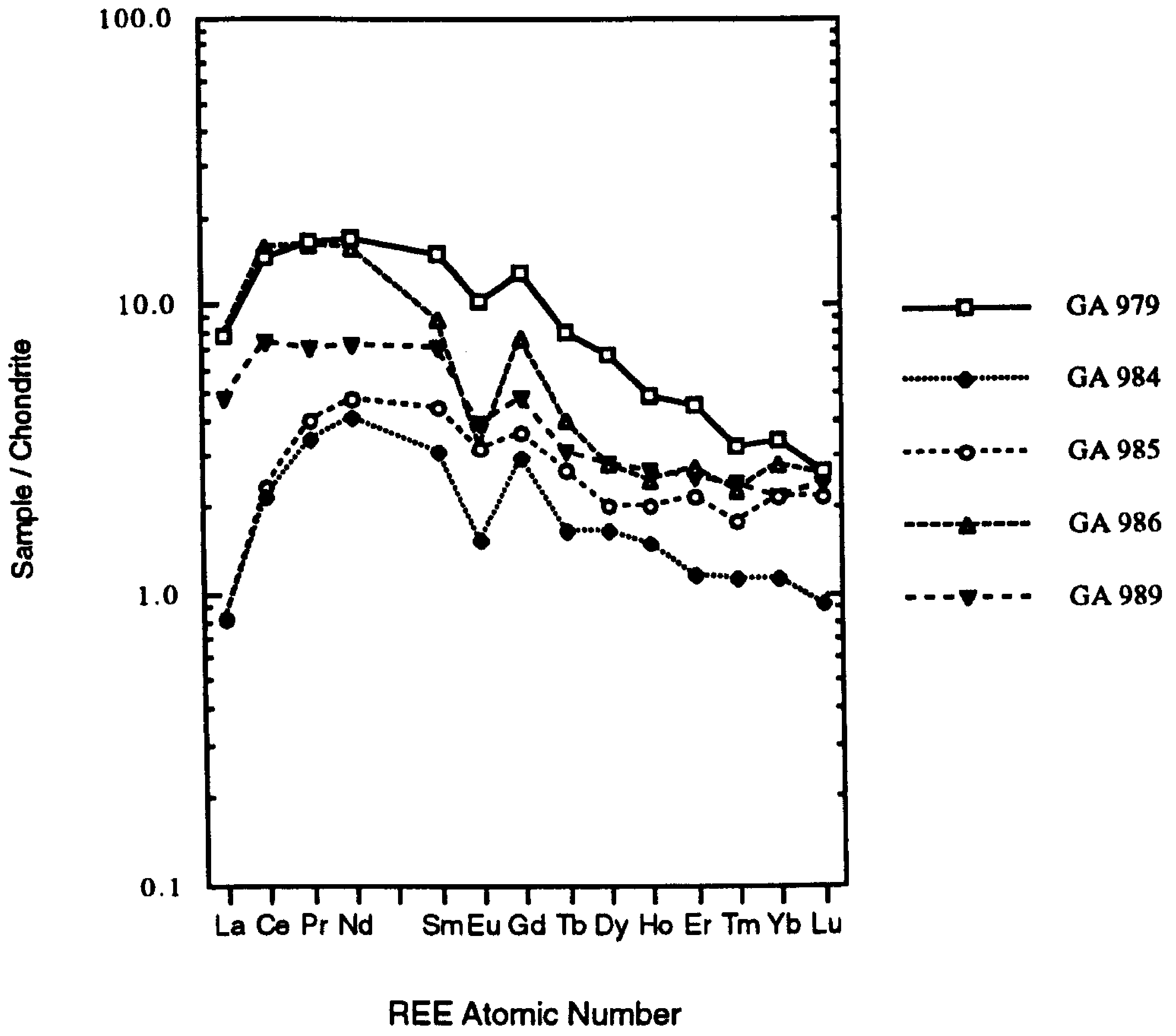
6.7.2 Comparison of artifacts and steatite source REE patterns

Having established the validity of using chondrite normalised REE patterns to characterise steatite quarries, in chapter 4, it is now possible to discuss potential resources procurement suggested by the comparison of results from artifacts and sources.

Visual matching of the REE patterns coupled with utilisation of chondrite normalised ratios was considered to be the optimum method of comparing artifacts and steatite sources. Characterisation and classification of chondrite normalised REE patterns have been possible by the use of chondrite normalised ratios. However, this technique presents a number of problems. Errors on single point used in the ratio calculation may result in values that are not representative of the general REE pattern. Also similar patterns may be classified differently due to the position of cut-off points between types. However, the ratio method does allow some numerically based comparison between sources.

The artifact samples display a number of different types of chondrite normalised patterns. All the samples from Dun Telve (GA 979, GA 984, GA 985, GA 986, GA 989) exhibit a general HREE depleted pattern, with La, Ce and Pr also showing depletion, figure 6.26. This is a characteristic pattern seen in many peridotites, particularly pyroxenites, see section 4.5. The relatively high REE abundances may also be result of a pyroxene bearing parental material. The samples all display negative Eu anomalies.

Figure 6.26 Chondrite normalised REE abundances in steatite samples from Dun Telve, Glenelg, (GA 979, GA 984, GA 985, GA 986, GA 989).



The samples from the Dun Beag (GA 1047), Caisteal Grugaig (AQ 116) and Carlungie I (HD 1748) show a similar pattern to those of the Dun Telve material, .exhibit a general HREE depleted pattern, with La, Ce and Pr also showing depletion, figure 6.27. This suggests that a quarry with a similar pattern the was source material for all these samples. The samples from Dun Troddan (GA 1132, GA 1133, GA 1134, GA 1136) display essentially flat REE patterns with large positive Eu anomalies, figure 6.28. This type of patterns suggests REE mobility during steatisation. Three Scottish mainland samples also show a similar REE pattern, figure 6.29. Again it is proposed that these samples come from a source with this type of REE pattern.

Figure 6.27 Chondrite normalised REE abundances in steatite samples from Dun Beag, Skye (GA 1047), Caisteal Grugaig, Lochalsh (AQ 116) and Carlungie I, Angus (HD 1748).

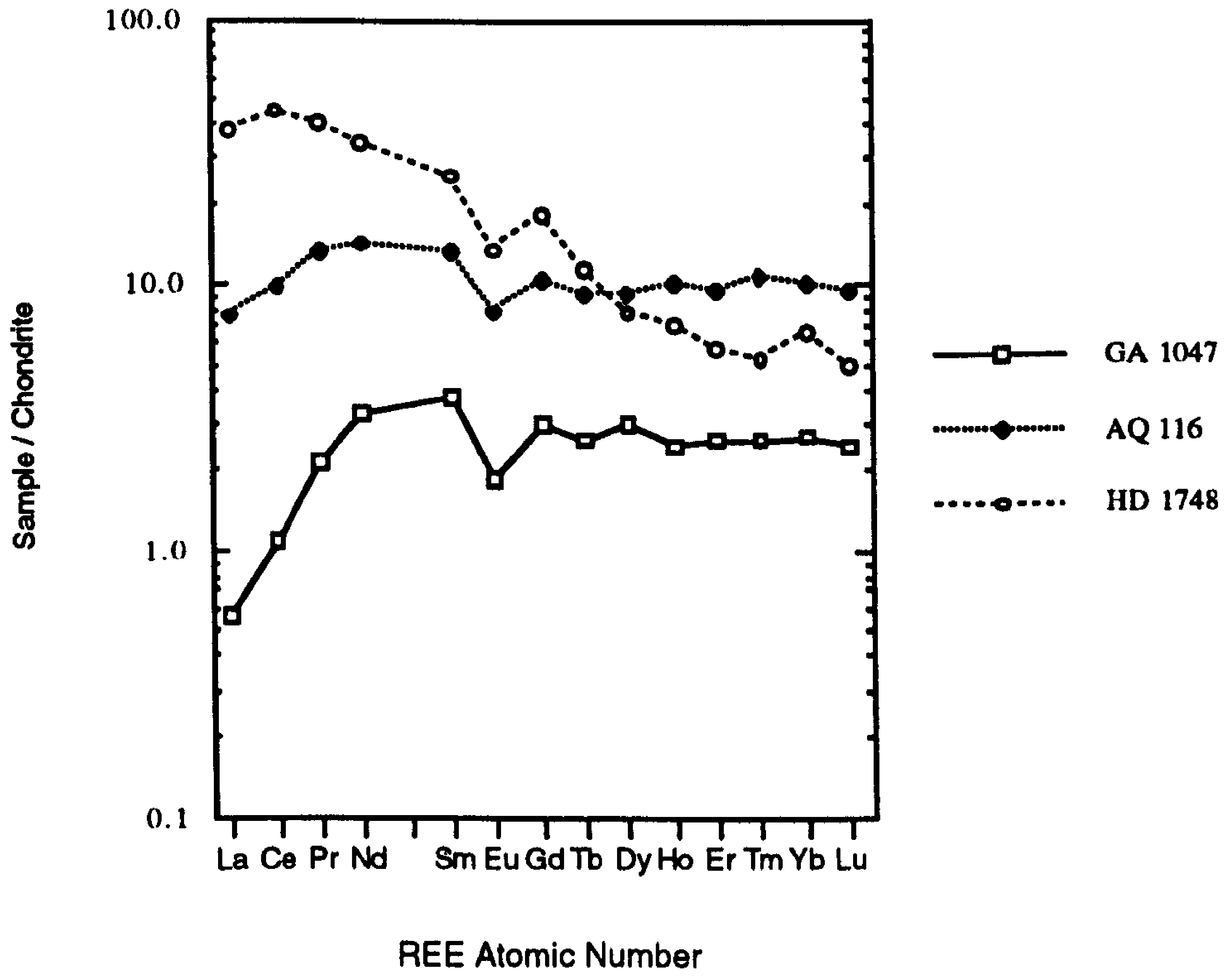


Figure 6.28 Chondrite normalised REE abundances in steatite samples from Dun Troddan, Glenelg (GA 1132, GA 1133, GA 1134, GA 1136).

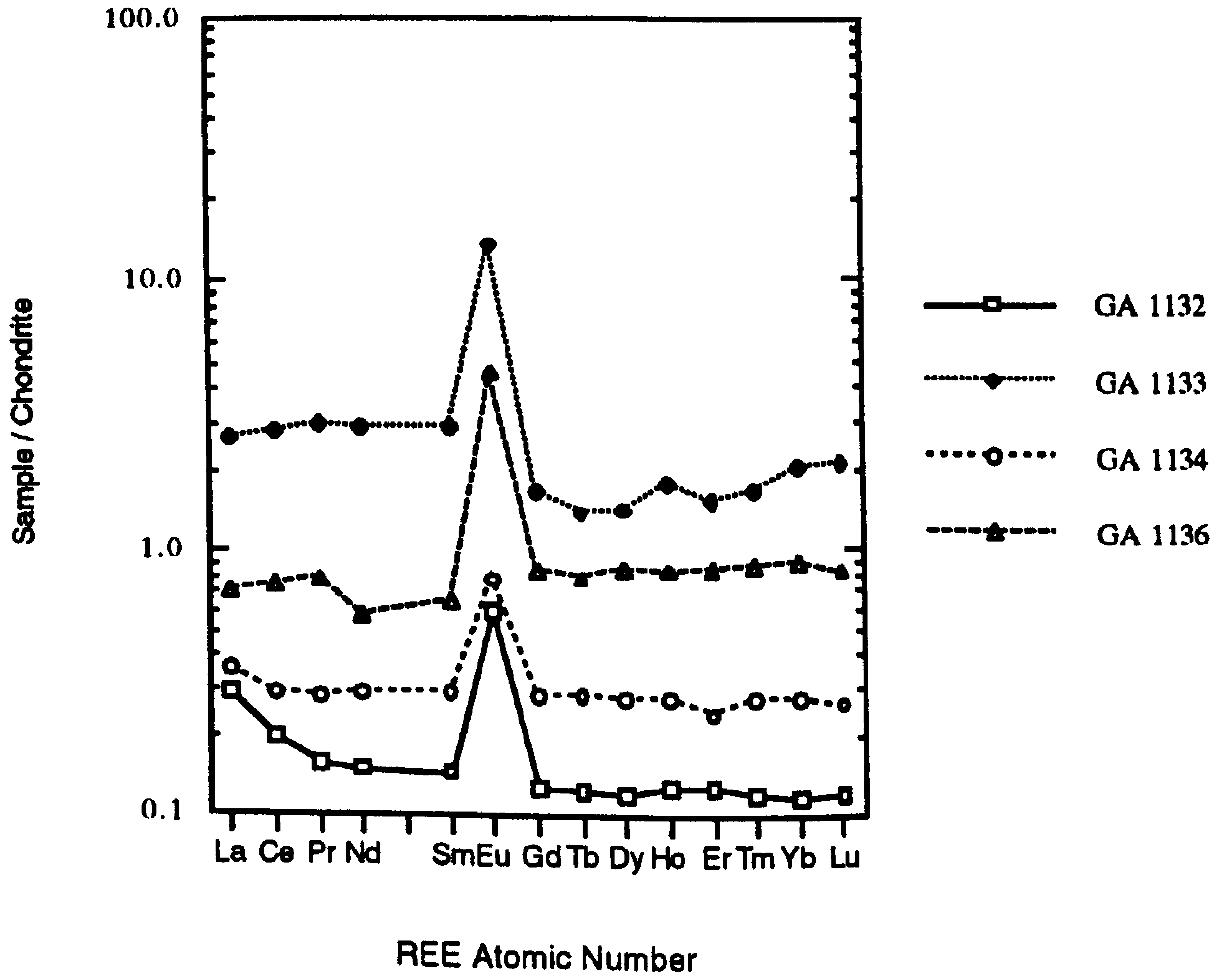
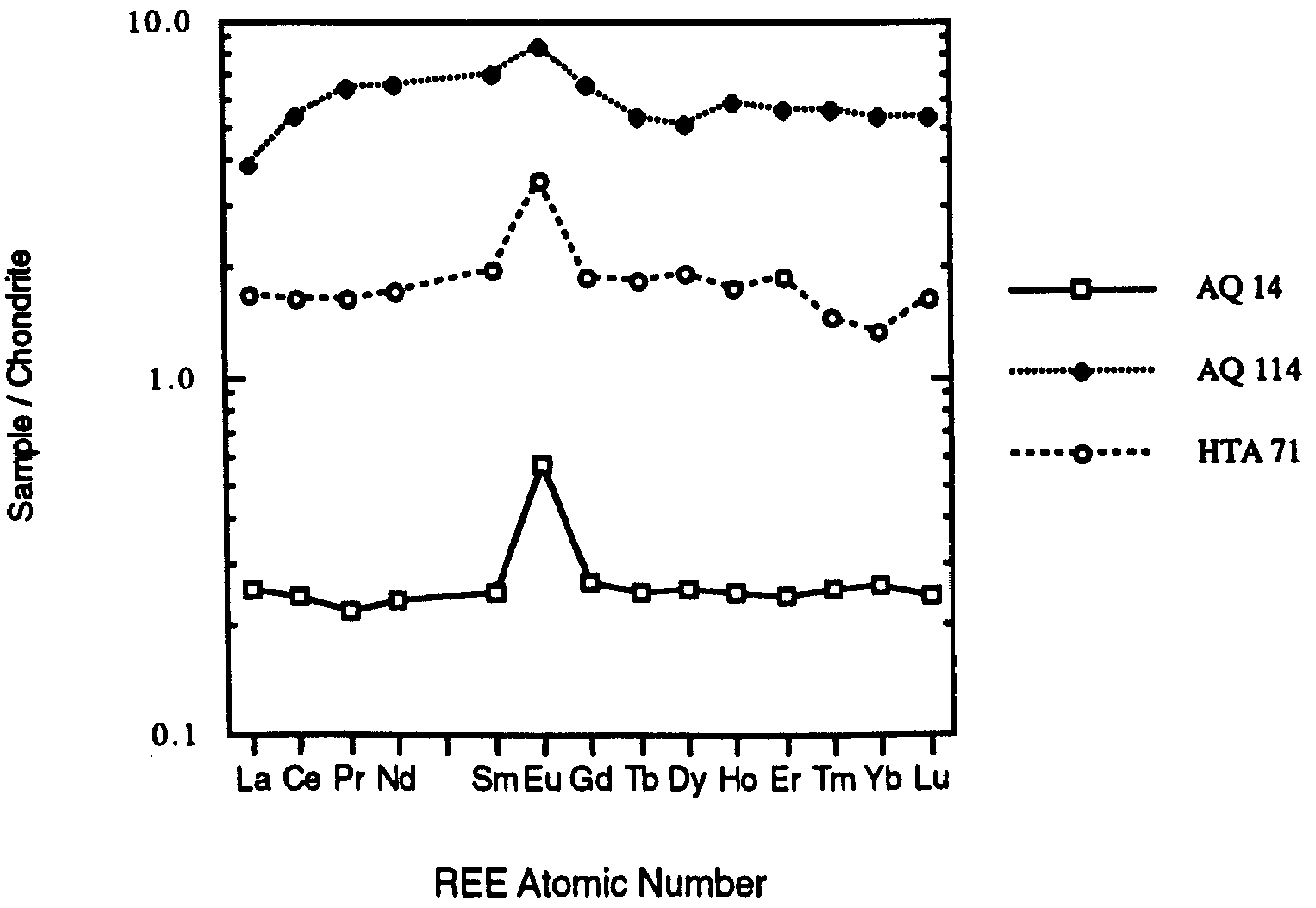


Figure 6.29 Chondrite normalised REE abundances in steatite samples from Killilan, Lochalsh (AQ 14), Dundonald, Ayrshire (AQ 114) and Hyndford, Lanarkshire (HTA 71).



The REE patterns for the samples of Shetland steatite are again different to those seen from the Scottish mainland sites. The samples from Jarlshof (HSA 672, HSA 681, HSA 688, HSA 722, HSA 726) show a typically HREE depleted pattern with a positive Eu anomaly, figure 6.30. The absolute REE concentration is very low in all these samples, typically HREE less than 0.1 times chondrite. Sample BD 35 has a different REE pattern to all the other samples. This sample show marked HREE depletion with no Eu anomaly, figure 6.31.

Figure 6.30 Chondrite normalised REE abundances in steatite samples from Jarlshof, Shetland (HSA 672, HSA 681, HSA 688, HSA 722, HSA 726).

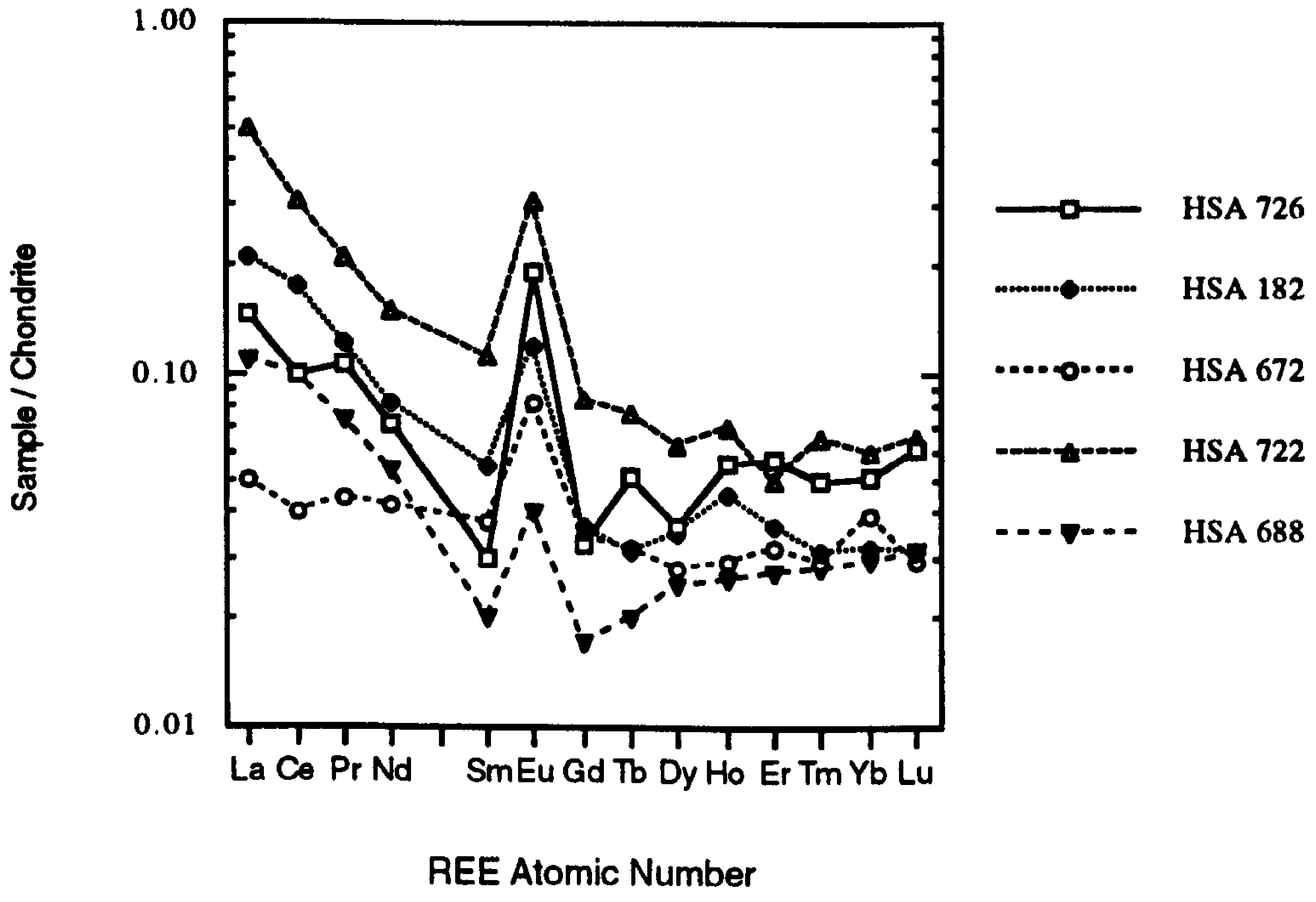
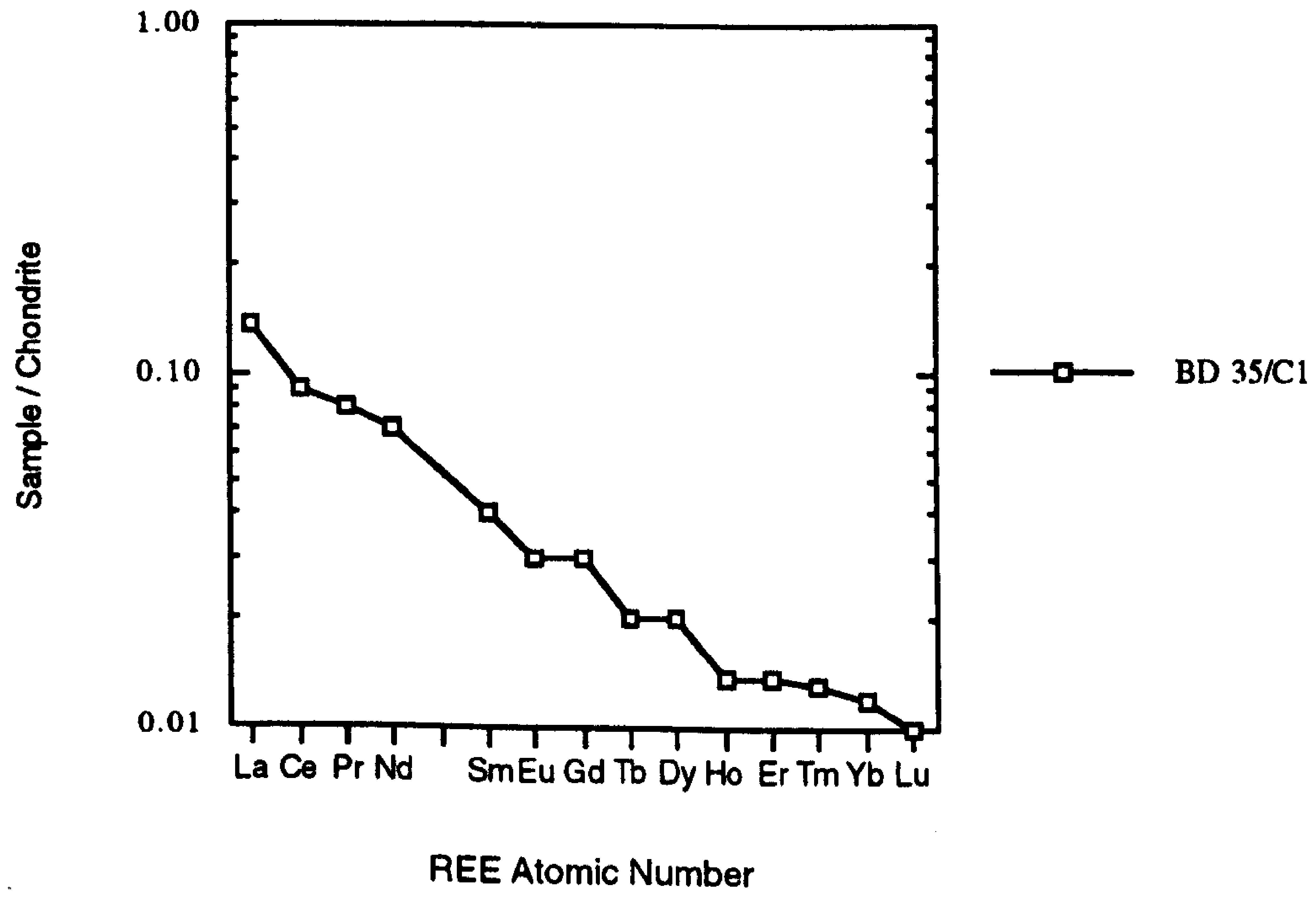


Figure 6.31 Chondrite normalised REE abundances in steatite samples from Muness, Unst Shetland (BD 35).



These patterns can be compared with those from British sources that have been analysed, by both a visual examination and comparison of various ratios. The samples from Dun Troddan and samples AQ 14, AQ 114 and HTA 71 display a typically flat REE pattern with a positive Eu anomaly. Examination of the chondrite normalised REE patterns from analysed British steatite sources reveal that only two sources have this typical REE pattern, Ardintoul Glenelg and Dammins Fetlar Shetland. Furthermore the REE pattern from Dammins Fetlar shows a slight enrichment in La and Ce that is not seen in the artifact samples. A comparison with the Ardintoul Glenelg source can be seen in figures 6.32 - 6.33.

Figure 6.32 Chondrite normalised REE abundances of steatite samples from Dun Troddan ((GA 1132, GA 1133, GA 1134, GA 1136) comparison with the source quarry at Ardintoul, Glenelg, shaded area.

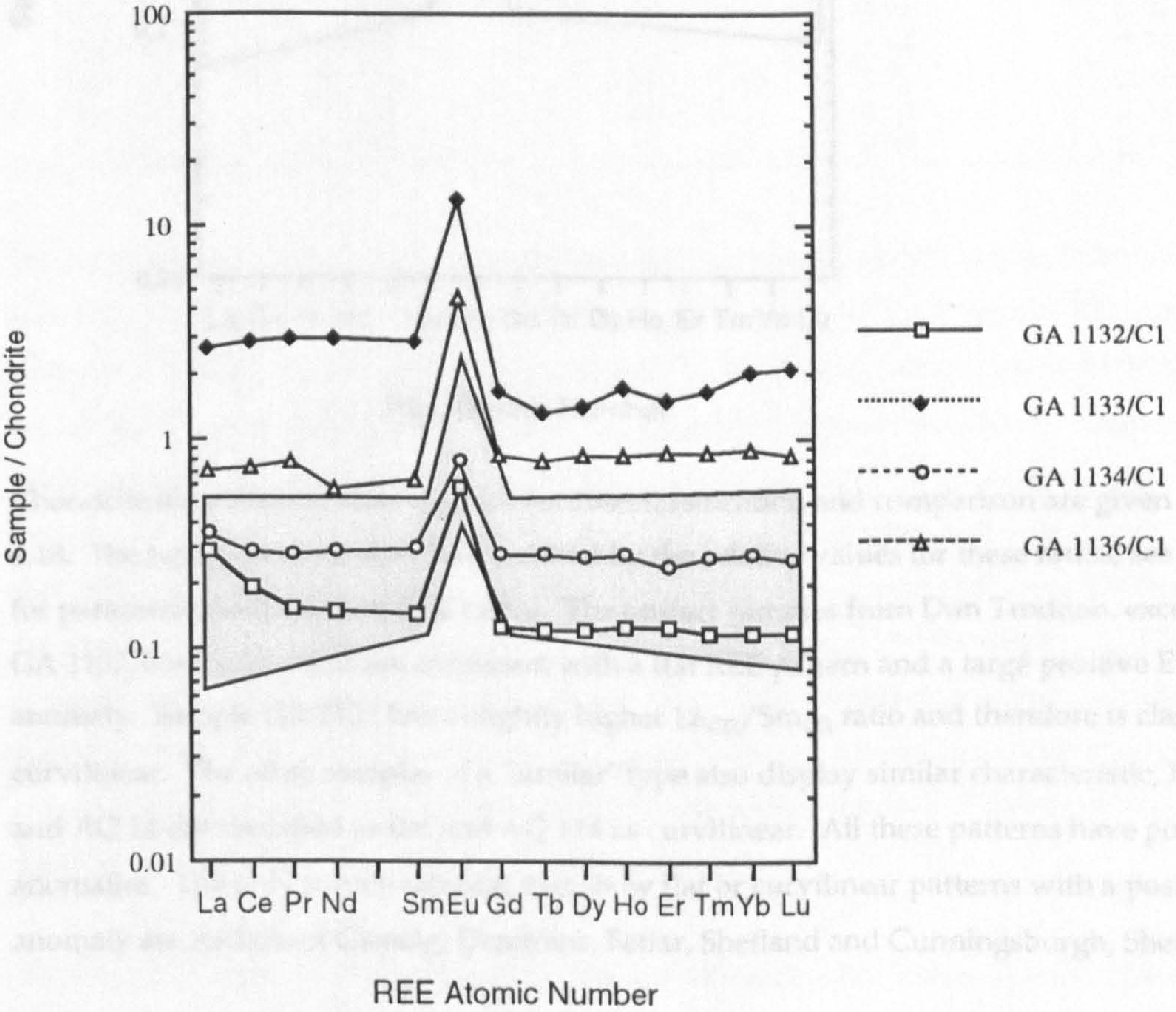
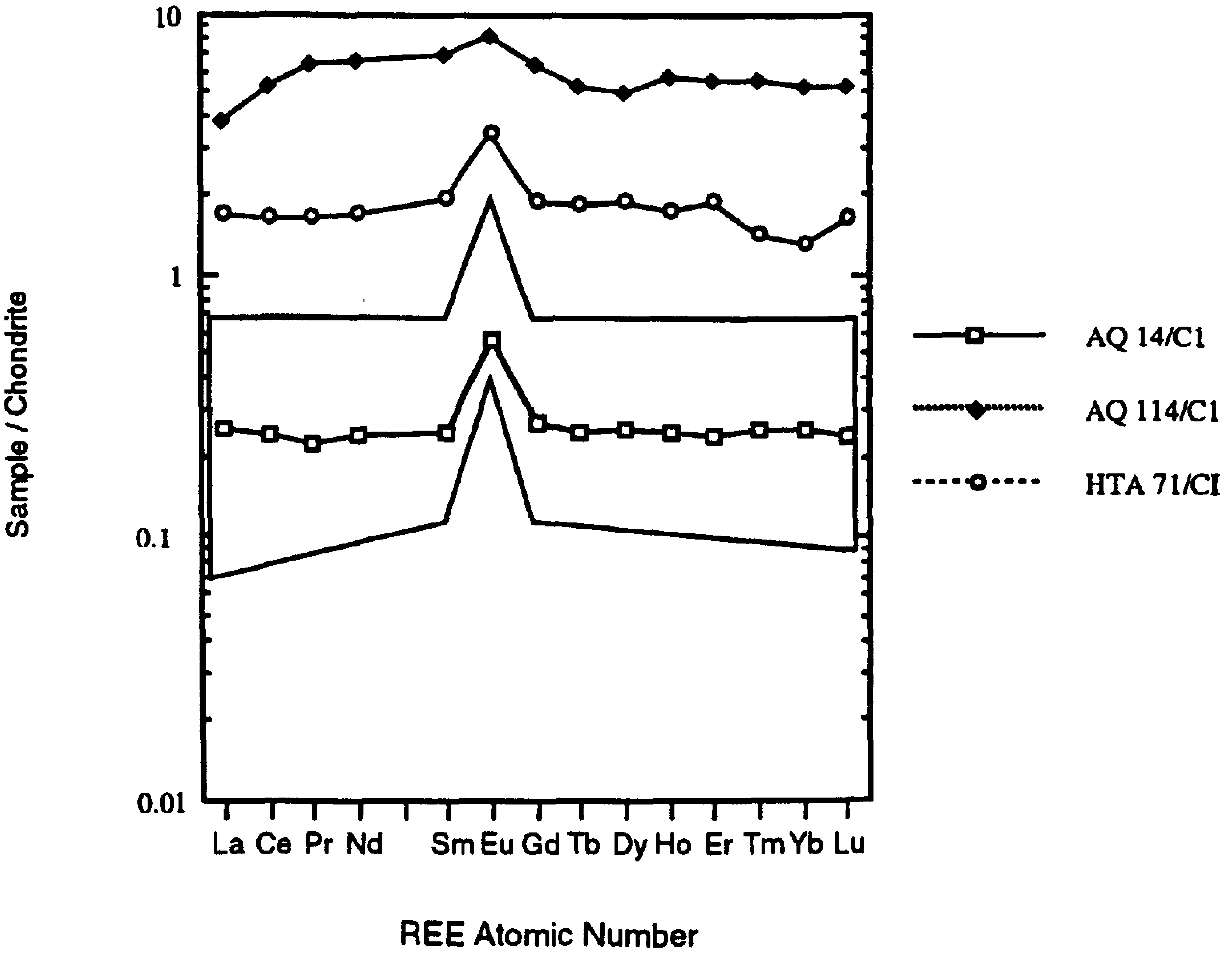


Figure 6.33 Chondrite normalised REE abundances of steatite samples from Killilan, Lochalsh (AQ 14), Dundonald, Ayrshire (AQ 114) and Hyndford crannog, Lanarkshire (HTA 71) comparison with the source quarry at Ardintoul, Glenelg, shaded area.



Chondrite normalised ratios used for further classification and comparison are given in table 6.18. The types of curves may be described by the relative values for these ratios, see chapter 4 for parameters and types of REE curve. The artifact samples from Dun Troddan, except sample GA 1132, have ratios that are consistent with a flat REE pattern and a large positive Eu anomaly. Sample GA 1132 has a slightly higher La_{cn}/Sm_{cn} ratio and therefore is classified as curvilinear. The other samples of a "similar" type also display similar characteristic, HTA 71 and AQ 14 are classified as flat and AQ 114 as curvilinear. All these patterns have positive Eu anomalies. The only source samples that show flat or curvilinear patterns with a positive Eu anomaly are Ardintoul Glenelg; Dammins, Fetlar, Shetland and Cunningsburgh, Shetland.

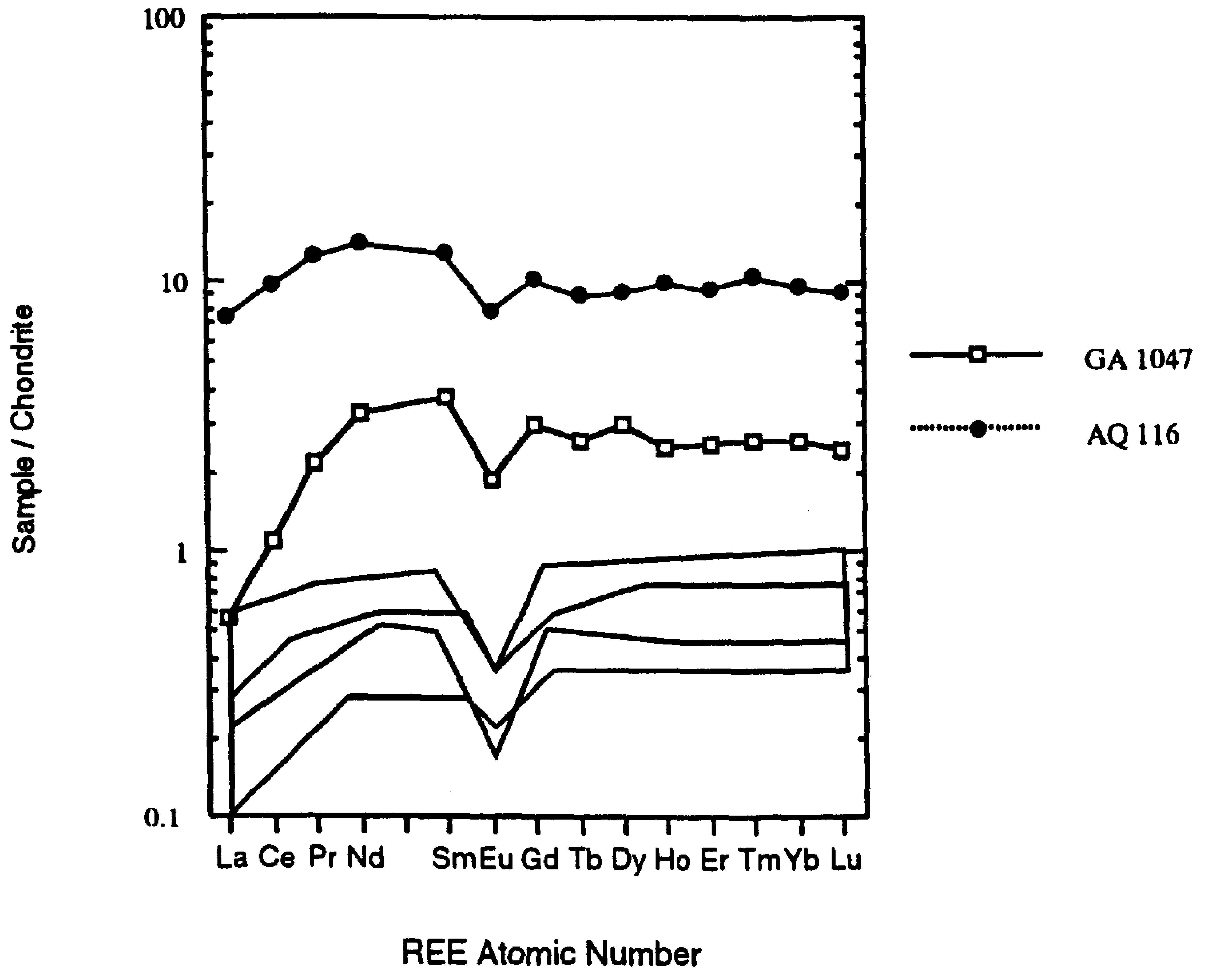
Table 6.18 Chondrite normalised ratios for artifact samples

Sample	La_{cn}/Lu_{cn}	La_{cn}/Sm_{cn}	Gd_{cn}/Lu_{cn}	Eu_{cn}/Eu_{cn}^*
GA 979	2.97	0.52	4.91	0.73
GA 984	0.89	0.26	3.19	0.51
GA 985	0.38	0.19	1.66	0.79
GA 986	3.03	0.89	2.97	0.40
GA 989	1.95	0.67	1.95	0.67
GA 1132	2.45	2.01	1.05	4.35
GA 1133	1.28	0.92	0.79	5.74
GA 1134	1.35	1.19	1.09	2.69
GA 1136	0.84	1.08	1.02	6.19
GA 1047	0.23	0.15	1.22	0.56
AQ 14	1.05	1.03	1.11	2.19
AQ 116	0.80	0.58	1.09	0.67
AQ 114	0.73	0.55	1.23	1.25
BD 35	13.57	3.39	3.00	0.86
HD 1748	7.61	1.49	3.70	0.61
HTA 71	1.03	0.85	1.15	1.80
HSA 726	2.41	4.90	0.54	6.06
HSA 182	6.81	3.91	1.19	2.59
HSA 672	1.69	1.29	1.17	2.28
HSA 722	7.55	4.46	1.29	3.19
HSA 688	3.52	5.45	0.55	2.16

The comparison of the chondrite normalised REE patterns from the samples from Dun Telve (GA 979, GA 984, GA 985, GA 986, GA 989) is more problematic if the type of REE curve is compared. These patterns are difficult to classify as the overall patterns show a HREE depletion, but most display a depletion of La, Ce and Pr. If these samples are compared with source patterns that exhibit a typically HREE depleted, negative Eu anomaly pattern, three sources can be identified Eilean Glas, Scalpay, Harris; Hillswick Ness, Shetland and Orra Wick Shetland. However, on further inspection these patterns display considerable differences from the artifact samples. None of the patterns from these sources show the depletion of La, Ce and Pr displayed by the artifact. Furthermore, the Eilean Glas sample shows some enrichment in these elements. Also, in the cases of the Hillswick Ness and Eilean Glas sources the general extent of the Eu anomaly does not reflect that of the artifact samples. Thus these source quarries seem unlikely sources for the artifact material.

If sources that show LREE depletion and negative Eu anomalies are considered, there are two possible source quarries; Clibberswick, Unst, Shetland and Fethaland, North Roe, Shetland. However, again on further inspection these sources show differences from the artifact samples. Although, displaying the initial LREE depletion neither of these REE source patterns feature the HREE depletion characteristic of the artifact samples. A similar comparison can be made for the artifact samples that displayed similar patterns to those of the Dun Telve material, Dun Beag, Skye (GA 1047), Caisteal Grugaig, Lochalsh (AQ 116) and Carlungie I, Angus (HD 1748). The sample from Carlungie I displays a similar pattern to that of the Dun Telve material and thus a similar conclusion can be made. However, the samples from Dun Beag and Caisteal Grugaig although similar do not show a marked HREE depletion. Thus these samples are in some respects comparable with both the Fethaland and Clibberswick material, figure 6.34. However, both artifact samples display much higher REE abundances than seen in the source material. The sample from Caisteal Grugaig also displays a more marked LREE depletion than the source samples. Thus there is no evidence at this stage to support an association with either of these sources.

Figure 6.34 Chondrite normalised REE abundances in steatite samples from Dun Beag, Skye (GA 1047) and Caisteal Grugaig, Lochalsh (AQ 116), compared with steatite sources Fethaland, North Roe, Shetland (unshaded box) and Clibberswick, Unst, Shetland (shaded box).

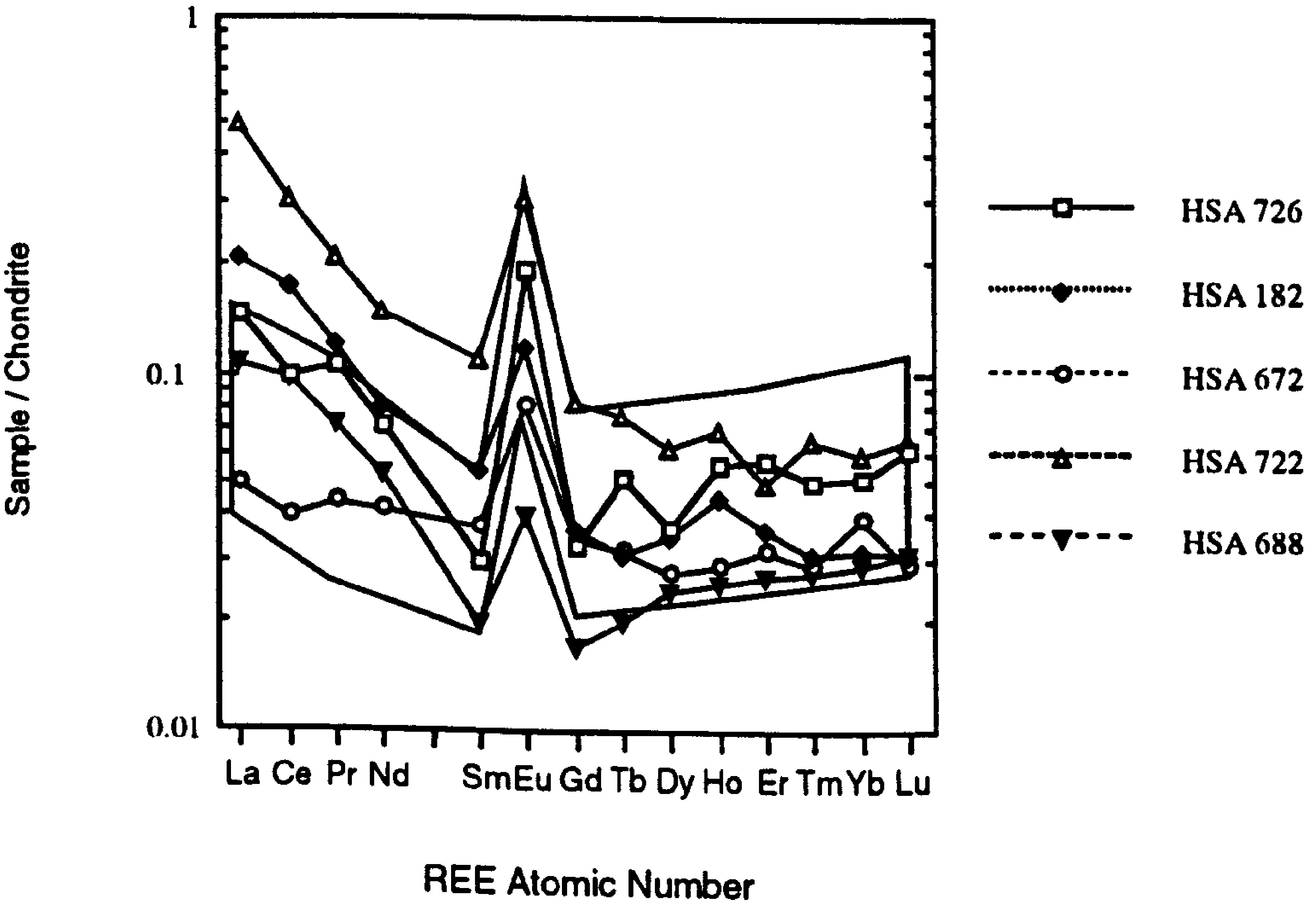


The chondrite normalised ratios for the samples from Dun Telve emphasis the limitations of this method in the determination of a classification scheme. These samples cannot be assigned to any present group. Chondrite normalised ratios for samples GA 979, GA 984, GA 985, GA 989 suggest a downward V-shaped pattern with a negative Eu anomaly. Sample GA 986 ratios suggest a flat LREE and strongly depleted HREE pattern. These suggested patterns are merely a reflection of the points on the curve used in the classification. The initial LREE depletion is not recorded as the depletion towards the HREE results in the La and Sm values being nearly comparable. Thus comparison with currently sampled source material reveals no similar patterns. There are several possible implications, either these samples comes from a British source not yet analysed, or from an overseas link, as yet not established.

The artifact samples with similar REE patterns to those of Dun Telve samples, Dun Beag, Skye (GA 1047), Caisteal Grugaig, Lochalsh (AQ 116) and Carlungie I, Angus (HD 1748) also can be classified by the use of chondrite normalised ratios. HD 1748 displays similar values to the unclassified GA 986, suffering from the same curve sampling problem as discussed above. GA 1047 is classified as LREE depleted concave with a negative Eu anomaly. Only source zmf-7 (Fethaland) is comparable with this pattern. The differences between this source and the artifact have been discussed above, figure 6.34. AQ 116 is classified as curvilinear with a negative Eu anomaly. Only sources sample zmf-1 and zmf-2 are comparable with this sample. However differences between these patterns have already been demonstrated, see figure 6.34. This REE curve does not show the sharp La and Ce depletion, and the general HREE depletion of the other samples of similar general trend. Therefore this sample may have to viewed as separate from the other groups.

Artifact samples from Jarlshof (HSA 672, HSA 681, HSA 688, HSA 722, HSA 726).are also compared to source material. The chondrite normalised REE pattern displayed by these samples is one of LREE depleted or V-shaped REE pattern, with a positive Eu anomaly. Only two source samples exhibit these characteristics, Cunningsburgh, Shetland and Damshead Quarry, Portsoy. A more detailed examination of the REE patterns shows the Portsoy source to exhibit marked HREE depletion with relatively high LREE abundances, characteristics not displayed in the artifact samples. However, the artifact samples display many of the features seen in the Cunningsburgh samples, figure 6.35.

Figure 6.35 Chondrite normalised REE abundances in steatite samples from Jarlshof ((HSA 672, HSA 681, HSA 688, HSA 722, HSA 726), compared with the steatite source at Cunningsburgh, Shetland (shaded).



The Jarlshof samples again emphasise the limitations of the REE classification system. Although all the patterns are comparable, the classification system places the samples in three separate groups and one is unclassified, HSA 726 V-shaped, HSA 182 and HSA 722 HREE depleted concave, HSA 672 flat and HSA 688 unclassified. All these patterns show positive Eu anomalies. The possible source quarries based on these classifications are Cunningsburgh, Shetland; Ardintoul Glenelg, Dammins Shetland and Portsoy. However, the visual inspection demonstrates that the Cunningsburgh source is the most likely, see figure 6.35.

The single artifact sample from Muness, Unst (BD 35) displays a HREE depleted pattern with no Eu anomaly. Only one source sample analysed exhibits a similar pattern, the source at Toward/Inellan, Cowal. However, this source seems unlikely for reasons that will be discussed later.

6.8 Provenance of Artifact Material

This section reviews the results of the univariate/bivariate analyses and multivariate analyses of the trace element data and REE analyses in order to assess the likely provenance of the artifact material analysed.

The samples from Dun Troddan are probably the easiest to deal with and therefore will be discussed first. The univariate/bivariate analysis and the multivariate analysis strongly suggest that the material is from a Lewisian source. Principal component analysis reveals some differences between these samples and the Lewisian sources, a fact that may account for the placing of two samples in the Dalradian region by discriminant analysis (although the other three discriminant analyses classified these samples as Lewisian). This may indicate that more sampling and analysis of Lewisian sources is required to fully characterise this source. The REE analysis demonstrated that only a single quarry site, of the sites analysed, shows a similar pattern to that of the Dun Troddan samples, Ardintoul Glenelg. This site is part of the Lewisian tectonic region and thus these results are consistent with the univariate/bivariate and multivariate analysis.

A Lewisian source is also suggested, by the univariate/bivariate and multivariate analysis, as the most likely origin of the artifact samples from Dun Telve. Results from both PCA and discriminant analysis imply that the Lewisian is the source region for all samples. Thus a fair degree of certainty can be attached to this interpretation. REE analysis reveals that all the samples have similar REE patterns, and hence a single quarry site is the most likely hypothesis. However, none of the quarries analysed so far have a REE pattern that matches these samples. Therefore an as yet un-sampled quarry site within the Lewisian appears to be the most likely explanation. Within the Glenelg region there are a number of small outcrops of steatite that have not been analysed, eg. in the left bank of the small unnamed burn that flows into Loch Duich 100 m south of Dhruideig cottages [NG 877 244], and 300 m up the Allt Mor

[NG 845 168]. A body is also reported by Wilson & Phemister (1946) in the Allt Utha, which flows into the Arnisdale River about 2 km from Loch Hourn, although no trace of it was found when quarry sites were visited. The site at Allt Mor appears the most likely source as Dun Telve is only 2 km away, although neither site showed signs of exploitation. An alternative is that an as yet undiscovered steatite body was the source of this material.

The sample from Dun Beag, Skye is similar in many respects to the material from Dun Telve. It exhibits similar trends in the univariate/bivariate and multivariate analysis, consistent with a Lewisian source. The REE pattern is also similar in many respects, although it does not show the same HREE depletion as the Dun Telve samples. Even with these slight differences this sample probably originates from the same source as the Dun Telve material, and as such may reflect some small variation in the REE abundances within this source.

The Caisteal Grugaig and Killilan samples have univariate/bivariate signatures that closely match the Lewisian sources. Although, in a number of respects they also resemble Dalradian and Ophiolite sources, eg. Killilan low Ba concentration. However, the results of the multivariate analysis place both these samples within the Lewisian field. Both samples appear similar from the univariate/bivariate and multivariate analysis, but the REE patterns demonstrate that they are from different source quarries. The Killilan sample has a REE pattern similar to that of the Dun Troddan samples, and it plots within the known field of the Ardintoul source. Thus this is most probably the source of the artifact. The Caisteal Grugaig sample has a REE pattern similar to that of the Dun Beag sample. Again the lack of HREE depletion seen in Dun Telve samples is apparent. A similar interpretation of small in-site variation is considered to be the most likely explanation. Therefore this sample is considered to have originated from the same source as the Dun Beag and Dun Telve samples.

The other samples from the Scottish mainland are far from potential steatite quarries and their presence on these sites implies some considerable movement. The Hyndford and Carlungie samples both have characteristics similar to that of the Lewisian source region in both the univariate/bivariate and multivariate analysis. The Dundonald sample displays univariate / bivariate results that offer no insight into the provenance, but the multivariate analysis suggests Lewisian characteristics. REE patterns are able to resolve some of the problems in these samples. The Carlungie sample has a similar REE pattern to that of the Dun Telve material. Although the absolute REE concentrations are slightly higher, the patterns are remarkably similar. Thus the same source is considered the most likely explanation. The possible sources have been discussed above. The REE patterns from the Hyndford and Dundonald artifacts display similar patterns to that of the Ardintoul source in Glenelg. Although the absolute concentrations are higher than the range described by the source samples, another source seems unlikely, as these results are consistent with the univariate/bivariate and multivariate results.

The Jarlshof samples display a univariate/bivariate character that is not Lewisian. As the other source groups cannot be resolved from one another no comment can be made as to the provenance. The multivariate analysis reveals a similar non-Lewisian source and demonstrates similarities to the Cunningsburgh source. Discriminant analysis places the samples in the Dalradian or Ophiolite tectonic regions. These results indicate that the Lewisian tectonic region is not the source of the Jarlshof material. REE patterns indicate that only the source at Cunningsburgh has a similar REE pattern to the artifact material. This source is the largest in Britain and was heavily exploited in the past (Smith 1989). Cunningsburgh is also one of the closest steatite sources to Jarlshof, which is only 20 km away. Thus it can be convincingly argued that Cunningsburgh is the most probable source of these samples, although the possibility of a small source within Shetland or a Norwegian source cannot be ruled out.

The Muness, Unst sample is very enigmatic. The univariate/bivariate analysis suggests that the sample is most closely related to the Lewisian source although in many cases the trace element values are dissimilar to all known tectonic regions. PCA suggests a source related to ophiolitic material, although the discriminant analysis suggests this as well as a Basement type source. The REE pattern is only similar to a single source; Toward/Inellan, Cowal. This is considered not to be a likely source, as Unst has a great abundance of potential steatite sources, including many that have been utilised in the past, whereas the Toward source is on the Firth of Clyde. The import over many hundreds of miles of a resource that is widely abundant on the island where the artifact was found is considered extremely unlikely. This sample may be from an as yet un-sampled source in Shetland. Alternatively the strange signature may reflect a source in Scandinavia that possesses a different signature from British material.

6.9 Implication of Artifact Provenance

In the previous section the probable provenance of the artifact samples was discussed. In this section the archaeological implications of these results will be discussed.

Characteristics of Iron Age settlement and material culture have long indicated a contrast between different areas in Scotland (Piggott 1966). Clearly in order to understand the social/economic and political structure in the Iron Age, conclusive evidence of contacts between these areas is vital. At present, traditional sources of information on such contacts, such as pottery, metalwork and glass, reveal little useful information. MacKie (1974) typologically distinguished two broad groups from Dun Mor Vaul, Vaul Ware, the antecedent of so-called "native pottery" which is considered to be for the most part local, and Everted Rim Ware, in which he saw parallels with pottery of the Wessex area. However, this long-distance connection has not been widely accepted (Lane 1987). Petrological analysis of the pottery from

Gurness indicated it was overwhelmingly local in origin, "exotic" material could not be assigned to any particular source and may also be from the local area (Williams 1987). Topping (1987) suggested that most ceramic production in the Atlantic Province was local and that there were no clear production centres or subsequent trade/exchange of the finished product. Thus it can be concluded that pottery is unable to provide good evidence for contacts during this period. Metalwork too has not yet proved a good indicator of contact. The subjective claims are based on art-historical interpretation (MacGregor 1976) and hence should be treated with care .

The study of glass beads has proved a little more promising. A number of different types of glass beads have been recognised from the Iron Age (Guido 1978). One of these types (Guido class 8) has been shown by analysis to have two production centres, one in Somerset and one in Moray (Henderson & Warren 1983). Beads of the North-east Scottish group have been found on two sites in the west. Henderson (1991) has suggested that glass making was highly specialised and took place at a number of centres for exchange. Although, by the nature of the material being used as a provenancing tool, particularly the widespread distribution of the raw materials and the effects of technological change on a combination of raw materials, this means that these studies cannot be conclusive. Henderson (1989) has argued for widespread trade/exchange in this material in Scotland during the late Iron Age, and cites examples of class 8 beads originating from Culbin Sands, Moray found at Dun Troddan, Glenelg; Dun Fiadhairt, Skye; Kirkmadden, Wigtonshire and Glenluce Sands Wigtonshire and may demonstrate contacts between different cultural areas. Two other bead types (Guido 1978, class 13 and 14) show a concentration in the north-east of Scotland, with a spread to the west.

Other artifact classes provide hints of inter-regional exchange. The distribution pattern of handled stone cups (Steer 1956) has been considered as evidence for exchange between regions. Clearly if the steatite cups, which make up 60% of the total, can be provenanced, this will provide much more conclusive evidence for these contacts.

The results obtained from the current steatite provenancing work sheds important new light on this thorny problem of resource use and movement in the Iron Age. The west coast artifact samples demonstrate the use of local resources. The samples of whorls from Dun Troddan appear to originate from the quarry at Ardintoul, which is only 10 km from the site, figure 6.65. The Killilan handled cup also originates from this source. The Dun Telve, Dun Beag and Caisteal Grugaig whorls and cups are all from a Lewisian source that is not the Ardintoul quarry. On the basis of their similar REE patterns, all these artifacts appear to originate from a single source. There are a number of possible sources in the Glenelg region; the burn near

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Dhruideig [NG 877 244], 300 m up the Allt Mor [NG 845 168] and a body in the Allt Utha. The Allt Mor source is only 1.5 km from Dun Telve, figure 6.36. One of these would appear to be probable, as other Lewisian sources are relatively distant (Scalpay, Harris Scara Rubha, Harris and Loch na h'Oidhche in the Sheildaig Forest), and these do not have the characteristic REE pattern of the artifact samples. The utilisation of local resources by the inhabitants of these brochs and duns demonstrates that the inhabitants of the Glenelg and Skye region were aware of this local resource and its potential as a raw material for both domestic and decorative items.

The other artifacts from the Scottish mainland all come from sites that are far removed from any steatite sources. Thus by their presence on these sites relatively long-distance trade/exchange can be inferred.

The cup/lamps from Hyndford and Dundonald have similar characteristics to the Ardintoul quarry in the Glenelg region. This demonstrates that the material from this region was traded across long distances, from the Atlantic Province to the lowland areas of Scotland. Similar evidence for long distance contact is provided by the Carlungie cup/lamp. This artifact has a chemical characteristic consistent with the premise that it originates from a Lewisian source (all Lewisian sources are within the Atlantic province), probably in the Glenelg region.

Steatite cups/lamps may have been regarded as a prestigious item in the southern and eastern provinces of Scotland, where steatite would not have been readily available either as goods or as a raw material. This steatite evidence is particularly important as there is little proof for contacts between the separate provinces during this period. Currently the only direct evidence of east-west contact that exists is a spiral snake armlet of eastern Scottish type (the distribution is concentrated in Angus) from Duntulm, Skye (MacGregor 1976), and the evidence from glass beads, mentioned above (Henderson 1989). This steatite evidence is the first material which can be shown to originate in the Atlantic Province and be distributed to the Solway-Clyde, Tyne-Forth and North-Eastern Provinces. This is very valuable evidence indicating that the Iron Age provinces of Scotland were not isolated from one another, but that contacts and trade did exist.

The Norse artifacts from Shetland were included to enable the technique to test material that was considered most likely to originate from a source other than Lewisian sources. It has been suggested for a number of reasons that Cunningsburgh is probably the source of these artifacts. In Shetland the possibility of these artifacts originating from Scandinavian raw material cannot be ruled out. As Scandinavian sources have, as yet, remained un-characterised a definite statement cannot be made as to the exact provenance. However if Cunningsburgh is the source, as seems likely, then it is clear that the inhabitants of Jarlshof either recognised and exploited Cunningsburgh as a local resource or traded/exchanged with the people that controlled the quarry area. This is consistent with excavation evidence of the Norse use of the quarry (Smith 1989).

The absence of any information as to the provenance of the Mu Ness, Unst artifact sample precludes any archaeological interpretation at the moment, and any suggestions would be unsubstantiated conjecture.

6.10 Conclusions

The importance of provenance studies to the study of cultural contacts and thus societies in the past has already been emphasised. This study, through the utilisation of trace elements selected from previous analysis, has demonstrated significant differences between Lewisian sources, confined to the west coast of Scotland, and all other sources. REE have also been used in order to allow more site specific source characterisation.

Twenty-one artifact samples, principally from Scottish mainland sites, have been compared to the known sources. As only British steatite sources have been characterised, artifact material and the Lewisian sources (west coast) were distinguishable from other sources. The artifact material selected was mainly of pre-Viking date and hence reduced the possibility of sampling Scandinavian source artifacts, as yet un-characterised, as there is no evidence for contact with Scandinavia in the Iron Age. A number of artifacts from Shetland were included for comparison as Lewisian sources were thought to be unlikely in these cases.

Analysis has revealed that artifacts from a number of Iron Age sites in Glenelg, Lochalsh and Isle of Skye have characteristics consistent with an origin from local Lewisian sources. Furthermore, in the case of artifacts from Dun Troddan and Killilan the quarry site at Ardintoul can been recognised as the source of these artifacts. These results clearly indicate that the inhabitants of these sites in the Iron Age were aware of this local resource and utilised it for a range of domestic and decorative items.

The other artifacts from mainland Scotland are from the southern and eastern Iron Age provinces. These also have characteristics similar to those of Lewisian sources, and in the cases of the Hyndford and Dundonald artifacts the Ardintoul source appears to be the probable quarry site. Thus the provenance of these artifacts gives important conclusive evidence for contact between different regions in the Scottish Iron Age, a period where there is little other direct evidence for such contact.

The artifacts from Jarlshof are comparable with the source at Cunningsburgh, Shetland. Although this source seems likely, it cannot be definitely established, as these artifacts may have Scandinavian sources with similar characteristics to the Cunningsburgh source. However, the probability is that Cunningsburgh, Britain's largest steatite quarry, which is close to Jarlshof, is the source of these artifacts. If this is correct then it shows the inhabitants of Jarlshof were utilising the local material in preference to imported material and other Shetland sources, although further analysis would be required to establish Cunningsburgh as the exclusive source.

Unfortunately no positive provenance can be established for the sample from Mu Ness, Unst. Its chemical characteristic is not comparable with any British source yet analysed.

The utilisation of local steatite sources by the inhabitants of the west coast brochs has been confirmed by this study. These sources were also the origin for a number of steatite artifacts from the southern and eastern provinces. Thus steatite provenance studies may be regarded as an important part of growing evidence, along with an armlet and glass beads, for contacts between the Iron Age provinces in Scotland. What scientific analysis cannot do is demonstrate how the artifacts were exchanged, whether a direct exchange between regions or hand-to-hand *down the line* trade from farmstead to farmstead and chief to chief (Renfrew 1975). However, analysis does provide the raw material for discussion.

This study demonstrates that extremely useful archaeological information may be gained from steatite provenance studies, although there are some remaining ambiguities and there is a need for further source characterisation. In order to better define the field of source regions, particularly the Lewisian source, a greater range of source samples should be analysed. Also, the intra-site variability must be assessed; if this variability is relatively low in elements that discriminate between sources then provenance may be established at the site specific level. Clearly, REE coupled with other techniques may potentially provide an excellent means of achieving this site specific provenance. Therefore REE analysis of all Lewisian sources may allow a more specific provenance to be established for the artifacts known to be of a Lewisian source origin.

These results clearly enable the provenance of artifacts to be positively established for the first time. However, in some cases the exact provenance cannot as yet be recognised, although in these cases the broad source region can often be established, which still enables useful archaeological interpretation to be made, or by negative inference, possible sources may be limited (i.e. the artifact did not come from that source). This can still be of use in interpretation and may in the future, with additional techniques, help in the establishment of the exact source.

CHAPTER 7 : DISCUSSION AND SYNOPSIS OF THE TECHNIQUES USED IN THIS STUDY AND THEIR IMPLICATIONS FOR ARCHAEOLOGICAL STUDIES.

7.1. Discussion of the Techniques used in this Study

In the previous chapters the importance to the study of cultures in the past of establishing artifact provenance was emphasised. If provenance studies are to be both useful and practicable two requirements must be fulfilled; the source material must be of limited abundance and of a restricted distribution, and the artifacts produced must now be found on sites at some distance from possible sources, so implying trade/exchange. It has been demonstrated that steatite satisfies these requirements in the northern Atlantic region from the Neolithic until early historic periods and in particular during the Norse Period.

The physical and chemical properties of the raw material, for which an origin is sought, impose certain limitations on the useful information that may be gained from such provenance studies. This was illustrated by several examples. In the case of obsidian the material displays desirable characteristics; homogeneous sources with distinct compositions that are unaffected by artifact manufacturing processes, hence artifact provenance has been established by a number of different techniques, including major elements (Cann *et al* 1969), trace element (Gordus *et al* 1971) and isotope ratio (Gale 1981) analysis. By contrast materials such as pottery (Wilson 1976) and glass (Sanderson & Hunter 1984), which also exhibit considerable compositional variability, encounter restrictions associated with the abundance of the raw materials and changes in the material brought about during manufacture. These factors present considerable obstacles for provenance studies, although information of a technological nature can be obtained from analytical work. Clearly, lithic materials, such as steatite, are largely unaffected by physical, chemical changes during the artifact production and the reuse of the raw material. Also steatite, along with many lithic materials utilised by cultures in the past, has a restricted geographical distribution, and thus the raw material is relatively scarce. However, as an essentially crystalline material, whose major chemistry is highly constrained by the formation requirements, it does not exhibit gross compositional differences from source to source. Steatite is thus an example of a material whose past utilisation, source distribution and relative scarcity are well suited to provenance studies, but whose physical properties present major analytical challenges to such work. It is a difficult material to provenance.

The use of steatite throughout prehistory and early historic periods, especially by island communities in the Northern Atlantic Region remote from posssible sources, make the successful provenancing of great archaeological value.

The complex formation processes that result in steatite were discussed, enabling techniques that might allow source characterisation and provenance establishment to be assessed. From this study it was apparent that because of the complex nature of steatite paragenesis and the resulting deposits, relatively simple techniques would not be suitable for unique source characterisation. These factors had not been considered by early workers (MacGregor 1956, Resi 1979, Kohl *et al* 1979, Buttler 1984, Olabanji 1991) in their attempts to provenance steatite. It was apparent that techniques such as hand identification, petrological examination, mineral phase identification by XRD and analysis of major elements by a range of techniques are unable to provide useful information for a provenance study.

Steatite and similar deposits form bodies that are mineralogically heterogeneous on the outcrop scale. Thus in order to obtain a "representative" sample of the body, for many elements, large samples are required. This is obviously impractical if artifacts are to be compared. Also, the conditions under which steatite forms are relatively restricted, so the major components in most deposits are similar. These factors are probably the source of the relatively simple provenancing techniques (MacGregor 1956, Resi 1979, Kohl *et al* 1979, Buttler 1984, Olabanji 1991) will be unable to characterise and separate individual sources or source regions. This fact was recognised at the outset and therefore it was considered that the most useful information could be obtained from trace elements and isotope ratios as these would be less affected by the general heterogeneity of the sources. These factors discussed above emphasise the importance of understanding the chemical and physical properties of a material and how these are affected during formation, thus enabling an educated decision to be made about the provenancing methods required. In the future more work will be required if trace elements are used in the characterisation and provenancing of artifacts in the comparision of error and sample size.

The challenge of the development and identification of a technique that would enable useful information to be gained from artifact comparison with source material was tackled from several different approaches. The initial approach utilised the multi-elemental capabilities of ICP-MS, that enabled 60 trace elements to be analysed. By a rigorous and structured statistical analysis, both univariate and multivariate, of the data obtained, the elements that displayed differences between steatite sources could be identified. This approach made no a priori assumptions as to the elements that might display differences between sources. The data were allowed to reveal their underlying structure and hence any elements that discriminated between the different sources. The other approach targeted elements that, due to their known geochemical behaviour, would be expected to demonstrate differences between the sources. It has been suggested that the REE are of use in steatite characterisation studies in North America (Allen *et al* 1975, Rogers *et al* 1983), although the information they provide was not proved to be conclusive. Studies of northern Atlantic steatite sources utilising REE have proved less successful (Buttler 1984, Moffat & Buttler 1986), due to lower absolute concentrations and poorer analytical precision than was obtained by the American workers. It was also thought that Sr isotopes might distinguish between different sources through differences in the steatite's host rocks; some are surrounded by metasediments with relatively high $^{87}Sr/^{86}Sr$ ratios whereas others are surrounded by ultrabasic and basic rocks with relatively low $^{87}Sr/^{86}Sr$ ratios. In the following paragraphs I shall review and discuss the results of these different approaches.

The multi-elemental trace element study is different from some studies undertaken in archaeological provenancing in that many trace elements have been analysed and their ability to discriminate between sources has been assessed by a structured use of both univariate and multivariate statistics. The ability of the ICP-MS to analyse trace elements with a reasonable degree of precision was required if differences between sources were to be established. This precision was evaluated during the period of the study in order that elements with poor precision could be recognised and thus allowances made in later analysis. During this study 20 elements were measured with a coefficient of variation of less than 10% and 34 elements less than 20%. Multi-element semi-quantitative analysis is claimed by the manufacturer to have a precision of around 20 - 30% (Date & Gray 1989), however as this and other studies (Taylor & Garbarino 1988), have shown, this figure varies considerably from element to element depending on the abundance of the specific isotope being monitored for the determination. Clearly ICP-MS, through its ability to analyse a wide range of elements from a relatively small sample with low detection limits, offers great potential for archaeological studies. The speed of analysis also makes this technique relatively inexpensive.

The analysis of a range of British steatite sources resulted in a data set with potentially complex multi-element relationships between a large number of variables. This study offers an example of a structured approach to the analysis of such data in order to extract the maximum useful information. This structured statistical approach adopted in the study enabled the identification of elements that distinguish between sources. The univariate and the multivariate analyses identified a number of trace elements that have the ability to discriminate between sources: Sr Nb, Ga, As, and Ba. Other elements, although unable to discriminate sources, but displaying great potential at resolving source regions, were also identified. Principal component analysis identified these and several other groups of elements that displayed differences between sources: REE, transition elements, and PGE.

Although analysis of these data was unable to resolve all the geological groups, several different combinations of variables; ie. i) soluble trace elements (Rb, Cs, Ba, Pb, Sr and B), ii) immobile trace elements (Zr, Hf, Nb, Ga, Ta, La, Ce), and iii) trace elements that were identified from univariate analysis (Sr, Sm, Nb, Ba, As, Sb, Ga), came close. The soluble trace elements and trace elements identified from univariate analysis were able to distinguish the Lewisian sources (confined to the west coast of Scotland) from all other sources. The important archaeological implications of this will be discussed in the following section.

This approach enabled the elements that demonstrated an ability to discriminate between sources to be identified and further investigated. Seventeen of these elements; B, Ga, As, Rb, Sr, Y, Zr, Nb, Sb, Cs, Ba, La, Ce, Sm, Hf, Ta, Pb, were analysed and sources compared to artifact samples, principally from Iron Age Scottish Mainland contexts. These analyses confirmed and extended differences observed between the Lewisian sources and all other sources, namely relatively high Ba, Nb, Ta, Pb concentrations and relatively low As concentrations. Bivariate scatter plots, using combinations of Ba, Cs, Nb and Pb, demonstrate that the Lewisian samples may be separated from the other tectonic groups. Further multivariate analysis, PCA and discriminant analysis, utilising all seventeen trace elements and selected sub-groups, were to further able resolve the Lewisian sources.

The REE were identified by PCA in the multi-element study as being potentially useful in discriminating between sources. Geochemical considerations, such as their large ionic radius and coherent group behaviour, also suggested their potential usefulness for provenancing studies. However, conflicting evidence existed from previous studies as to the potential use of selected REE for steatite provenancing. Allen *et al* (1975), Allen & Pennell (1978) and Rogers *et al* (1983), from NAA of between five and eight REE, demonstrated considerable differences in chondrite normalised REE patterns existed between individual sources, and that these differences are not recorded within a source. However, the data of Buttler (1984) and Moffat & Buttler (1986) showed that variation within individual quarries is as large as that noted between sources. This study has demonstrated that ICP-MS can produce accurate and precise results for the analysis of all fourteen REE, thus providing for the first time accurate and precise results, at the low levels encountered in most steatites, of all the REE, displaying much more detailed information than previous studies.

The analysis of a set of samples from British steatite sources has demonstrated that the REE show considerable variation in both concentration and chondrite normalised pattern between different sources. Furthermore, steatite samples from a single source show that although the absolute concentration may vary, the chondrite normalised patterns remain essentially unchanged. These results resolve the apparently anomalous findings of Buttler (1984) and Moffat & Buttler (1986). In the light of these new results their analytical data must be considered of questionable validity and thus the interpretation they inferred unsound. The results of this study, with far superior analytical conditions available, demonstrate that the REE are extremely promising as highly specific indicators of provenance, the important implications of which are reviewed in the next section.

While at the outset the problem was apparently intractable, there is now justification for continuing detailed investigation of intra-source variability. There was little justification for a detailed study unless significant differences could be established between different sources. A number of challenging areas still exist with this method. Firstly, the method of comparison of REE patterns is considered. Geochemists generally use a simple visual comparison, however for artifact comparison this is rather subjective and may prove time consuming if a large source data base is established. A numerical means of pattern classification based on chondrite normalised ratios has been suggested, but further work will be required if such methods are to be practicable with respect to artifact studies. It may be that some form of pattern recognition algorithm, or PCA of ratios, that does not have the problems of the ratio method suggested here, will be the solution to artifact-source comparison. Secondly, as no inference can be made about un-sampled quarries, all potential sites must be analysed before artifacts can be provenanced with certainty. However, this study has shown that the REE may provide an important tool in any provenancing study, especially as an individual quarry site may be identified.

Strontium isotopes may be useful for the provenancing of steatite. The different lithologies that host steatite deposits are thought to result in a range of $^{87}Sr/^{86}Sr$ ratios. A range of British sources have been analysed displaying a wide range of $^{87}Sr/^{86}Sr$ ratios. The internal variation within a single quarry site has been documented for a number of different sources. These results demonstrate that artifacts of unknown provenance cannot be assigned to an individual quarry. However, they are able to separate ophiolite and Dalradian sources, although the Lewisian overlaps both of these fields. Other isotope techniques, Pb and Ar, demonstrated great potential, although futher work will be required if these finds are to be confirmed and used for provenance studies. PGE, δD and $\delta^{18}O$ have also been suggested as other techniques that might prove successful for provenancing studies.

7.2 Implications for the Provenancing of Steatite

In the previous section the main techniques considered in this thesis have been discussed. In this section the implications of the results of these different techniques for the provenancing of steatite in Britain and the wider northern Atlantic region will be discussed.

This present study has demonstrated that by analysing all REE, Y, Ba, Cs, Nb, Sr and Pb accurate provenance may be established within Britain. Although no single technique considered in this thesis is able to provide all the "answers" to the provenancing question, many problems can be resolved, and by the use of multiple criteria precise artifact origins have been established. This was not totally unexpected as steatite has geochemical characteristics that make simple source characterisation, useful for provenance studies, difficult. Ultimately the ideal situation would enable the exact quarry an artifact originates from to be identified, and it is highly significant that this has been shown to be a possiblity in certain cases by the use of REE. However, valuable archaeological information may still be obtained from provenance studies that are less site specific, that is if a regional characteristic, the scale of which will dependent on the particular method used, can be utilised. Future work must concentrate on the refinement of these multiple techniques used. Currently ICP-MS offers relatively rapid analysis of many elements and is thus cost effective. Furthermore having dissolved the sample it is possible to conduct a number of related ICP-MS and TIMS from a single samples. In addition the data handling and statisics must be defined in order to enable a routine provenance to be established at different levels.

The trace element analysis by ICP-MS and subsequent statistical analysis identified certain trace elements as having potential for discriminating between the different geological provinces outlined in chapter 2. These elements were able to discriminate between the Lewisian sources, confined to the west coast of Scotland, and all other sources. Subsequent higher precision analysis in chapter 6 confirmed and enhanced this source characterisation. This ability to discriminate between Lewisian and all other sources is particular relevant to the utilisation of steatite in Scotland, outwith the Northern Isles in the period prior to the Viking invasion/settlement. Although steatite use was limited, the Lewisian sources appear to have possibly been exploited during this period, if the abundance of the material on local sites is taken as evidence, see sections 1.3 and 6.2. Application of ICP-MS trace element and REE analysis has confirmed this. These methods have enabled the confirmation of this exploitation of a local resource by the inhabitants of Iron Age sites: Dun Troddan, Dun Telve, Dun Beag, Caisteal Grugaig and Killilan, in the Glenelg, Lochalsh and Skye region. However, more significantly this technique has allowed artifacts from sites in the southern and eastern Iron Age regions of Scotland, Carlungie, Hyndford and Dundonald, to be provenanced to the Atlantic Province, and more specifically to the Ardintoul source in certain cases. During the Scottish Iron Age traditional sources of information on cultural contacts, such as pottery (Lane 1987, Williams 1987, Topping 1987), glass (Henderson & Warren 1983), and metalwork (MacGregor 1976) provide little conclusive evidence, see section 6.10. This study provides very valuable information on resource use and movement between and within the Iron Age regions and is the first known occasion on which it has been possible to associate steatite artifacts positively with certain sources. The probable source of artifacts from Norse Shetland has been established as the local Cunningsburgh source rather than the product of the much larger Norweigian industry.

The $^{87}Sr/^{86}Sr$ results demonstrate that Dalradian and Ophiolite sources may be separated from one another, although the Lewisian sources overlap with both the Dalradian and Ophiolite sources. It has already been shown that the Lewisian sources may be identified by separate means hence $^{87}Sr/^{86}Sr$ ratios may be used, in conjunction with trace element data, to separate other two sources. This may have important implications for the provenancing of steatite in

Shetland. Shetland has the greatest concentration of steatite sources in Britain and these were exploited extensively from the Neolithic until the late Norse Period. Sr isotopes may be used to discriminate between sources on the more northern islands of Unst and Fetlar (ophiolite) from that from Mainland Shetland and a minor quarry on Unst. This ability to distinguish these sources may have important implications for the study of steatite utilisation in Shetland, in particular the question of local utilisation of a raw material.

The REE were also considered as potentially useful for steatite provenancing. Results from a selection of British sources indicate that differences in the chondrite normalised REE pattern may be used for source characterisation. This chondrite normalised REE pattern technique is particularly powerful as it may enable site specific provenance to be established. However, due to similarities in the chondrite normalised REE pattern from different quarries this method alone cannot always attribute the origin of an artifact to a single source. The method also has the disadvantage of requiring all relevant sources to be sampled before absolute certainty can be given to results. However, as can be observed from the analysis of the artifact samples for both REE and the selected transition elements, REE can provide unique evidence for the prehistoric exploitation of individual steatite sources. With further parameterisation of source material, both un-sampled quarries and intra-site variabilty the full potential of REE to steatite characterisation may be ascertained.

These methods for the first time individually provide effective steatite source characterisation and provenancing for certain source region and individual sources. Clearly in order to obtain useful information steatite provenancing will require a range of techniques, eg. trace element and REE, to be utilised. This may on the surface alarm traditional archaeologists and museum curators, but most of these techniques require some form of sample dissolution and thus aliquots of this dissolution may be used for several analysis, the proportion depending on the technique and the elemental concentration. Thus a sample of between 100-200 mg may enable multiple analyses to be made. Also the information gained from successful provenance studies can reveal much about cultural contacts and thus the cultures themselves, the ultimate goal of archaeology.

The results of this study have important implications for the study of the difficult problem of resource use and movement, from prehistoric to early historic periods. However, scientific analysis cannot demonstrate the organisation of the resource exploitation and the type of artifact exchange or movement that occurred. Questions still remain as to the extent of professional craftsmen's use of quarries (Skjølsvold 1976, Buttler 1989) and the organisation of quarrying and finished product distribution. The type of trade or exchange is also open to debate. However, analysis and its subsequent implication do provide the evidence that allows substantiated discussion of these topics.

It has been successfully demonstrated that groups of steatite sources and individual sources can be characterised and hence that in certain circumstances the provenance of prehistoric steatite can be ascertained with confidence. It is now possible to contemplate extension of this work in the future studies of trace element and REE characterisation of Scandinavian sources, hence allowing the extension of provenancing to Norse artifacts, probably the most intensive period of steatite utilisation. as well as the provenancing of prehistoric, particularly Iron Age, artifacts. The initial Sr isotope feasibility study may also be extended. $^{40}Ar/^{39}Ar$ of single grains with higher K contents and higher precision Pb isotopes may be potentially useful. Other possible new areas that may enable source characterisation included Platinum Group Elements and stable oxygen and hydrogen isotopes.

7.3 Synopsis

This study is concerned with steatite as a raw material utilised by cultures in the past and traded/exchanged far from its source. Consequently its successful provenancing would provide much valuable information about these cultures, the ultimate aim of archaeology. For the first time all the sources of steatite in Britain have been identified and their geological framework investigated. Clearly the identification of all sources is critical to any provenance study before artifacts can be assigned an origin. This has not been accomplished in a number of previous steatite provenancing studies. The investigation of geological processes that result in steatite formation has enabled educated decisions to be made as to the techniques that might allow successful provenancing. This crucial stage is often not considered before provenancing studies are carried out and thus inappropriate techniques are used with lack of success.

The importance of this work is that, for the first time, it has been possible to demonstrate an ability to distinguish between individual sources within a region, between different regions and to make specific associations between artifacts and steatite sources. Trace elements, and cerain isotope ratios have been identified as the most likely to enable source characterisation. Several different approaches have revealed that a number of discriminating trace elements, the REE and Sr isotopes all display great potential in their ability successfully to provenance steatite. Although no single techniques is able to totally resolve all sources, a combination of the methods discussed in this study allows much important information to be gained from artifact comparison. A relatively small artifact sample may still enable multiple technique analyses to be carried out if appropriate preparation is undertaken. This combination of techniques has proved successful in a study in particular of Iron Age steatite from Mainland Scotland and Norse material from Jarlshof. Cultural contacts have been established, through the trade/exchange of steatite, between the different Scottish Iron Age provinces. This is particularly important during a period when little is known about these links and there is scant evidence from other studies.

With the further refinement of the techniques developed in the thesis, as well as other techniques of which some possibilities have also been suggested, it may be possible to further refine steatite provenance studies thus enabling their extension to new areas and hence new and more challenging problems, such as Norse utilisation, may be resolved. Steatite may no longer be considered the intractable problem it once was considered.

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APPENDIX A

Geological field-description of Sources of Steatite in Great Britain.

This section contains, for the first time, information on the location and a geological description of all of the potential quarry sites within Britain. In Shetland only the largest possible steatite quarry sites and quarries that and those that show signs of working in the past have been included as it was considered that the addition of un-worked bodies would not be beneficial to the provenancing of steatite artifacts. It does however include all possible sites on mainland Britain and other surrounding islands. A description of any signs of working present at these quarries can be found in Section 1.3. The information on these potential quarry sites was collected during visits to these sites in order to obtain samples for characterisation, and from various literature sources. Wilson & Phemister (1946) list talc deposits. Ritchie (1978) also gives much the same information and Buttler (1984) lists many of the Shetland sources.

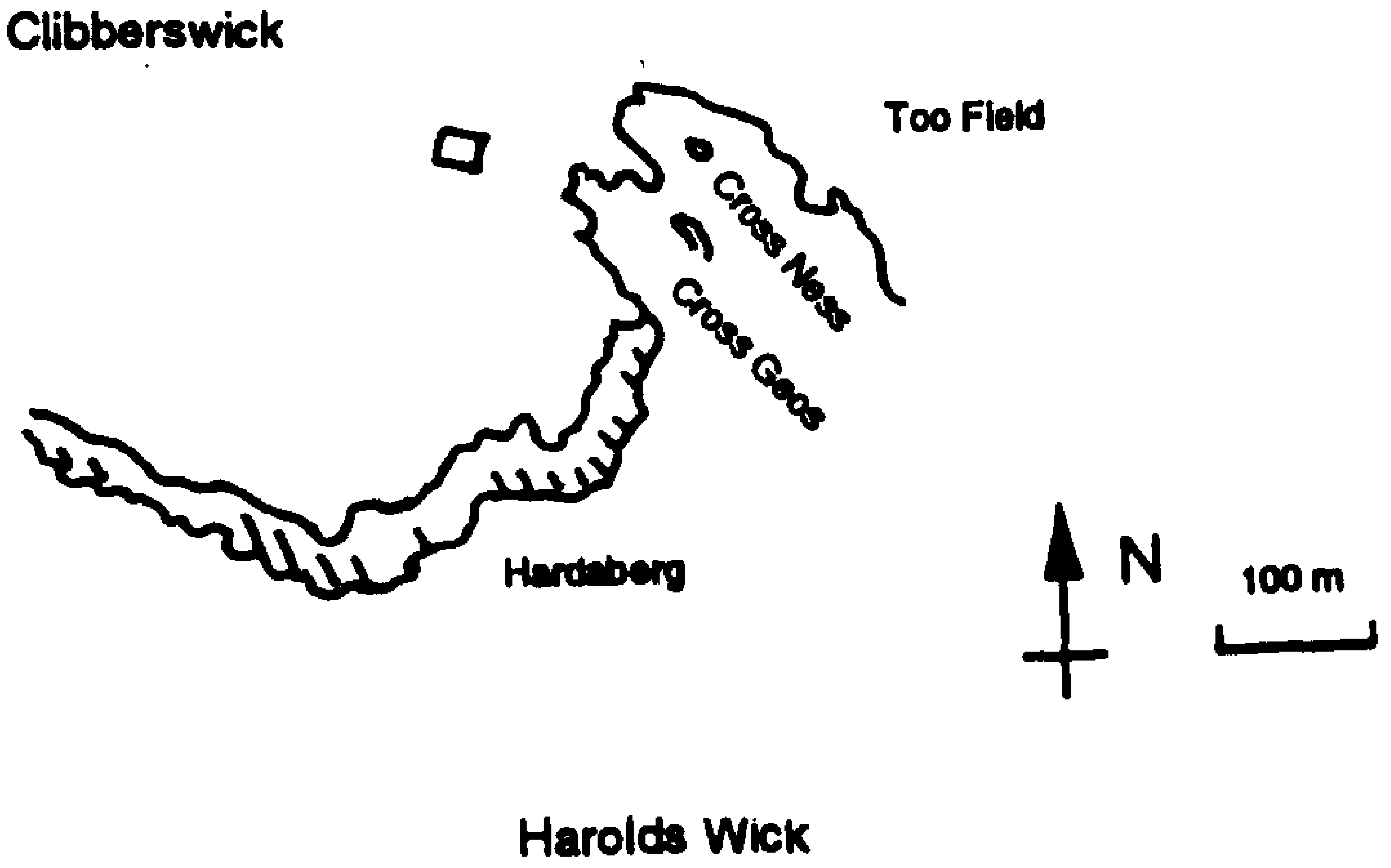
These descriptions represent all the potential sources in Britain, in general the larger quarries and the quarries that display considerable working have been described in greater detail than other sources. This section enables general comparisons to be made between different sources in respect to the style of steatisation. A limited period to time was spent at each site, therefore it may be useful if more detailed comparisons could be made between a sub-set of these sources in the future. For reference to the geological province see table 2.1. Locations of individual bodies are shown in figures 1.1, 1.2 and 1.3, for Shetland, Mainland Scotland and England Wales respectively. More detailed locations are shown by maps of individual localities.

Shetland

Cross Geo, Clibberswick, Unst [HP 652 122]
A large steatite body outcrops on the cliffs at Cross Geo, figure A.1. This body formed where the Clibberswick Serpentine Block is thrust against the Main Serpentine Block. The contact zone shows evidence of being a conduit for fluid flow resulting in steatisation of the serpentinite of the Clibberswick Serpentine Block. The contact is only well exposed where it meets Harolds Wick in Cross Geo [HP 652 122] and in the north at The Taing [HP 654 146]. Small exposures of steatite occur inland along the trace of the thrust zone, but these are mostly small and insignificant. The steatite is cream to pale greenish grey and appears fairly homogeneous with a foliation parallel to the thrust. It is equigranular, 0.5 mm grain size of carbonate surrounded by finer talc with small 0.1 mm opaque minerals which form stripes and sheets parallel to the foliation. Greenish grey serpentine, probably antigorite, also appears in places as amorphous patches. An apple green annabergite also occurs as plates in patches within the deposit. The steatite shows a fine grained phases contact, 20 mm pure chlorite, with

the surrounding serpentinites. The surrounding serpentinites are chloritised and small fractures are filled with vein carbonate.

Figure A,1 Map of Cross Geo area of Clibberswick, Unst.

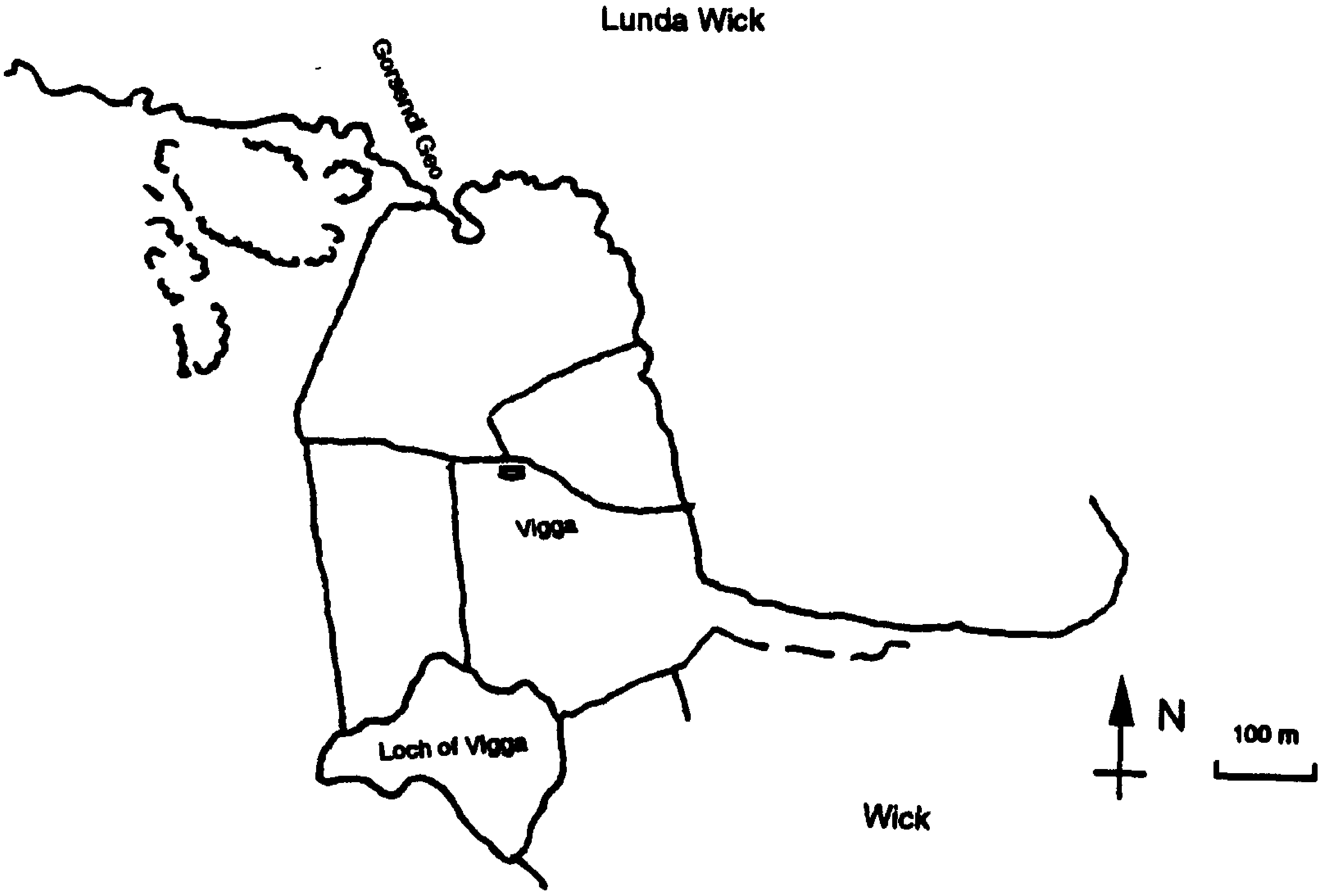


Clammel Knowes, Unst [HP 586 064]
A small remnant of an altered ultrabasic body outcrops to the west of the summit of the small hill of Clammel Knowes. This body occurs within the retrograde tourmaline garnet biotite gneiss of the Valla Field Block occur zoned bodies of altered serpentine that contain cores of talc (Read 1934b). The mass at Clammel Knowes is ca 8 m in diameter. Its relationship to the surrounding country rock is unclear due to poor exposure. The centre of the body is talc surrounded by actinolite-chlorite. Although not much of the talc remains. It is mostly white to pale greenish, 0.3-0.5 mm carbonate-talc-chlorite; small opaque grains form patches.

Gorsendi Geo area, Lund, Unst [HP 565 044]
In the area of Gorsendi Geo and along the shore to the west there are many zoned bodies seen in the Valla Field Block, figure A.2. The largest is a free standing ball on the shore, ca 2m high, figure A.3a. The country rock is purplish semi-pelitic and pelitic gneiss. The orderly zonal sequence is separated from these country rocks by a sharply defined surface made by the smooth skin of the outermost layer, biotite. In some cases later shearing has disturbed this surface. A few metres to the west of the largest body is a spherical ball of steatite that has been sheared into a series of lenses, which are a mixture of various zones. The largest zoned body shows an antigorite core, talc margins, surrounded by talc-schist in which are nodules of actinolite and wisps of biotite occur. The margin of the country rock shows a thin skin of biotite, figure A.3b. Other zoned bodies show different features, spherical interior of talc rock, talc-carbonate-chlorite, surrounded by a complete zone of actinolite, ca 60 mm thick and rimmed by 30 mm of biotite. Others show a simple actinolite-biotite association with no talc present. Here crystals of actinolite radiate from a medium plane to form a lens shaped nodule,

which is surrounded by a biotite sheath. Some examples show a central zone of talc and carbonate with actinolite prisms.

Figure A.2 Map of the Wick area of Lund.



The antigorite zone within these bodies is fine grained grey and green. A little talc appears as wisps and patches and rarely carbonate as irregular patches and a little magnetite.

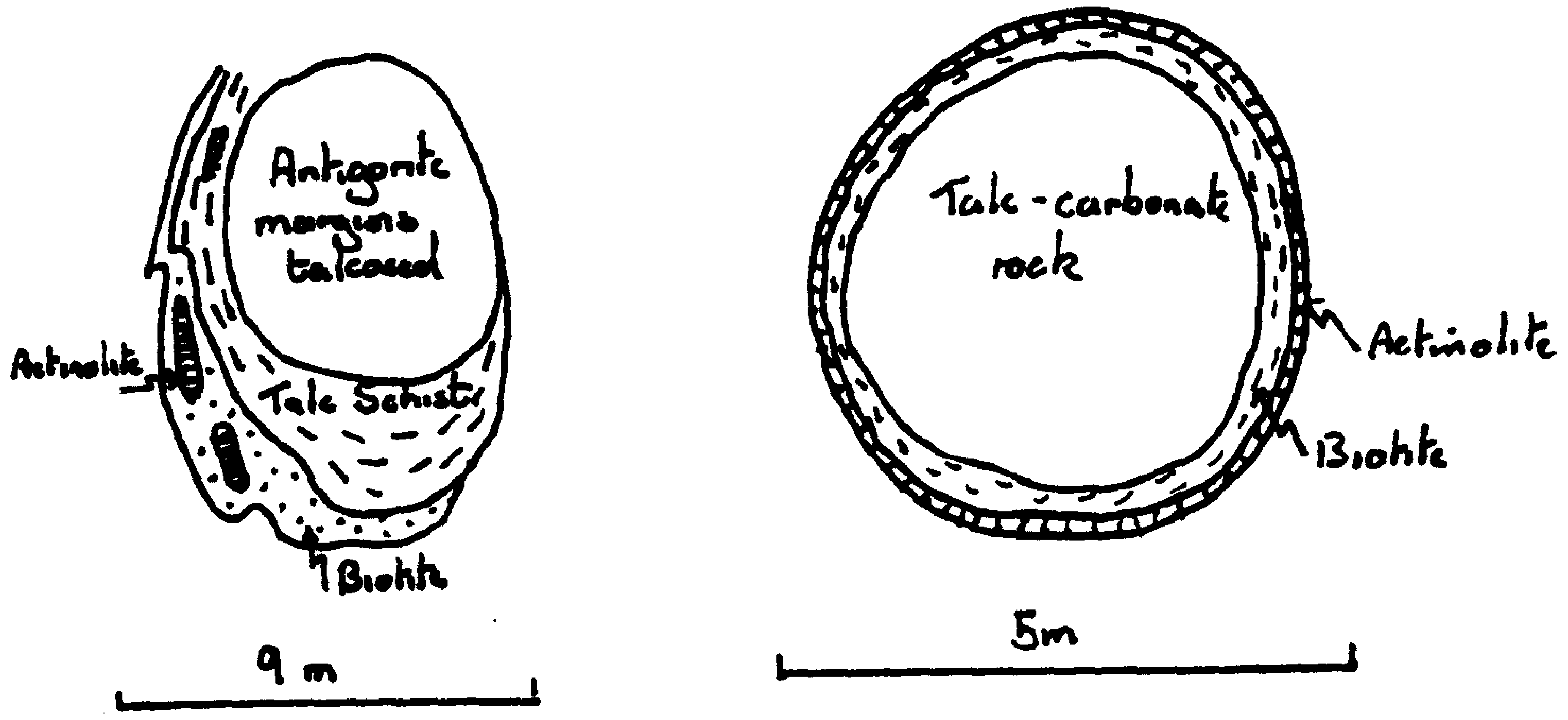
The talc zone is composed of massive talc or foliated talc schists. This foliation is probably a result of the late shearing that affects these bodies. The talc is white or pale green in colour and forms confused wisps and flakes; pale carbonate is fairly abundant along with small knots of chlorite. The talc schists show more chlorite. Foliated carbonate forms in zones between the talc and chlorite. In some case the zone is cut by later veins of green talc and brown dolomite. The edge of the talc zone immediately adjacent to the surrounding actinolite zone increases in the content of amphibole as pale green flat prisms up to 20 mm in length. Generally the main constituent is talc with actinolite, chlorite and small patches of phlogopite.

The actinolite zone is characterised by a bright green rock made up of interlacing sub radial actinolite up to 60 mm in length. This zone is almost pure actinolite with only a few interstitial crystals of chlorite and talc. The proportion of talc increases closer to the border with the talc zone. A similar increase in the chlorite content can be observed near the border of the surrounding chlorite zone. Where this zone is not present the passage to the biotite zone is characterised by biotite and chlorite interstitial between actinolite.

The chlorite zone shows large plates of deep green chlorite with a small percentage of interstitial talc and actinolite.

The biotite zone is pure biotite made up of plates with a poorly expressed alignment. The margin to the country rock is clean cut, defined by the smooth surface of the biotite.

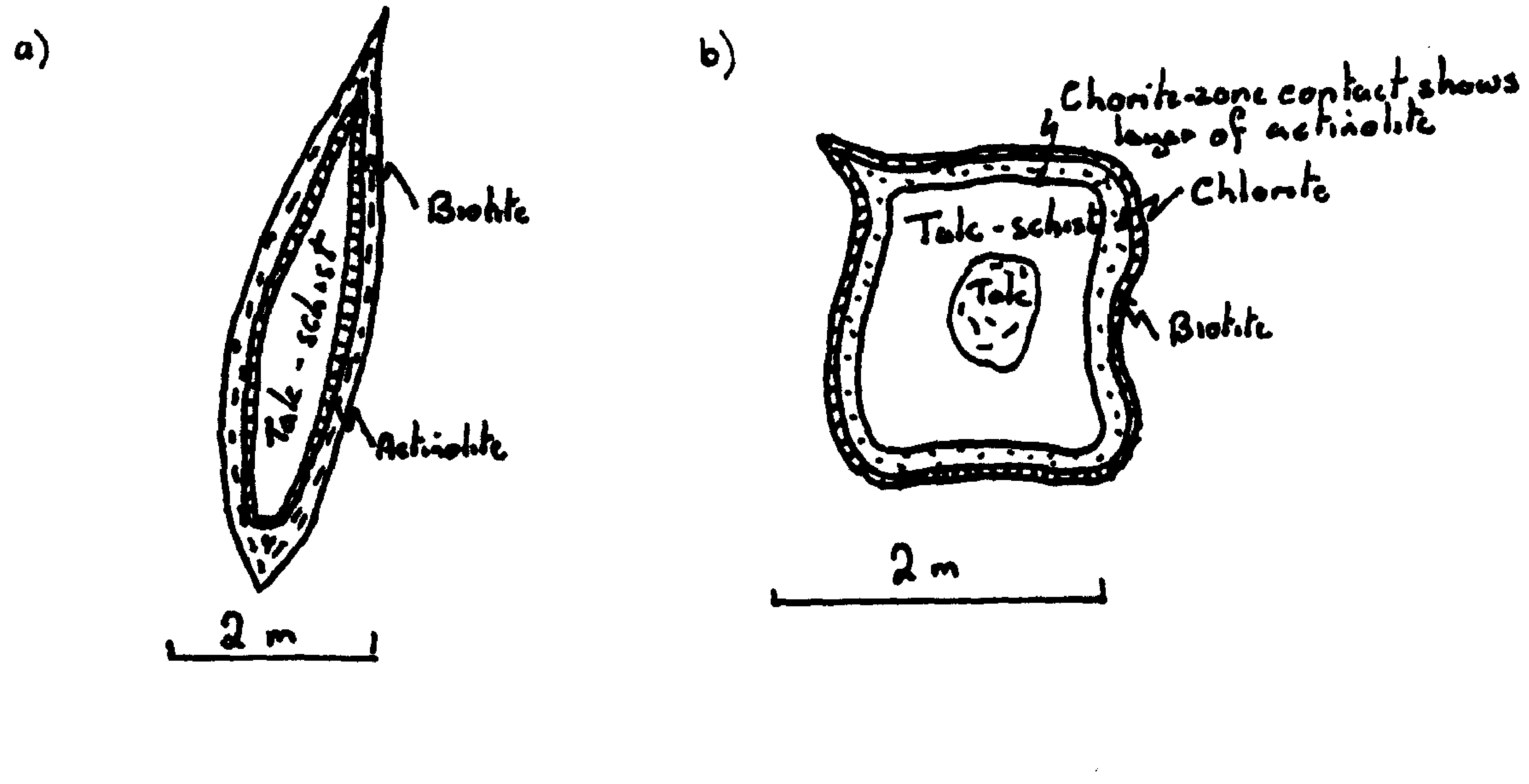
Figure A.3 Field sketchs of the zonal associations of antigorite, talc, actinolite and biotite at Gorsendi Geo.



Houllans Ness, Unst [HP 567 054]

On the west coast of Unst on the shore of the promontory of Houllans Ness a small zoned ultrabasic body outcrops. This body occurs within a mixture of hornblende and pelitic gneiss there are a number of bodies similar to the zoned bodies at Gorsendi Geo. At this locality many are distorted by the late shearing, figure A.4a.

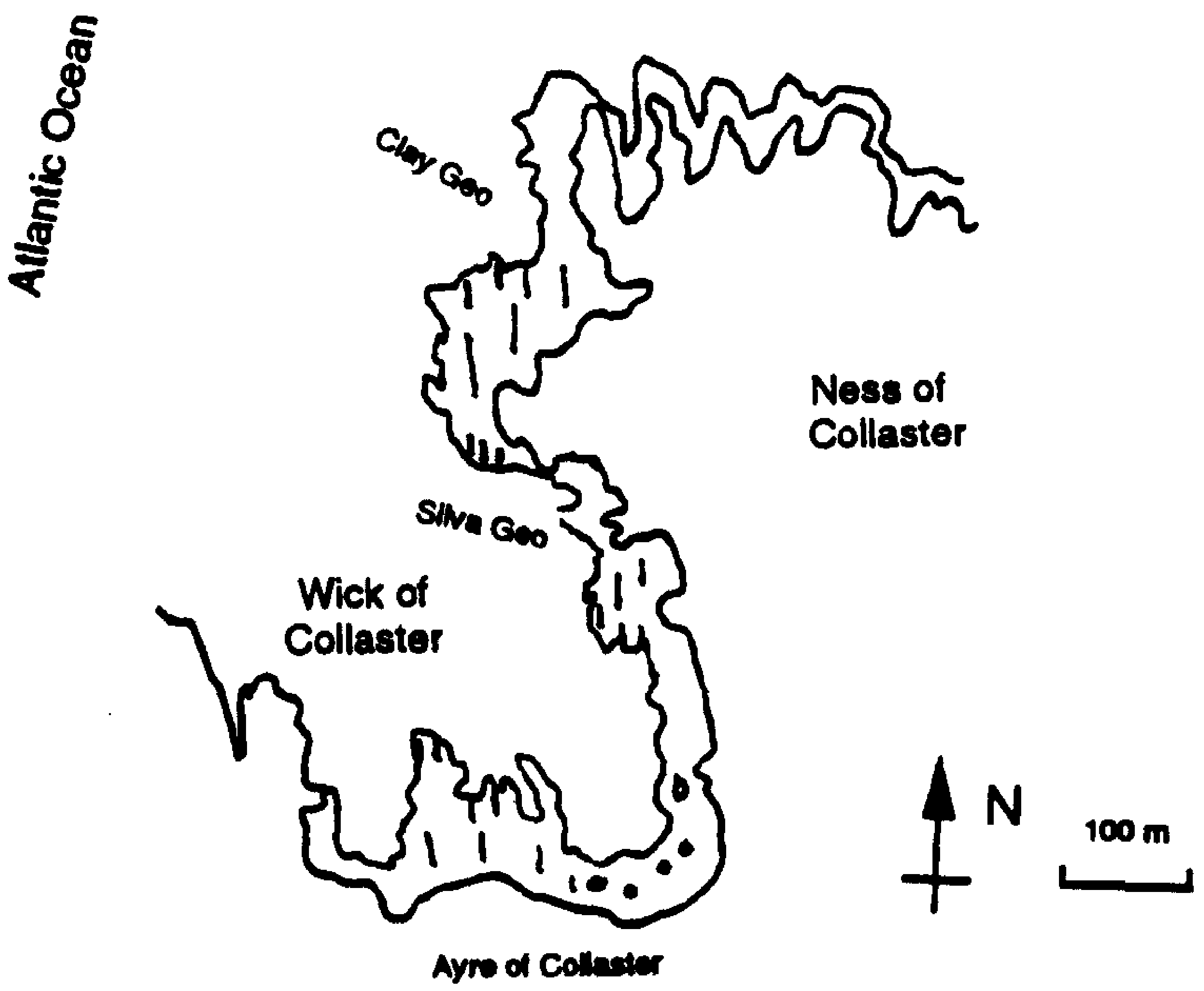
Figure A.4 Field sketchs of the zonal associations of antigorite, talc, actinolite, chlorite and biotite at a) Houllans Ness and b) Ness of Collaster.



Wick of Collaster, Unst [HP 596 077]

A small 2 m diameter zoned body is present on the Wick of Collaster,on the west coast of Unst, figure A.5. The body occurs within the gneiss small zoned bodies similar to those of Gorsendi Geo, consisting of knots of bronze biotite and radiating actinolite occur. However the talc rich zones are poorly developed thus making exploitation improbable.

Figure A.5 Map of the Collaster area of Unst, Shetland.



Clay Geo, Ness of Collaster, Unst [HP 576 077]

On the small cliffs at Clay Geo on the Ness of Collaster a number of small 2 m diameter zoned ultrabasic bodies outcrop. At this locality good examples of the zoned bodies similar to those of Gorsendi Geo occur, as well as deformed bodies, figure A.4b. These have been cut by a large shear plane that runs through the area. The country rock is a striped hornblende granulite cut by many thick pegmatites. The largest body of zoned ultrabasic is 4m by 10m. It consists of white talc schist sheathed in biotite with an irregular zone of actinolite between. Some of the smaller bodies show the complete zoning structure as described before.

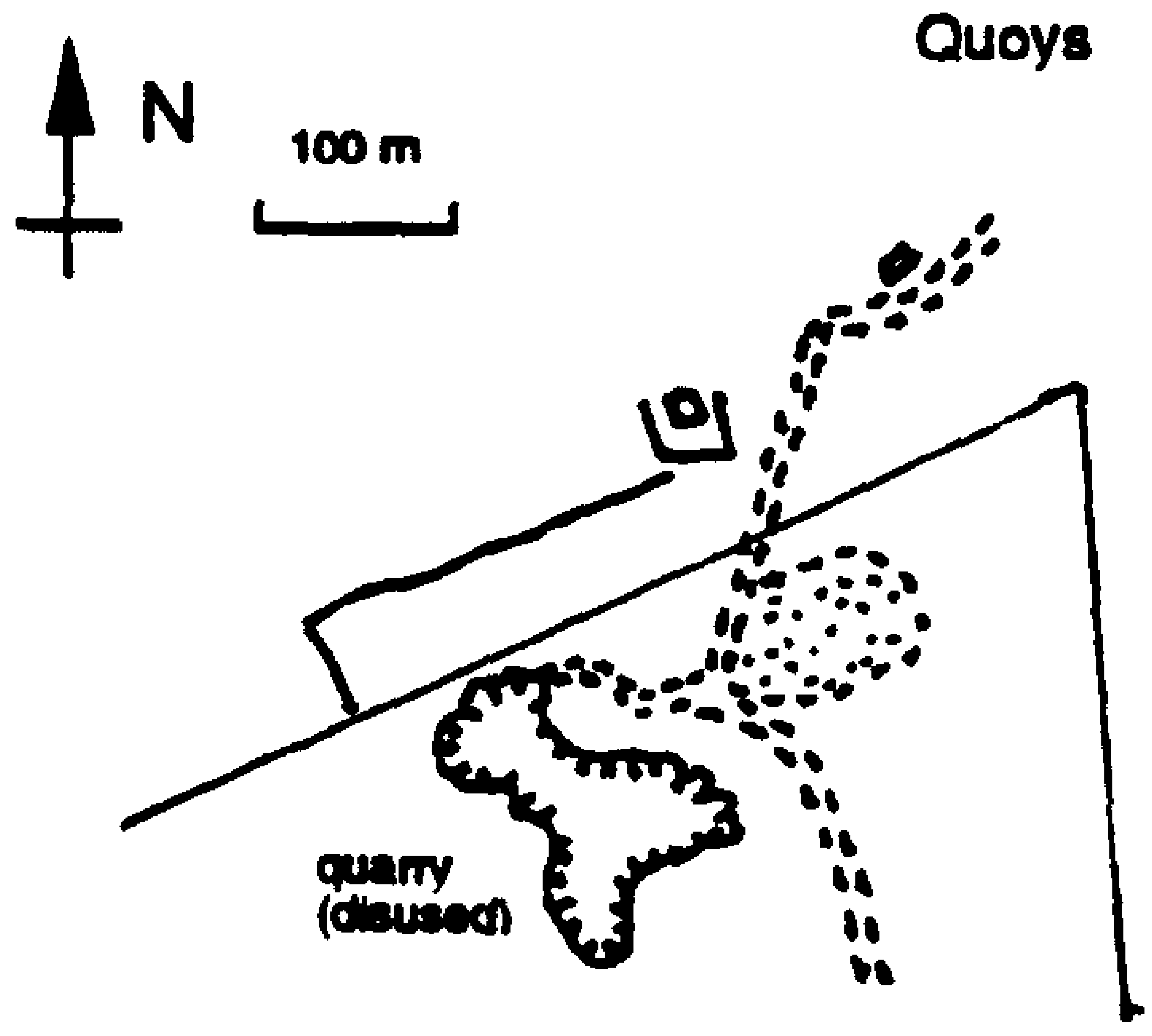
Fiska Wick, Unst [HP 614 156]

An altered ultrabasic body, 4 m diameter, outcrops on the cliff at Fiska Wick in the Burra Firth. The country rock consists of massive feldspathic and siliceous granulites with lesser quantities of semi-pelitic and pelitic bands; pegmatite veins are abundant. In the cliff north of the cove where Burger Stack is, there is an elongate mass of talc schist. It consists of talc-carbonate with wisps of bronze biotite and nodules of actinolite.

Queyhouse, near Burra Firth, Unst [HP 614 123]

A large ultrabasic body, whose diameter is estimated to in the order of 100 m from current outcrop, and which has been highly steatised, outcrops south of Queyhouse, figure A.6. This body occurs within the Main Serpentine Block in which are a number of altered serpentinite masses. The surrounding country rock is an olivine gneiss, composed of mostly olivine with a little tremolite and chlorite, and an antigorite serpentinite. Within these ultrabasic masses altered steatites occur; white and a pale green talc form as plates and clusters between the cream carbonate and rare chlorite. These minerals are generally equigranular ca. 5 mm grain size with smaller 0.1 mm opaque grains which form stripes and sheets. Small 10 mm patches of serpentine remain as relics in some places. The talc deposits occur on shears and incipient thrusts parallel to the main thrust between the Serpentine Block and the Saxa Vord Block. A talc schist, composed of fine grained talc, chlorite, carbonate and magnetite, occur along the thrust zone. This is similar to the talc schist and antigorite above the Stackaberg Thrust on Fetlar. The fact that the alteration occurs on tectonic dislocations suggests that the edges of these bodies are not igneous features but reflect the extent of the original alteration. Read (1934a) suggests that the serpentinisation took place during emplacement of the Serpentine Block, and steatisation not long after or at the same time.

Figure A.6 Map of the Quoys area og Unst, Shetland.



Wick of Hagadale, Unst [HP 641 106]

On the Wick of Hagadale on the east coast of Unst an elongate, 10 m in length, ultrabasic body outcrops. A zone of alteration similar to that at Queyhouse occurs here. However, the body is oriented perpendicular to the main thrust direction. This is probably due to tears or shears within the Serpentine Block during thrusting. The body exposed at [HP 643 165] shows a talc deposit similar to that at Queyhouse, white to grey talc surround slightly larger, 0.4 mm, cream coloured carbonates; small chlorite appear between the carbonates and talc.

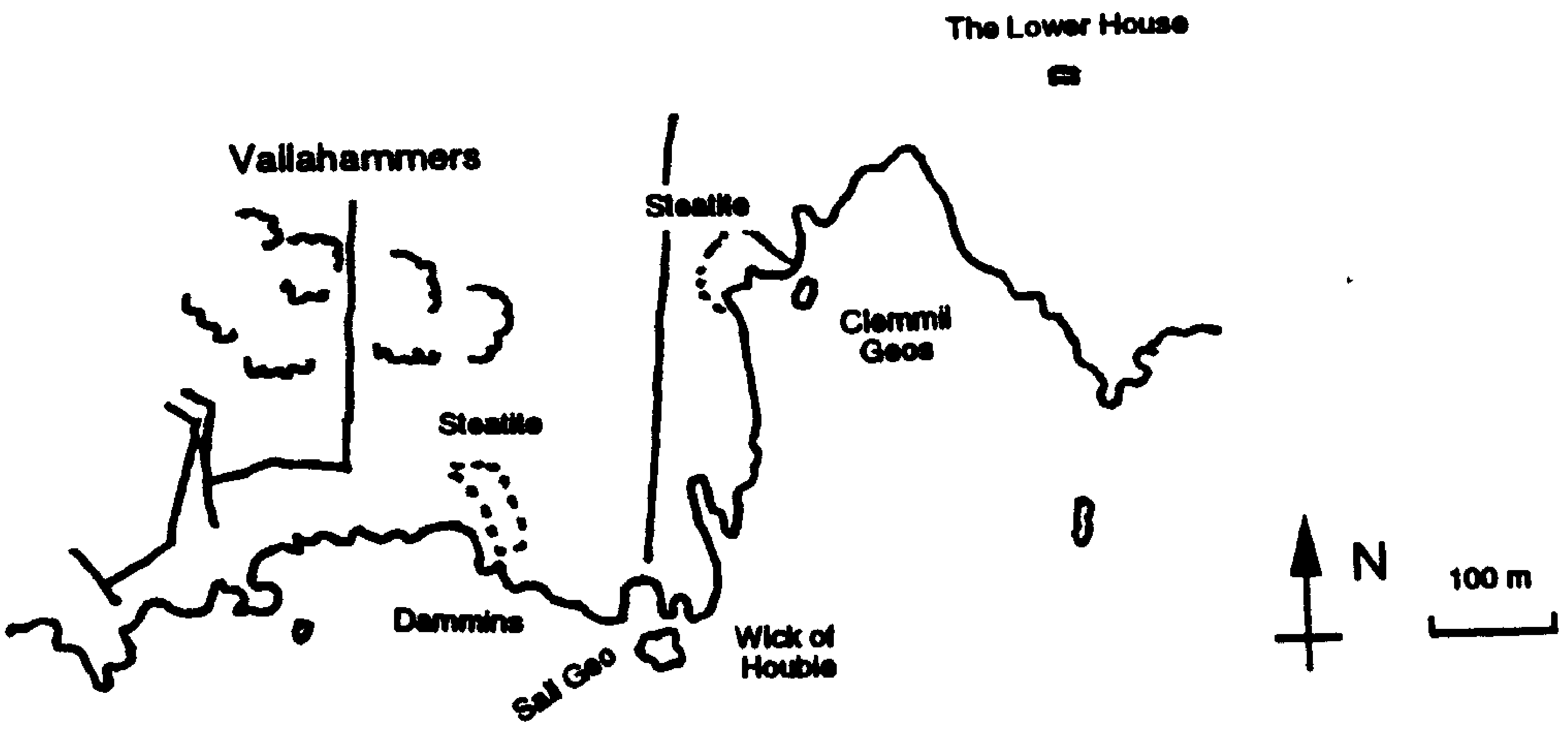
Uyeasound, Unst [HU 599 011]
A small, elongate, 3-4 m wide, steatised ultrabasic body outcrops on the shore at Uyeasound. This body occurs above the main ultrabasic body within the Greenstone Belt. Within this zone there are a number of ultrabasic bodies, especially running from Balta by Longa Water, Vord Hill, Housegarth to Uyeasound. Read (1934a) suggests that these were tectonically emplaced, the greenstone being schistosed against the ultrabasics. These ultrabasics are similar to those in the upper part of the this body. They were originally olivine-pyroxene rocks or pyroxenites, but now they are replaced by tremolite, chlorite, talc and carbonate, and occasional antigorite occurs. The centres of the bodies are coarse pyroxenite with the talc, tremolite and carbonate surrounding them.

Belmont to Head of Mula, Unst [HU 566 966]
A number of mostly small ultrabasic pods, diameter 1-4 m, outcrop from south of the ferry terminal at Belmont to the Head of Mula. These bodies are similar to the other ultrabasics on the thrust between the Main Serpentine Block and the Saxa Vord Block. On the coast at the Head of Mula, the junction of the Serpentine Blockwith the Greenstone Belt shows an altered body of talc schist and talc-serpentine schist.

Scolla Wick, Mu Ness, Unst [HP 634 007]
A small, 3 m diameter, steatised ultrabasic body occurs on the shore at Scolla Wick on Mu Ness, SE Unst. This body, a sheared serpentinite, occurs at the contact between the Mu Ness phyllites and the Mu Ness Greenstone Serpentine Block. This shearing results in a small talc deposit, ca. 1.5 m wide. The talc schist is highly foliated grey green and very fine grained. Occasional opaques are present.

Clemmil Geo, Hubie, Fetlar [HU 620 905]
A large steatised ultrabasic body outcrops on the cliffs above the twin geos at Clemmil near Hubie on Fetlar, figure A.7. This ultrabasic body crops out just within the phyllites of the Aith Block. It has been completely altered to steatite. The contact with the phyllites is not clear. The boundary fault with Tresta Block to the west is not exposed at this point, but is fairly close and may have acted as a conduit for fluid flow during steatisation. A strongly foliated mass of steatite, which shows a large variation in grain size. Most the body is coarse grained, >2 mm, although some of the material to the west of the body is much finer, <0.2 mm. The coarser material is composed of platy grey green talc surrounded by pale brown carbonates which form in patches and clusters; these patches tend to be oriented along foliation planes. There is also occasional green chlorite.

Figure A.7 Map of the Hubie area of Fetlar, Shetland



Dammins, Hubie, Fetlar [HU 618 903]

A large serpentinised ultrabasic outcrops across the whole of the low angle cliff, 200 m X 50 m, at Dammins near Hubie, figure A.7. This ultrabasic body occurs within the phyllites of the Tresta Block. It has been completely serpentinised and patches have subsequently been steatised. Similar to the steatite mass at Clemmil Geo this site occurs close to the thrust contact between the Tresta and Aith Blocks that may have acted as a conduit for fluid flow, probably during or soon after thrusting. This staetite apparently is formed from a large serpentinite mass. The steatite is grey green mottled, with a high carbonate content, and contains large grain of green talc.

Leagarth, Fetlar [HU 627 905]

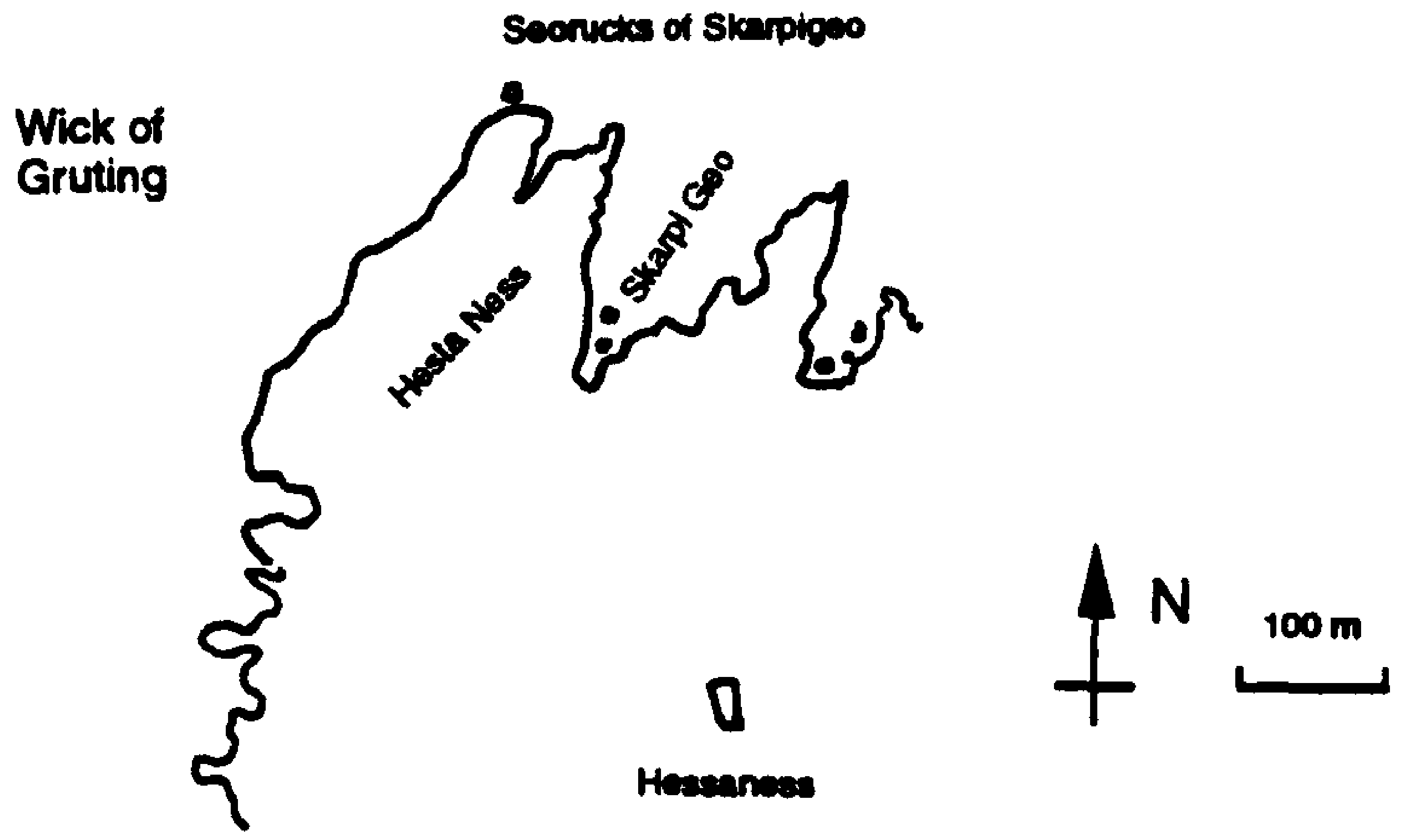
On the shore below Leagarth a small ultrabasic body has been steatised. This body occurs within the Aith Block of Fetlar which contains a number of small talc schist bands. On the shore at Leagarth a thin 4 m wide talc schist is present within the phyllites and serpentinites. It occurs at the contact of the phyllites with a hornblende schist, which may have provided a suitable pathway for steatisation to occur.

Hesta Ness, Fetlar [HU 664 927]

On Hesta Ness there are several steatised ultrabasic bodies. The largest of this group is on the top and half way down the cliffs at Scarpi Geo, figure A.8. These ultrabasic bodies occur within the Strand Block of Fetlar the Hesta Ness serpentinite occurs. This serpentinite has been highly altered to antigorite and steatite. Several outcrops of steatite occur along the east side of the Wick of Gruting and on Hesta Ness itself. The largest body occurs at Scarpi Geo [HP 664 927].

The body is medium grained, 1-2 mm, and is composed of grey talc surrounded by pale carbonates which form patches and clusters. Small opaques occur less commonly.

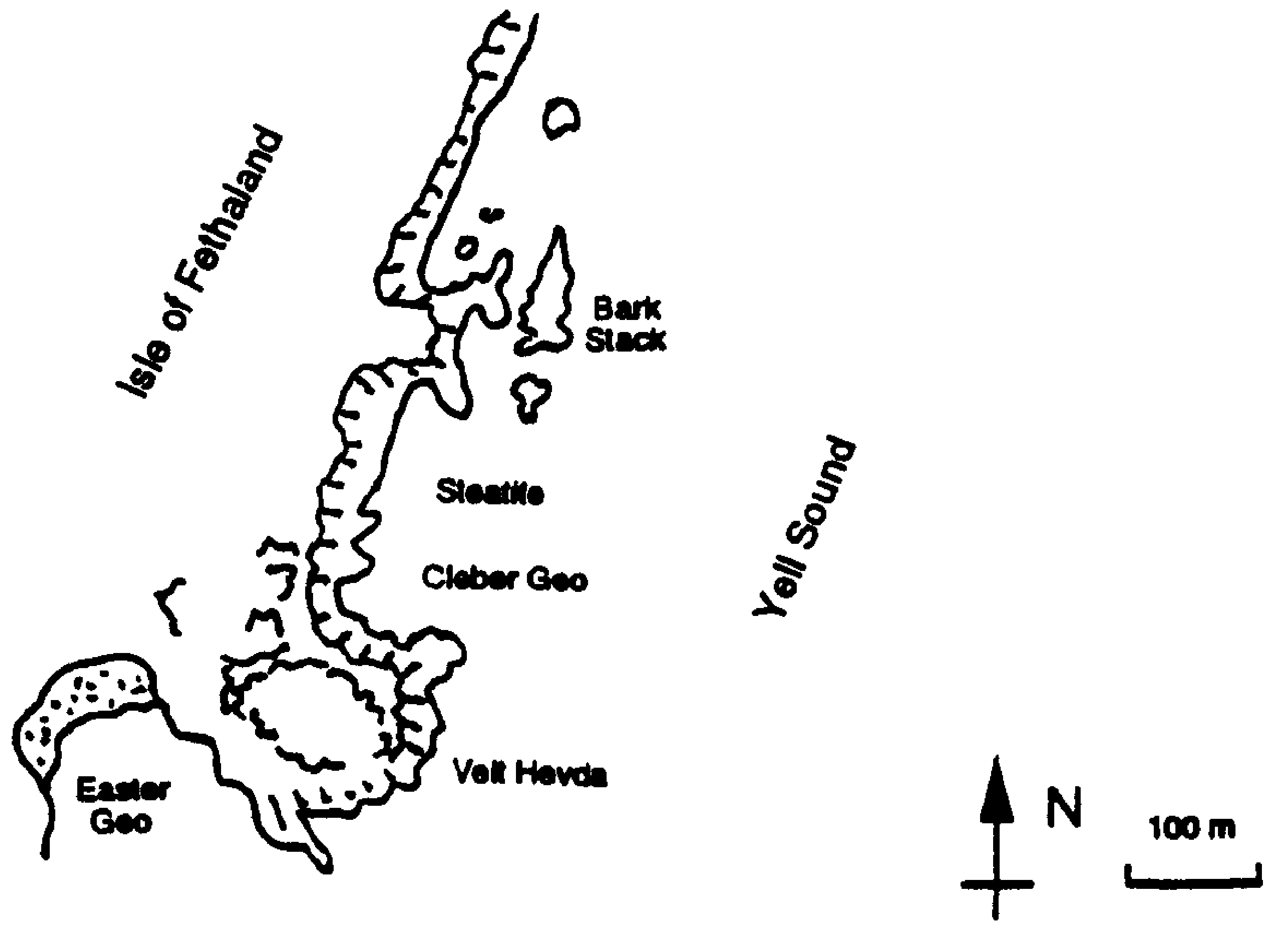
Figure A.8 Map of the Hesta Ness area of Fetlar, Shetland.



Fethaland, North Roe, Mainland [HU 378 943]

Part of a large steatised ultrabasic body, diameter ca. 10 m, outcrops at Cleber Geo on the top part of the cliff on the east coast of Fethaland, figure A.9. This outcrop occurs within the interleaved cover and basement west of the Wall Boundary Fault. At Fethaland a serpentinite occurs within the Queyfirth Group, a unit of fine grained grey schists. Large zoned serpentinite bodies occur within this group at Fethaland, Pundy Geo and Head of Calasta, and these bodies are similar in nature to those seen at Gorsendi Geo Unst. These bodies are within semi-pelitic units interbanded with flaggy impure quartzites. The bodies have been sheared and folded after steatisation with the fine grained, pale green actinolites sheared into lenses parallel to the schistosity. The zonal arrangement is confused due to the high degree of shearing and folding, but the centre appears to be characterised by a massive chlorite zone, then talc-chlorite and the centres of actinolite. The steatite is dark grey and fine grained, < 0.1 mm, is composed mostly of talc with few grains of carbonate. Where present, the carbonate is white and weathers to a reddish brown. This body is close to the fault contact of the Queyfirth Group and Sand Voe Groups of the West Mainland Succession. This contact may have been the locus for fluid flow. Another possibility is that steatisation occurred as a result of the convection system set up in the metasediment after the intrusion of the Ronas Hill Granite, which is only 5 km away. However this seems unlikely as steatisation occurred before the deformation of the metasediments and this deformation further is cut by the granite.

Figure A.9 Map of the Fethaland area of North Roe, Shetland.



Pundy Geo, Breibister, North Roe, Mainland [HU 377 938]
Two small, 5 m diameter, steatised ultrabasic bodies outcrop half way down the cliff at Pundy Geo, Breibister on the North Roe. These two bodies are similar to the serpentinite at Fethaland. These bodies are also within the Queyfirth Group of the Fethaland Block. Two bodies of yellowish steatite, approximately 20 m across are contained within the amphibolite gneisses of the West Shetland Group. The steatite is medium grained, 1-2 mm diammeter, and composed of talc and carbonates, and sparse opaque grains.

Head of Calasta, North Roe, Mainland [HU 377 878]
A steatised ultrabasic body outcrops on the north facing cliff on the Head of Calasta. This serpentinised ultrabasic mass is similar to those seen at Fethaland and Pundy Geo and occurs within the Queyfirth Group of the Calasta Block. The zoned body is highly sheared and very little of the original arrangement is clear. However, a folded steatite zone produces two separate outcrops that are surrounded by massive chlorite and serpentinite. Two steatite outcrops are 5 m across. The steatite is dark grey fine grained, < 0.1 mm, and is composed mostly of talc with few grains of carbonate. Where present, the carbonate is white and weathers to a reddish brown.

Cleber Geo, Hillswick Ness [HU 276 749]
A steatised ultrabasic body occurs part the way down the large cliff, figure A.10. There is a serpentinite associated with a gabbro within banded hornblende gneiss with sheets of felsic material of the Queyfirth Group in the Hillswick Block. The serpentinite has a typical mesh structure indicative of an dunite source rock. It has been high altered and crushed in many places. The alteration is in the form of retrograde chlorite and less often anthophyllite. At the contact of the serpentinite with a felsic gneiss a zonal arrangement is present. The serpentinite

grades into a 5 m layer of anthophyllite which grades into a pinkish steatite, approximately 14 m across. The steatite is massive showing no foliation. It is principally composed of talc and cream coloured carbonate, up to 1.5 mm in diameter. Magnetite also occurs as wisp and clusters. This layer then grades into a talc schist that contains nodules, 50 cm across. There is then a sharp contact with the felsic gneiss

Figure A.10 Map of the Hillswick Ness area of Mainland Shetland.

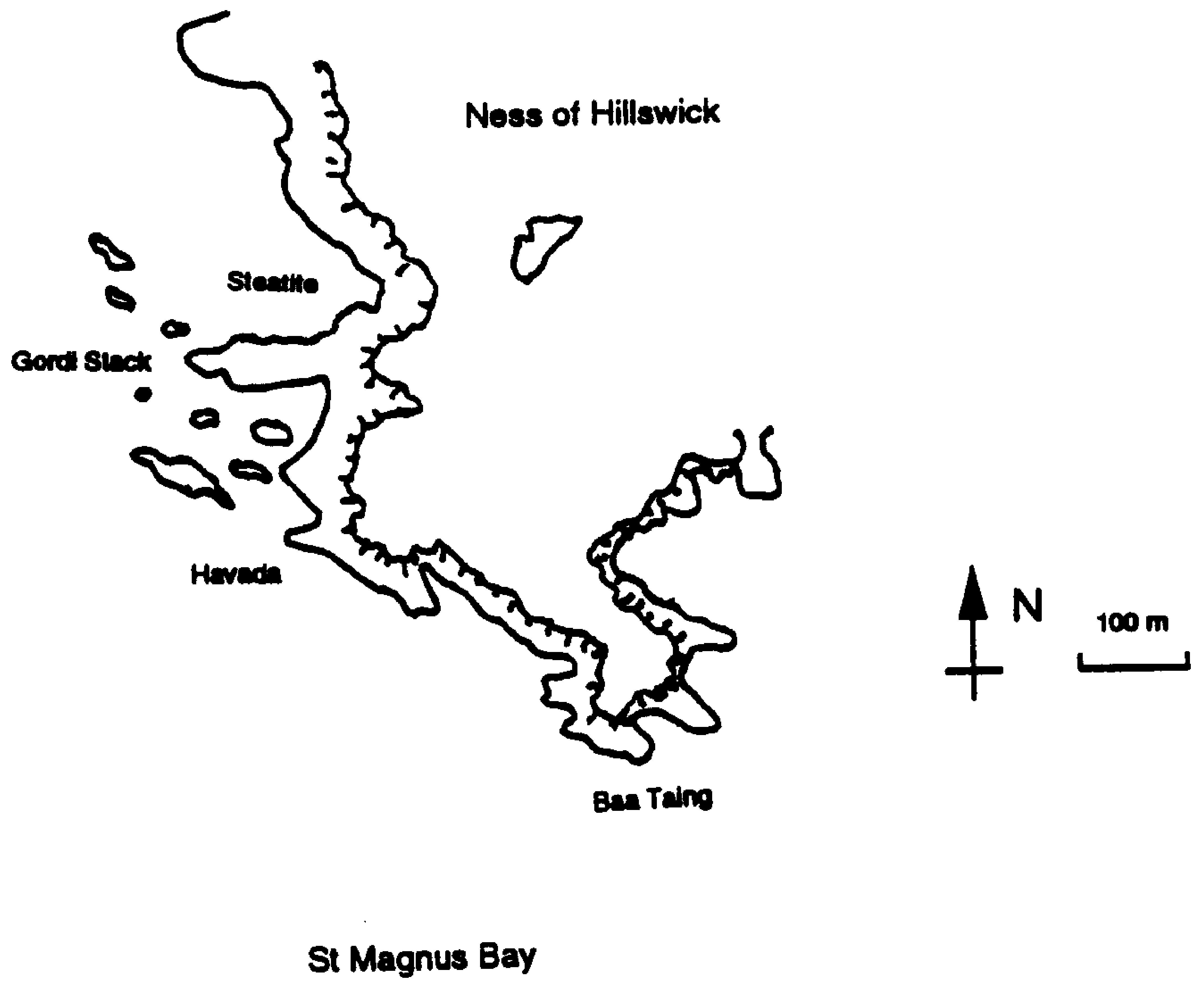
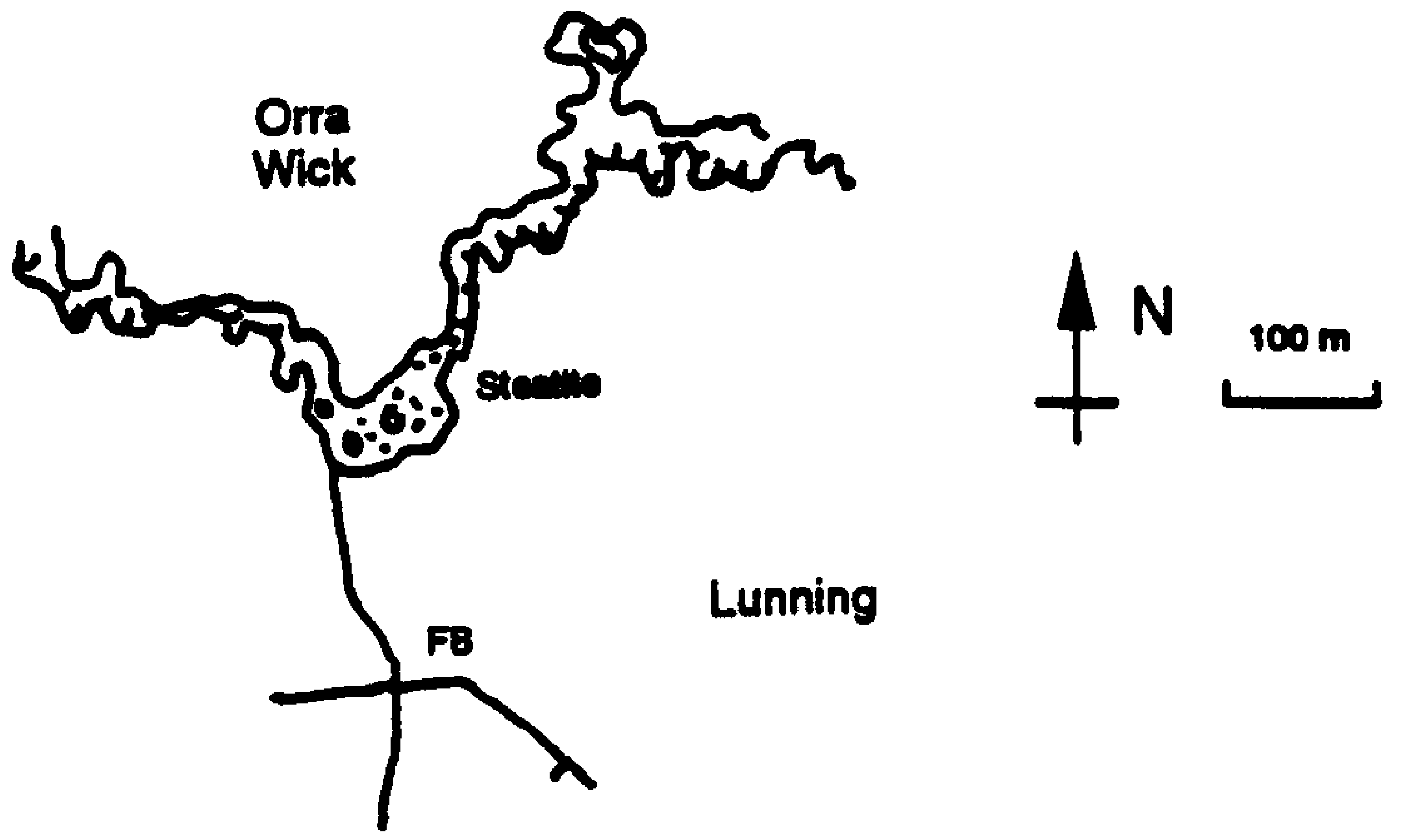


Figure A.11 Map of the Orra Wich area, Lunning, Shetland.



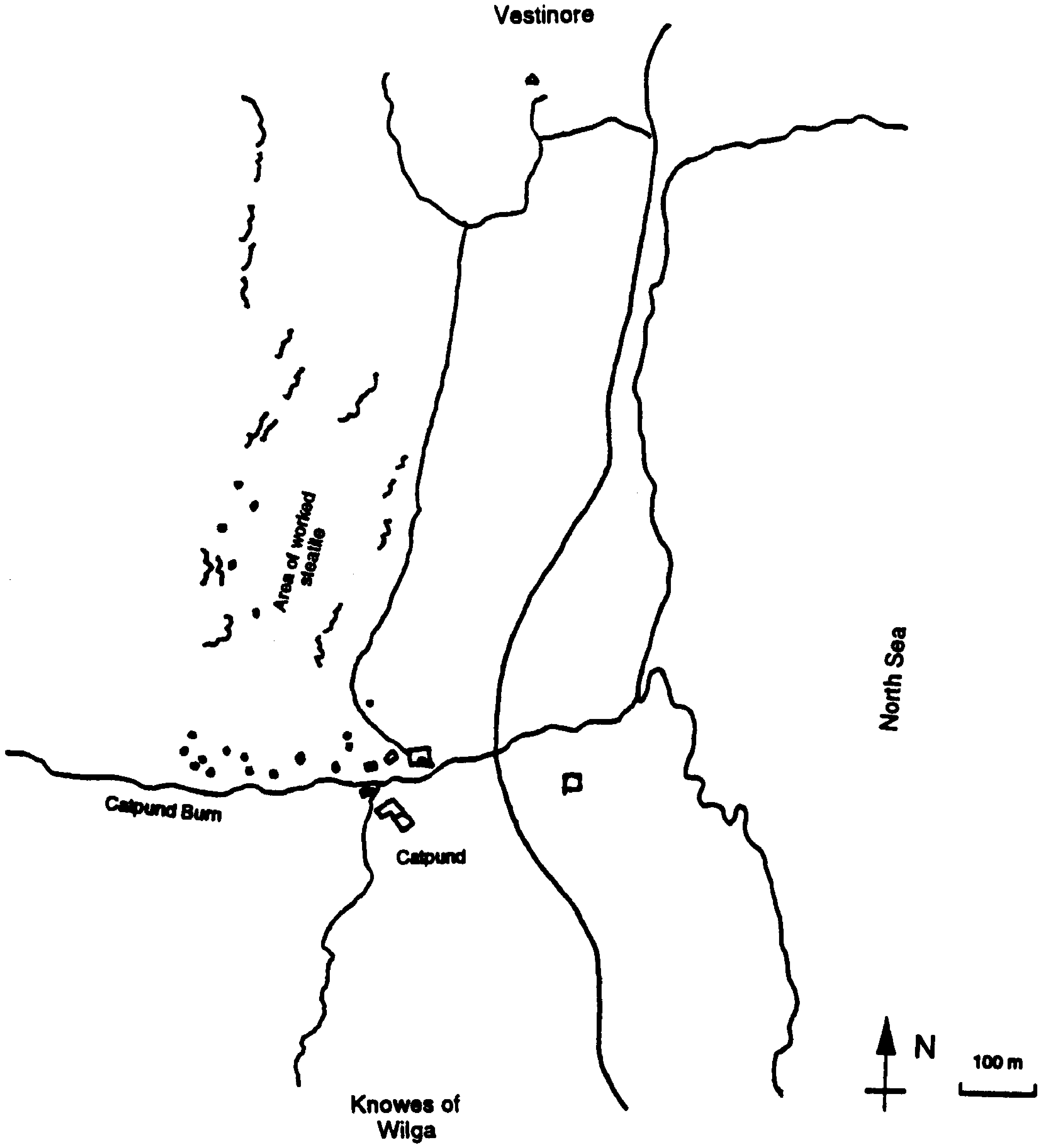
Orra Wick, Lunning [HU 505 670]

On the east coast of Mainland at Orra Wick there is a small steatised ultrabasic body on the shore some 40 m east of the stream, figure A.11. This body occurs within highly deformed interbedded quartzite and pelitic to semi-pelitic schists of the East Mainland Succession. Small lenses of serpentinite , 2-4 m across occur, that have been completely altered to steatite. The edges of these bodies show a slight schistosity. The steatite is medium grained, ca 1.5 mm, weathering brownish grey and containing cream coloured carbonates in a fine blue grey matrix of talc. These carbonates form irregular aggregates. Chlorite occurs as blades between the carbonate and talc. Magnetite occurs as clusters and strings.

Cunningsburgh, Southern Mainland [HU 425 271]

Southern Mainland contains a number of steatised ultrabasic bodies, the largest being at Cunningsburgh. The body covers a large area from Vestinore in the north to Knowes of Wilga in the south and extends onto the beach north of the Catpund Burn and some 500 m west of the road up the Catpund Burn. This serpentinised and steatised ultrabasic body occurs within the

Figure A.12 Map of the Cunningsburgh area, Shetland.



phyllites of the Dunrossness Series, the upper most unit of the East Mainland Succession. The serpentinites are thought to be alteration products of a peridotite (Moffat & Buttler 1986). These serpentinites are highly altered mostly to patchy steatite. The steatite shows considerable variation across the body. In general it is coarse grained, >2 mm, weathering brownish yellow and containing large cream coloured carbonates in a fine blue grey matrix of talc. These carbonates form irregular aggregates. Relic serpentine is also present in certain areas of the body. Chlorite occurs as blades between the carbonate and talc. Magnetite occurs as clusters and strings.

The Berg, Dunrossness [HU 426 228]
To the south of Cunningsburgh there is another steatised ultrabasic body at The Berg, Hoswick. This body forms the tip of the point and extends into the intertidal zone. It is a similar serpentinite to that at Cunningsburgh occuring within the phyllites of the Dunrossness Series. However, this is a much smaller serpentinite body that only covers some 100 m^2. The serpentinite has been highly altered and forms large masses of steatite. In general it is medium grained, ca 1.5 mm, weathering brownish grey and containing large cream coloured carbonates in a fine blue grey matrix of talc. These carbonates form irregular aggregates. Relict serpentine is also present in certain areas of the body. Chlorite occurs as blades between the carbonate and talc. Magnetite occurs as clusters and strings.

Mainland Scotland and surrounding islands

Eilean Glas, Scalpay, Harris [NG 246 948]
A serpentinised and steatised ultrabasic body occurs on the narrow isthmus joining Eilean Glas and Scalpay, figure A.13. This sill-like serpentinite mass, 5 m thick, has been emplaced into the surrounding gneiss. The centre of the sill has been altered to produce a talc chlorite rock. The edges of the body are sheared resulting in a steatite; dark green chrysotile veins cut the steatite. The steatite forms a fine greenish white to grey rock composed of carbonate and talc; there is also a more massive fine grained greenish white talc rock. Of note at this locality is the apparent lack of any opaque minerals. The shearing and fluid movement that formed this body may be related to the Outer Isles Thrust. There is currently no universally accepted view as to either the age of initiation or the number and dates of the main phases of movement of the Fault Zone, although the late Caledonian normal movement appears to be well established (Park 1991)

Scara Ruadh [NG 056 884] to Dun [NG 034 940] near Borve Lodge and on to the coast at Sgeir nan Sgardh [NF 025 950], Harris
A number of ultrabasic bodies that have been steatised outcrop from Scara Ruadh to Sgeir nan Sgardh. These bodies are the exposed parts of a large ultrabasic dyke has been intruded into

the metasediments of the Lochlangavat succession (Scourian). The dyke is 40 m wide at Scara Ruadh, but it has been tectonically pinched out along its strike. Scara Ruadh is the largest of these bodies, and shows some of the original igneous features. It has a distinct layered structure on its southern margin; the centre and the north of the body are massive with little alteration of the original rhombic olivine, pyroxene, mica and magnetite. In places the micas have been altered to green chlorite. At the edges of the body the parent material has been converted into a green talc schist that weathers reddish brown. It is composed of talc, tremolite needles, up to 40 mm, chlorite, opaque minerals are not abundant. The actinolite forms star shaped groups oriented along the foliation plane. Livingstone (1976) suggested that the ultrabasics were serpentinised and steatised during the late Laxfordian, 1 700-1 500 Ma.

Figure A.13 Map of the Eilean Glas area of Scalpay, Harris.

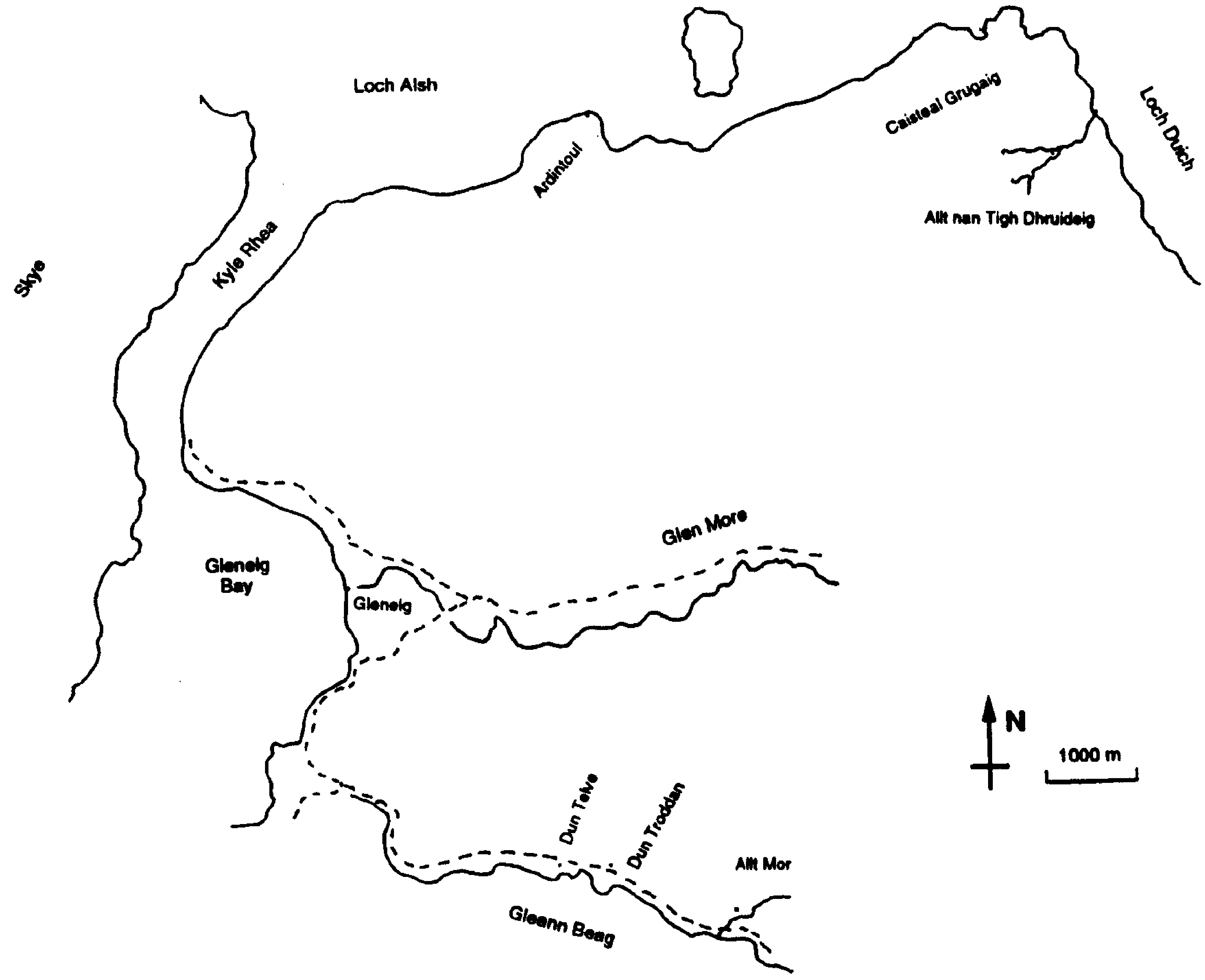
Loch na h'Oidhche, Shieldaig Forest [NG 895 628]

A large serpentinite body, 300 m by 100 m, occurs within a Lewisian inlier to the south of Loch na h'Oidhche. The serpentinite is highly variable in mineralogy and ranges from a pale grey to a blue grey to an orange grey. It weathers pale grey. Most of the body shows no foliation, but near the western edge are steep dipping, well-foliated serpentinite occurs. The rock is very fine gained light brown containing scales of talc-carbonate and chlorite. The edges of the body show carbonate filling veins within the talc-carbonate material.

Ardintoul [NG 834 244], Tigh Dhruideig [NG 877 244], Allt Mor [NG 845 168], Glenelg

A number of steatised ultrabasic bodies outcrop in the Glenelg area, figure A.14. Firstly, on the shore near Ardintoul; secondly in the left bank of a small burn that flows into Loch Duich 100 m south of Tigh Dhruideig, just below the confluence of the two burns, and in Glenn Beag 200 m up the Allt Mor. These bodies are hornblendite or biotite hornblendite within the Lewisian inlier that have been altered to an impure serpentinite that weathers to a yellowish brown. The edges of these bodies are composed of talc schist. At Allt Mor the talc schist is variable in character, but its overall composition is of talc with needles of tremolite and brownish carbonate. At Ardintoul a talc schist is 2 m across, containing fine talc, pale green tremolite needles and pale brown carbonate.

Figure A.14 Map of the Glenelg region showing steatite deposits.



Damshead, Portsoy [NJ 575 636]

A belt of foliated serpentinite runs 8 km from the coast west of Portsoy to Badenyouchers. At Damshead the serpentinite is some 400 m wide. The serpentinite contains thin strings of reddish chyroslitee and veins of greenish and brownish serpentine. At the western edge of the serpentinite near the junction with basic rocks, it passes into a pale greenish chlorite tremolite schist. Pale green chlorite in streaks and and intermingled with elongate tremolite blades. The eastern margin contains a green talc-serpentine-chromite rock. The talc occurs in lenticular crush zones within the shattered serpentinite, which are up to 2m thick, generally vertically oriented parallel to the general strike of the serpentinite. The talc occurs in as both a white and pale green varieties. Pale carbonate occurs as confused aggregates and clusters. Fibrous antigorite also occurs within the crush zones.

Shinness, Sutherland [NC 552 139]

Steatite occurs in a small quarry on the north side of Loch Shin as nodules within a limestone. This limestone occurs within psammites and amphibolites of the Moine. The steatite is fine grained, grey in colour, samples appear to be pure talc, no carbonates or chlorite is present.

Grummore [NC 600 369] and Meall a'Bhrollaich [NC 588 368], Altnaharra

There are a number of ultrabasic bodies within the Lewisian inliers on the hill at Grummore and Meall a'Bhrollaich. These bodies represent the largest in a number around the Loch Naver area that are relatively abundant and well exposed. The largest is on Grummore and is 200 X 150 m. This body is intensely sheared and highly altered. These ultrabasics have been highly altered to form coarse serpentinite, > 2 mm, which also contain, talc, tremolite chlorite and relict olivine. Carbonate forms small clusters and aggregates. The serpentinite is greenish black and finely fibrous, and contains some relic olivine. The talc and tremolite appear to be associated and form together as small laths of confused aggregates within the serpentinite. Pale green tremolite that forms large blades is often grouped in radiating clusters as result of the alteration of olivine and sometime subparrallel. At the edge of these bodies well foliated talc schists occur. These are composed of grey talc, pale green plates of chlorite, dark green tremolite and long colourless prisms of what appears to be anthophyllite that lie on the foliation plane.

Druim Klibreck [NC 605 352], River Mudale [NC 554 358], Altnahara

There are a number of ultrabasic bodies within the Moine of Sutherland at Druim Klibreck and on the small hill above the River Mudale. These are serpentinite which prominent features in the landscape. The serpentinites are dark green black antigorite with relics of olivine. In some places there are long blades of pale green tremolite and green chlorite. The edges of these serpentinite bodies are altered to talc schists. These contain pale green plates and wisps of talc, aggregates of pale grey carbonate, green chlorite, cluster and trails of magnetite and long blades of anthophyllite.

Allt na Dionach-caridh [NC 556 422]

At Allt na Dionach-caridh a large sheet-like serpentinite has been altered in places to steatite. The best example of this is present in the bank of the burn at [NC 556 422]. At this locality a dark green blue serpentinite that contains may veins of chrysolite as well as chlorite-tremolite has been altered to steatite. The serpentinite occurs within a major Lewisian enclave within the Moine The upper contact of the serpentinite with the surrounding hornblende gneiss forms a 1 m wide pure talc rock. It is composed of confused aggregates or large flakes of talc in which are large rhombs of pale brown dolomite and plates of pale green chlorite.

Glen Urquhart [NH 763 354]

The Glen Urquhart Complex is an ultrabasic body of serpentinite, approximately 3.5 km^2 in area, intruded into semi-pelites and psammites of the Loch Eil Division of the Moine. The serpentinite and surrounding schists have previously been identified as an infold of Lewisian (Horne & Hinxman 1914), but Francis (1958) showed them to be Moine. Geochemical studies by (Rock 1983) have not confirmed this conclusion and their stratigraphical position is still under investigation. The outcrop is characterised by a varied assemblage of calc-silicate rocks and skarns, the product of the contact metamorphism related to the intrusion of the serpentinite. There are a number of zoned hydrothermally altered bodies associated with the serpentinite. Most of these bodies are intensely folded and composed of very friable and are composed of dark green biotite and white laths kyanite, both upto 5 mm long. In the centre of the bodies is normal mesh-texture serpentinite. However, between the biotite/kyanite and serpentinite is a zone of talc chlorite rock. The talc forms confused aggregates. The boundaries of the zones are gradational and no sharp contacts are apparent. Within the talc-chlorite zone there is small amount of actinolite.

Corrycharmaig, Glen Lochy [NN 622 358]

In Glen Lochay, there is a large serpentinite body to the west of the farm at Corrycharmaig on the south west side of the River Lochay about 5 km north west of Killin. The serpentinite body, measuring 600m by 300m. forms the craggy hill of Dun Garbh Beag. The foliation within the serpentinite body is similar to that of the surrounding garnet mica schists that also contain smaller serpentinite bodies. The serpentinite is mostly massive, containing serpentine, actinolite, talc and magnetite. Thin veins of chrysolite are abundant. Pyrite and chromite occur in patches within the body. Carbonate rich serpentine is common throughout the deposit. On the western side of the body greenish steatite, composed of talc, carbonate with a small quantity of antigorite and chromite occurs in patches and stripes.

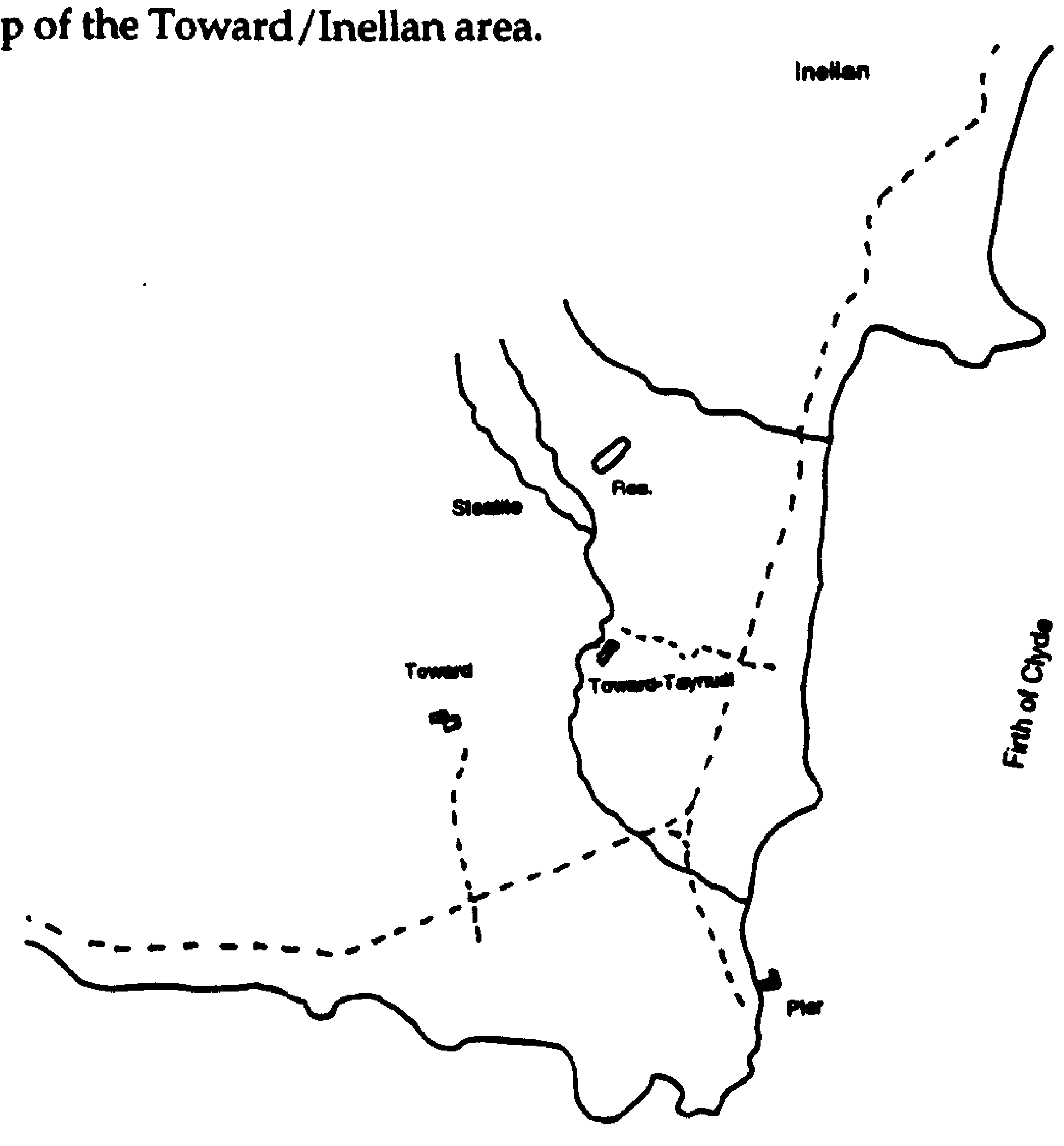
Bolfracks Hill, Aberfeldy [NN 836 477[

Near Aberfeldy on the east side of Bolfracks Hill, 3 km south west of Aberfeldy a ultrabasic body outcrops. This body is sill-like is appearance and contains a dark green talc chlorite phase occurs on the contact of an epidiorite sill and the surrounding metasediments. The samples are very soft and appear to be a homogeneous mixture of talc and chlorite. The contact zone is relatively small and only 1 m of talc chlorite rock exists.

Toward, Inellan [NS 134 687]

A steatised ultrabasic body is present in the vicinity of Inellan and Toward, figure A.15. Steatisation is present at the junction of the two streams north of Toward Taynuill and in the eastern branch of the stream 5m above the confluence. These steatised bodies between Toward and Inellan represent tectonic slivers of non-pseudomorphic serpentinite that are thrust against the contact metamorphosed Dalradian metasediments. Henderson & Richardson (1982) recognised the serpentinite to be the oldest part of the Highland Border Complex. They also suggested that the serpentinite was part of an ophiolite, which may be comparable with possible ophiolites within the Dunrossness Series in Shetland. The serpentinite has a characteristically mottled dark grey and green matrix, cross-fibres of chrysotile veins are widespread and appear to have developed contemporaneously with the shears that resulted in the talc formation. These shear zones occur in some areas within the serpentinite, resulting in a red crush rock of carbonate and talc with chrysotile veins. The carbonate forms larger reddish brown minerals surrounded by brown/grey talc. These shear zones are probably related to movements on the Highland Boundary Fault.

Figure A.15 Map of the Toward/Inellan area.



England and Wales

Porth Delise [SH 282 845], Brondell [SH 268 764], Anglesey

There are two ultrabasic bodies within the late Proterozoic Mona Complex, original dunites and harzburgite, that have been altered to form serpentinites. These serpentinites have been sheared and form steatite-carbonate-serpentinites. On the west coast of Porth Delise and at Brondell layers of fine well foliated, talc-carbonate occur. At Bronddell the serpentinite has been sheared to form a well foliated tremolite talc schist. Needles of green actinolite form on the foliation planes. At Porth-Delise the peridotite has been hydrothermally altered to form a talc-carbonate 2-4 m wide rock. It contains mostly fine grey talc, with a few scales of pale brown carbonate and pale green chlorite.

Kennack Mullion [SW 666 178], the Black Head [SW 775 162], Pentreth [SW 685 135], west of Kyanance [SW 674 174], Gew-graze [SW 674 144], Lizard

Within the serpentinite of the Lizard Complex there are many small occurrences of talc-carbonate alteration, near Kennack, Mullion, the Black Head, Pentreth and west of Kyanance, Gew-graze In zones of crushing the serpentinite is transferred into anthophyllite talc schist. Fell & Hill (1946) suggest the fluid that formed these talc schists was a result of the granite intrusion.

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APPENDIX B

Description of Inductively Coupled Plasma-Mass Spectrometry

ICP-MS is a relatively new technique that provides rapid multi-element analysis with low detection limits and few of the problems of conventional optical plasma techniques (Pickford and Brown 1985). Since the production of the first commercial instrument in 1978 it has become a widespread technique in many branches of analysis (Gray 1989, Jarvis et al 1992). The rapid ultra-trace element capability is derived from the combination of the high ionisation power of argon ICP sources, which have been successfully utilised for many years in Inductively Coupled Plasma Spectrometry (Walsh and Howie 1986, Meyer 1987), with the precise and rapid mass analysis of the quadrupole mass-spectrometer system used in routine organic analysis (Gurka et al 1988). A major developmental problem was enabling the system to sample efficiently the high yield ions in the ICP at atmospheric pressure and transmit those ions to a mass analysis system at high vacuum. Gray (1975) initially developed a system that could produce useful analytical data from solutions sampled by plasmas at atmospheric pressure. The rapid development that followed resulted in the release of the first commercial machine by SCIEX, Canada in 1978 after much development by Houk (Houk et al 1980, Houk 1986). Detailed reviews and discussion of the development of the technique are included in the reviews by Gray and Date (1983), Gray (1985), Houk and Thompson (1988), Gray (1989) and Jarvis et al (1992).

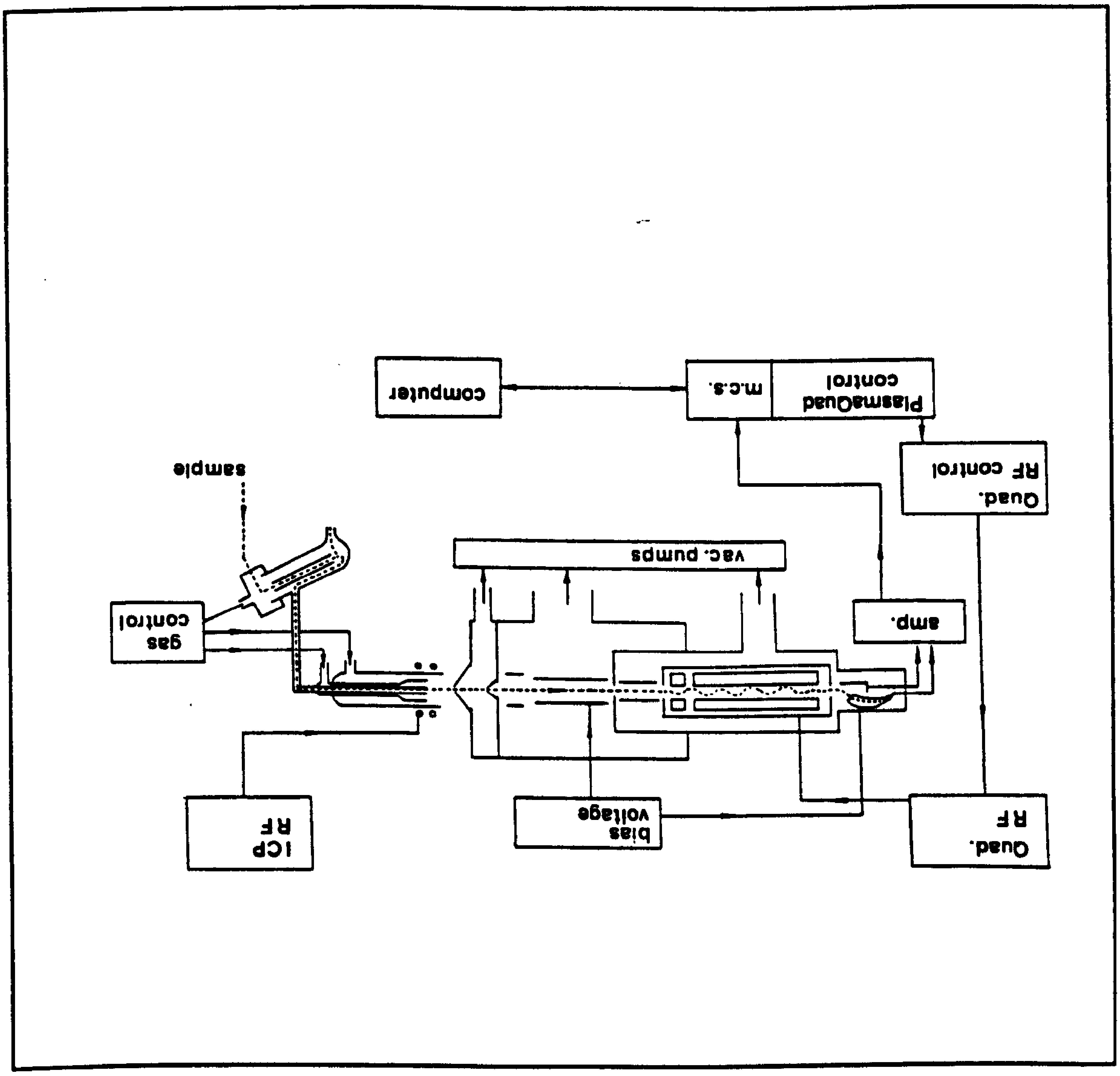
The main features of the system used in this study are described below, since these are many characteristics that influence the performance and behaviour of the machine that must be appreciated in order to develop and apply the technique to specific problems. Figure B.1 is a schematic diagram of the VG PlasmaQuad instrument used in this study. It can be divided into four sections: (i) sample introduction, (ii) ICP torch/ion generator, (iii) ion extraction and (iv) quadrupole mass analyser. Each feature will be described in turn below. The horizontally mounted torch is the same as that used for optical systems in vertical configuration. The ions generated are fed into a mass analyser through sampling and skimmer cones lying in front of an array of electromagnetic lenses, which focus the ion beam. The large pressure difference between the torch and the analyser is obtained through a combination of rotary and diffusion pumps. The ion detection system comprises an electron multiplier and amplifier. The whole system is controlled by a central microprocessor that allows the data acquisition parameters and quantification procedures to be defined and collects and analyses data.

(i) sample introduction

The method most commonly used for sample introduction into the plasma is through the aspiration and nebulisation of aqueous solutions. The particles generated should be less than

10 mm, ideally 3 mm, in diameter (Houk and Thompson 1988). In general most samples are introduced in the form of aqueous solution although organic liquids have been used (Hutton 1986). In order to generate an aerosol the most frequently used technique is pneumatic nebulisation. This is produced by a high velocity jet of gas disrupting the flow of sample.

Figure B.1 A schematic diagrams of the PlasmaQuad (PQ1) used in this study (VG isotopes 1988).



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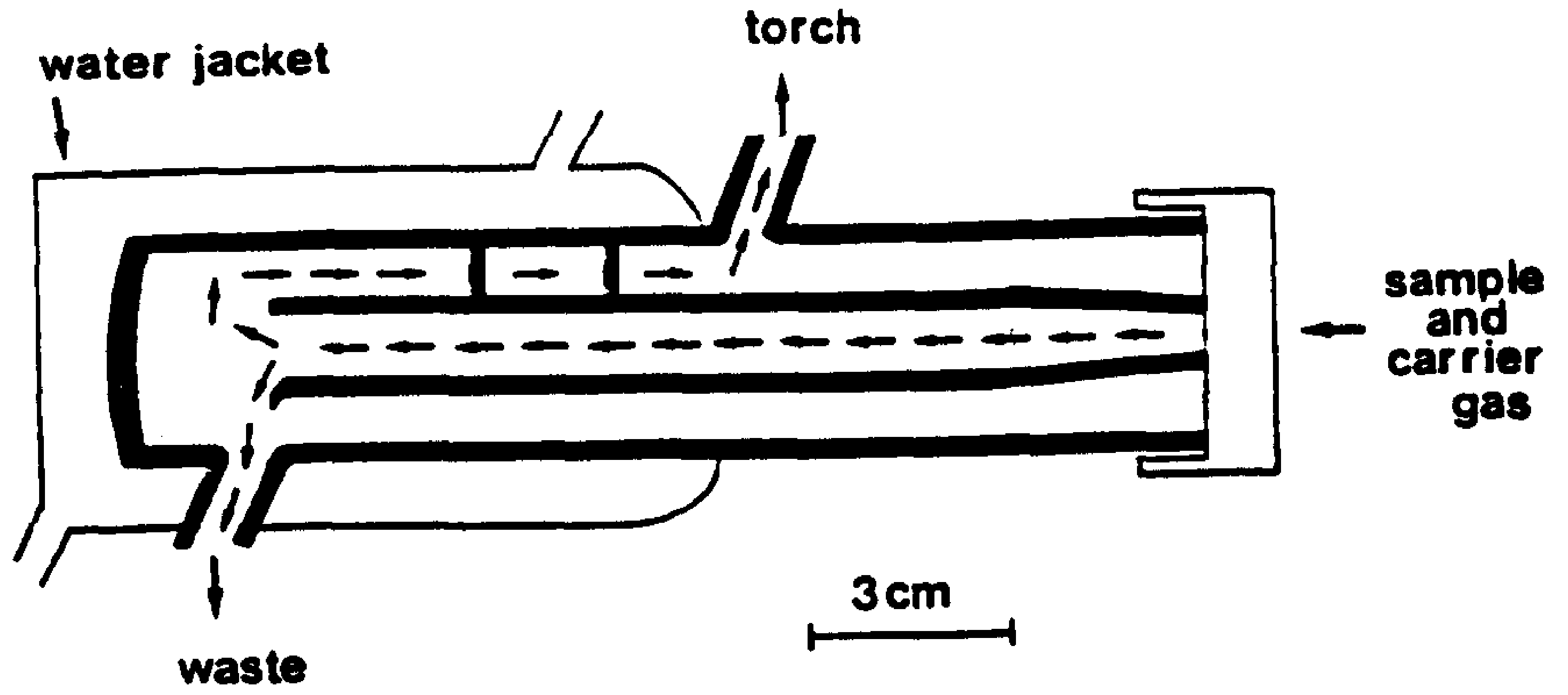
The method most commonly used for sample introduction into the plasma is through the aspiration and nebulisation of aqueous solutions. The particles generated should be less than 10 mm, ideally 3 mm, in diameter (Houk and Thompson 1988). In general most samples are introduced in the form of aqueous solution although organic liquids have been used (Hutton 1986). In order to generate an aerosol the most frequently used technique is pneumatic nebulisation. This is produced by a high velocity jet of gas disrupting the flow of sample.

Different configurations of the two incidental fluids are available to cope with either relatively high solid loading or to produce very stable aerosol flow. Ultrasonic nebulisation can also be used and has the advantage of up to 3 to 10 times greater aerosol generation efficiency (Olivares and Houk 1986). The aerosol then passes into the spray chamber where condensation of the larger droplets occurs and a more uniform aerosol is produced with droplets of < 10 mm in diameter. A representation of the aerosol flow through a standard spray chamber is shown in figure B.2. This selection step allows only 1 to 2% of the aspirated sample to be introduced into the plasma. The efficiency of sample introduction can be increased by the use of a recirculating spray chamber, which can allow up to 30 minutes of measure on 1 ml of solution (Gray and Date 1983). The spray chamber is jacketed by water that is used to lower the water loading in the aerosol in order to reduce plasma cooling. It also reduces oxide levels, improves ion sensitivity and reduces thermal buffering of the plasma (Hutton and Eaton 1986, Long and Browner 1988). Other methods of sample introduction to the plasma include; sparking, laser ablation, slurry nebulisation and electrothermal vaporisation, although many of these are only in the development stage (Gray and Date 1989, Gregoire 1988, Dean et al 1989, Gray 1989, Hager 1989, Jarvis et al 1992)

Figure B.2 Diagram of the spray chamber (double pass Scott-type) used on the PQ1 showing aerosol flow.



(ii) the inductively coupled plasma

The ICP is a very efficient source of ions in a controlled, uncontaminated region of sufficiently high temperature to produce the required sample conditioning and excitation. Furthermore, it allows the rapid and complete introduction of the sample into that region (Gray 1989). The sample is introduced via a laminar flow of argon gas to the point of atomisation and excitation. The typical form of an ICP torch is shown in figure B.3. Three different gas flows meet at this point. The nebuliser gas containing the sample is introduced along the middle axis where it

Figure B.3 Schematic of ICP torch, gas flow and induced magnetic field. The shaded zones are observed when nebulised sample containing Y is introduced along the central channel in the injector gas flow (Houk 1990).

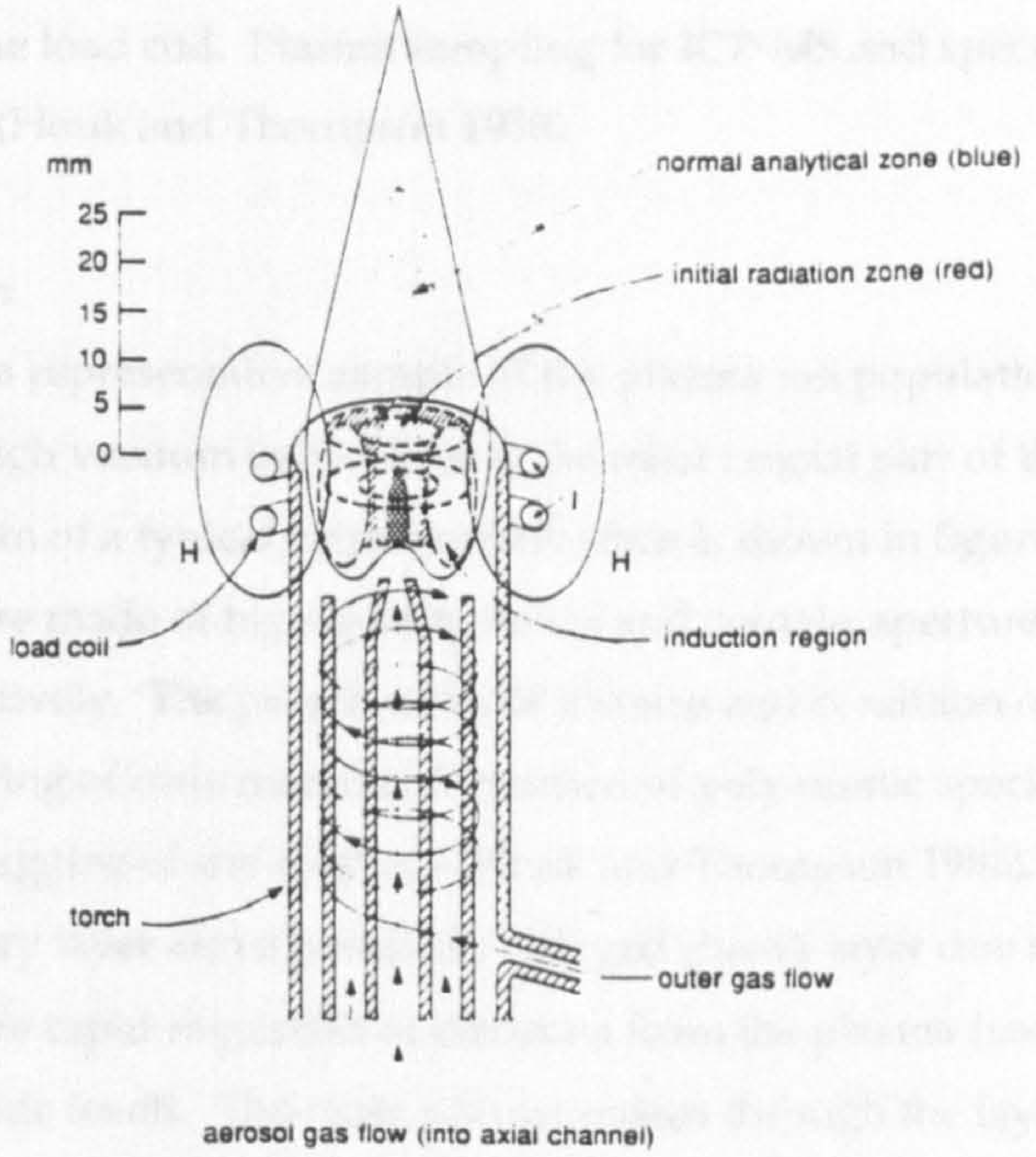
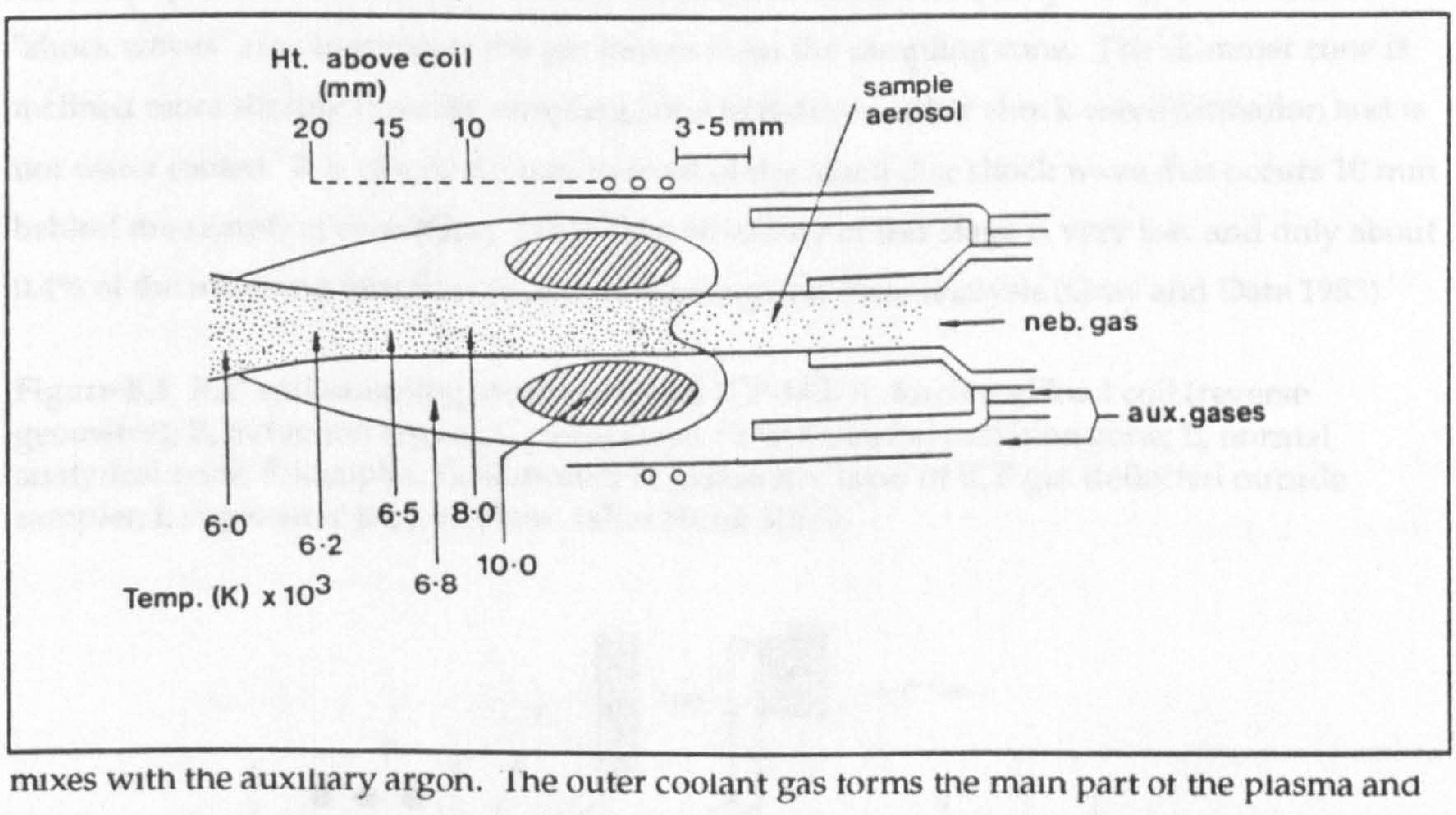


Figure B.4 Detail of the ICP torch showing plasma temperature variation and sample introduction point (Gray 1989).

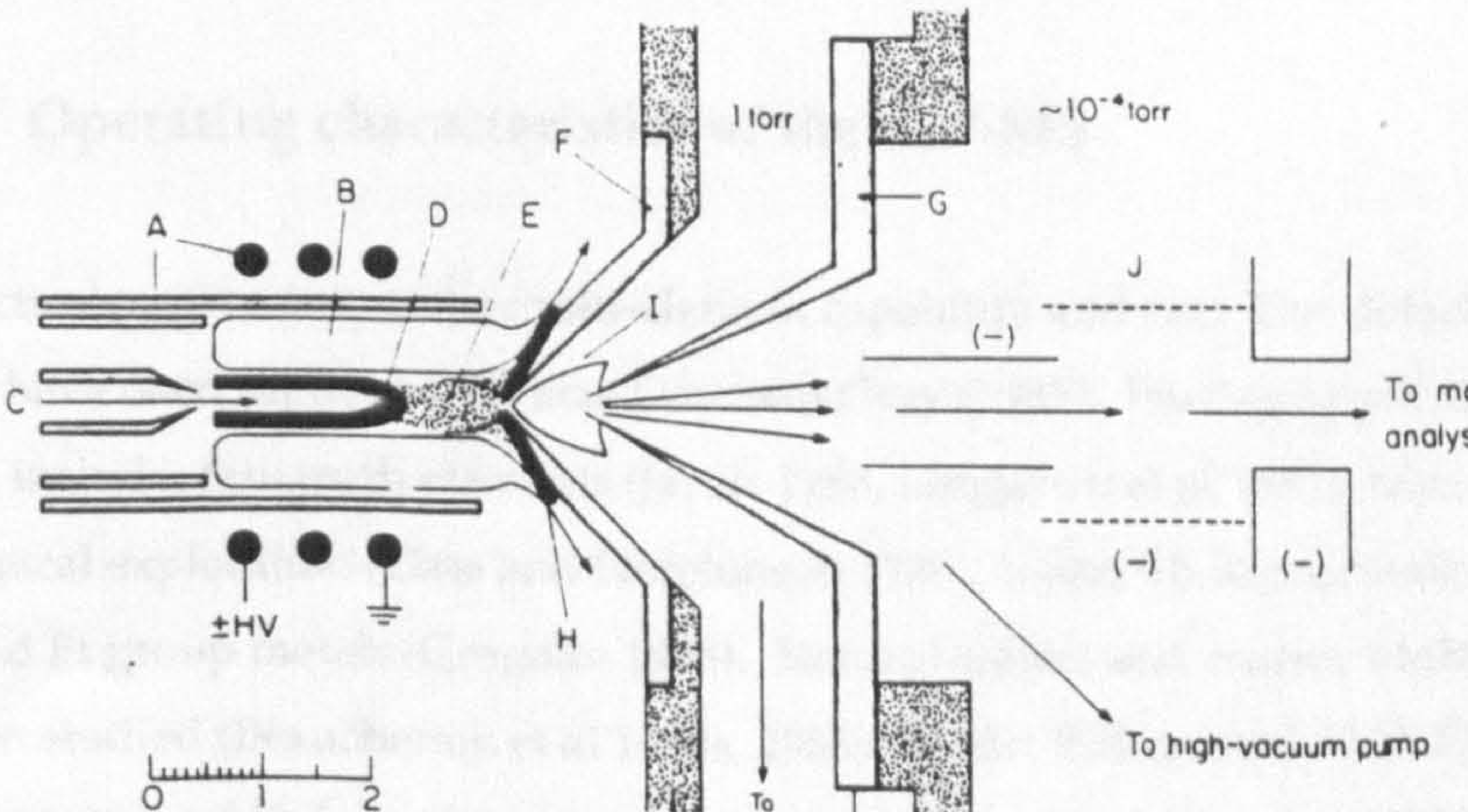


mixes with the auxiliary argon. The outer coolant gas forms the main part of the plasma and cools the torch (Walsh and Howie 1986). The plasma is generated by a fluctuating magnetic field induced by the RF coil (at 1 to 1.5 kW) which transfers energy to the plasma by accelerating free electrons which heat by collision. The plasma is induced by a Tesla coil which allows the introduction of free electrons to overcome the dielectric resistance of the gas. The energy is transferred to the central gas stream via conduction. The distribution of temperatures induced and the plasma shape is shown in figure B.4. Sample aerosol is desolvated and salt particles vaporised as they are introduced into the plasma. The molecular vapour is atomised and ionised. These processes take a few milliseconds to occur (Houk 1986), the exact position at which these processes take place being dictated by the gas flow and dielectric field pattern (Gray 1989). On leaving the torch, the gas streams mix and the temperature falls to 6000 K at 10 to 12 mm from the load coil. Plasma sampling for ICP-MS and spectral observation for ICP-AES occurs here (Houk and Thompson 1988).

(iii) ion extraction

The transport of a representative sample of the plasma ion population from atmospheric pressure into a high vacuum (<10-5 torr) is the most crucial part of the ICP-MS system. A schematic diagram of a typical extraction interface is shown in figure B.5. The sampler and skimmer cones are made of high quality nickel and contain apertures of 1.0 mm and 0.75 mm diameters respectively. The preservation of the size and condition of the surfaces is important to reduce sputtering of cone material, formation of polyatomic species and a build up of solids leading to the plugging of the aperture (Houk and Thompson 1988). The impinging plasma creates a boundary layer and a positively charged sheath layer due to the cooling effect of the cone and the more rapid migration of electrons from the plasma (see figure 3.5). This region contains high oxide levels. The main plasma passes through the layers. Behind the cone a moderate vacuum, 2 mBar, results in the supersonic expansion of the gas, cooling and freezing the ion population and thus preventing reactions between ions (Gray 1989). A number of "shock waves" are observed as the gas moves from the sampling cone. The skimmer cone is inclined more sharply than the sampling cone to reduce further shock wave formation and is not water cooled. It is placed 6.5 mm in front of the Mach disc shock wave that occurs 10 mm behind the sampling cone (Gray 1989). The efficiency of this stage is very low and only about 0.4% of the incoming ions pass on to ion focusing and mass analysis (Gray and Date 1983).

Figure B.5 ICP and sampling interface for an ICP-MS. A, torch and load coil (reverse geometry); B, induction region; C, aerosol gas flow; D, initial radiation zone; E, normal analytical zone; F, sampler; G, skimmer; H, boundary layer of ICP gas deflected outside sampler; I, supersonic jet; J, ion lens. (after Houk 1986).



(iv) ion focusing, mass analysis and detection

A stack of electrostatic lenses is used to focus the ions that pass on from the sampling interface, the configuration being shown in figure B.5 The different components of the lens system are held between -1000 and +30 V. The precise settings are variable and are part of the fine tuning procedure for routine analysis. The extraction electrode is at a negative bias and extracts positively charged ions, whilst repelling negatively charged species and leaving uncharged molecular species to diffuse away. The currents to the lenses can be of the order of 1 mA (Houk and Thompson 1988) and within the threshold for space charge effects which can change the spatial distribution of the beam. Although this has been used to explain some non-spectroscopic interferences, the mechanics is far from easy to determine (Gillson et al 1988).

The mass analysis of the ions is performed by a quadrupole system similar to, but slightly larger than that used in organic analysis (Gray 1989). The quadrupole system can tolerate fairly high pressures and significant spreads in ion velocities and can scan rapidly and transmit a larger fraction of the injected ion beam (Houk and Thompson 1988). However, the resolution obtained is not as high as other types of mass-spectrometer but can be finely adjusted to give better resolution. The ion analysis system compromises three sets of radically arranged poles, two smaller units acting as filters. A sinusoidally varying voltage and a fixed DC potential on the central pole unit permits only ions of a narrow band of mass : charge ratio to have a stable path through the fields. This also determines the resolution of the analyser (VG Isotopes Ltd. 1988). The ions selected by the quadrupole are detected by a continuous dynode electron multiplier, which can tolerate high count rates and operating pressures. The detector may be used at lower gain to give linear response for high ion densities. In the pulse counting mode, linear response over 5 decades in concentration is possible and can be improved to 8 decades using a mean current detection system (Gray 1989).

The signal analysis is similar to that used for radiometric counting devices using a 4096 channel multi-channel scaler. Scan times can be as short as 10 ms and under the control of the central computer skip scanning and total mass scans can be performed rapidly.

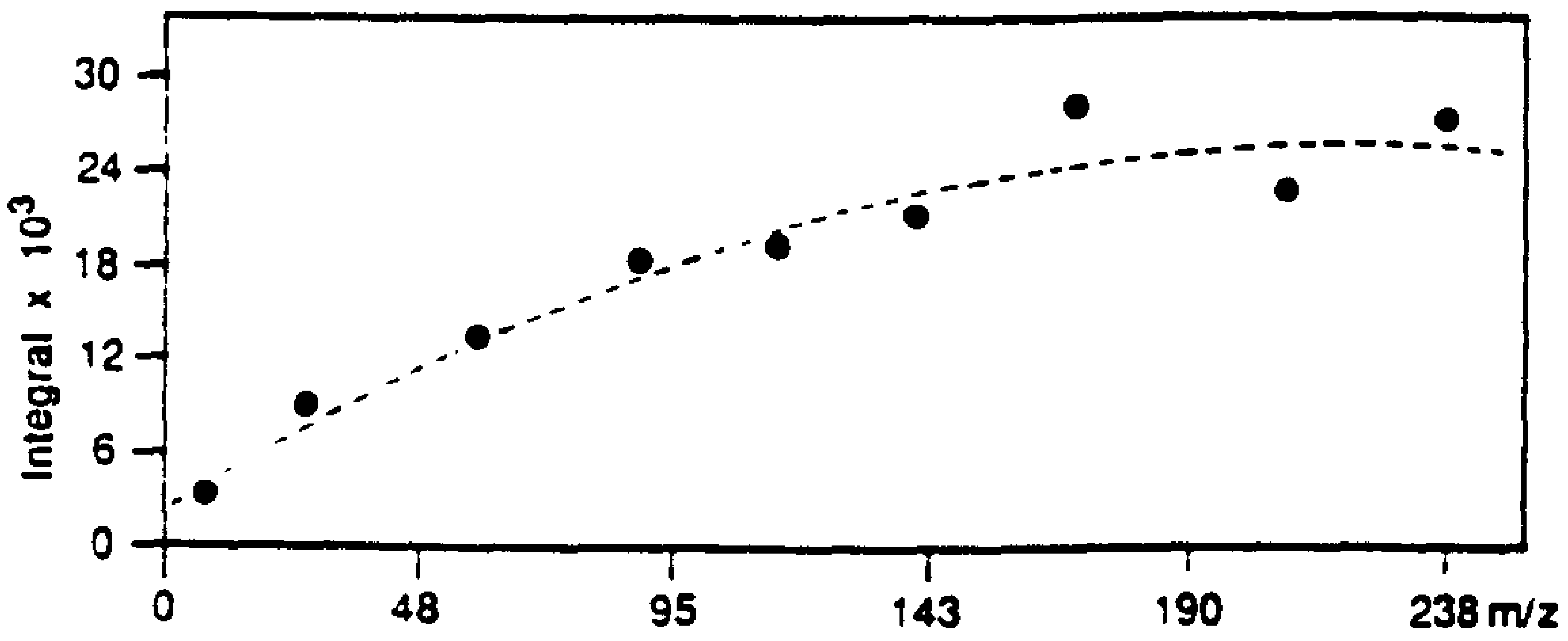
Operating characteristics of the ICP-MS

The practical application of the multi-element capability and very low detection limits of the ICP-MS have been rapid and diverse Date and Gray (1989). Further applications in the earth sciences include; rare earth elements (Jarvis 1988, Longerich et al 1987), trace elements in geochemical exploration (Date and Hutchinson 1986), U and Th in tourmalines (Kantipulty et al 1988) and Pt group metals (Gregoire 1988). Natural waters and marine biological samples have also been studied (Beauchemin et al 1988a, 1988b, 1988c; Ridout et al 1988; Garbarino et al 1987). Clinical analysis of biological specimens for trace elements (Lyon et al 1988) and studies of ultrapure materials (Paulsen et al 1986, 1987; Luck 1989) are further applications. During these studies there has been considerable improvement in practical detection limits, control of interferences and ion beam stability.

(i) plasma ion population and system response

The plasma equilibria are controlled by the properties of Ar and O and to a lesser extent, H. The introduction of a sample matrix does not perturb those equilibria up to 1% concentration. The ion population is balanced by electronic charge and the system response for any element is the same for identical concentrations. However, this depends on the precise instrument settings that vary across the mass range and must be set at a compromise (Gray 1989). When the mass range is scanned in the semi-quantitative mode, using single conditions, the response curve over the mass range shown in figure B.6 is obtained. This can be used to calibrate for approximate (+/- factor of 3) concentration. More accurate determinations can be made using sets of standards.

Figure B.6 Instrument response curve from 4 to 240 m/z (after Jarvis et al 1992)



(ii) backgrounds and peak interference

It is important to be aware of background levels and potential peak interferences. Spectral contributions of non-analyte counts can be derived from: continuum background and background peaks, oxide and doubly charged ions, polyatomic ions, isobaric overlap, matrix suppression and physical or non-specific effects (Riddel et al 1988)

(iii) continuum background and background peaks

When aqueous solutions are introduced there are no background interferences above mass 80 except for Xe+ and Kr+ impurities in the argon gas (Gray 1986, Houk and Thompson 1988). The general background continuum is very low, of the order of a few counts and is mainly derived from stray photons that pass the photon stop, the detector being particularly sensitive to vacuum UV photons from the plasma (Gray 1986, Kawaguchi et al 1988). There is also some contribution of charged species from contamination, memory effects and random noise (Gray 1975, Kawaguchi et al 1988). The main peaks observed in the background spectrum are due to the isotopes and species of Ar, O and H as well as contributions from the acid solution used to introduce the sample and air entrained by the plasma (Tan and Horlick 1986, VG Isotopes 1988). Table B.1 lists the interferences derived from water and plasma gas and from a number of mineral acids over the mass ranges affected. The recommended medium for sample introduction is nitric acid since this produces the lowest abundance of interfering species. The first row transition metals are the most affected group of elements.

Table B.1 Potential isobaric interferences derived from plasma gas, water, hydrochloric, perchloric, nitric, sulphuric and phosphoric acids (VG Isotopes 1986)

Mass	Species	Interfered isotope
19	OH_3^+	^{19}F
20	$^{40}Ar_2^+$	^{20}Ne
28	N_2	^{28}Si
29	N_2H	^{29}Si
30	NO	^{30}Si
31	^{15}N, NOH	^{31}Si
32	O_2	^{32}S
33	O_2H	^{33}S
34	$^{16}O\,^{18}O$	^{34}S
35	$^{16}O\,^{18}OH$, O_2H_3	^{35}Cl
36	^{36}Ar, $^{18}O_2$	^{36}S
37	$^{18}O_2H$, 36ArH	^{37}Cl
39	^{38}ArH	^{38}K
40	^{40}Ar	^{40}Ca
41	^{40}ArH	^{41}K
47	PO	^{47}Ti
48	^{32}SO	^{48}Ti
49	^{32}SOH	^{49}Ti
50	^{34}SO	$^{50}Ti/^{50}V/^{50}Ca$
51	^{34}SOH, ^{35}ClO	^{51}V
52	$^{35}ClOH$	^{52}Cr
54	$^{37}ClOH$, ^{40}ArN	^{54}Cr, ^{54}Fe
55	$^{40}ArNH$	^{55}Mn
56	^{40}ArO	^{56}Fe
63	PO_2	^{63}Cu
64	^{32}S, $^{32}SO_2$	$^{64}Zn/^{64}Ni$
66	$^{34}SO_2$	^{66}Zn
70	$^{35}Cl_2$	$^{70}Zn/^{70}Ge$
71	ArP	^{71}Ga
72	$^{35}Cl^{37}Cl$	^{72}Ge
74	$^{37}Cl_2$	$^{74}Ge/^{74}Se$
75	$^{40}Ar^{35}Cl$	^{75}As
76	$^{40}Ar^{36}Cl$	^{76}Se
77	$^{40}Ar^{37}Cl$	^{77}Se
78	$^{40}Ar^{38}Ar$	^{78}Se
80	$^{40}Ar_2$	^{80}Se

The abundance of interference peaks varies with the operating conditions and the behaviour of the plasma, that is uncertain (Long and Browner 1988). The presence of water in the plasma has been shown to be important and can be reduced by cooling the spray chamber (Hutton and Eaton 1988). If high stability of these peaks is found, simple background subtraction may be used to remove the interference.

(iv) oxide, hydroxide and doubly charged species

The formation of these species may cause isobaric interferences with other masses. If they are formed from the analyte, the population of the monocharged analyte ions is reduced and hence the instrument response suppressed. Under normal operating conditions, oxide levels are the most important and are expected to be of the order of 5% (Houk et al 1980, Gray 1989). The precise level depends on operating conditions, elemental composition of the plasma, bond energies of the species and ionisation energies of the elements under consideration (VG Isotopes 1987). The potential spectral interferences have been tabulated for a wide range of elements (Vaughan and Horlick 1986). The instrumental parameters that have most effect on the levels have been studied in some detail and include the RF power and nebuliser flow (Gray and Date 1983, Long and Brown 1986, Lichte et al 1987, Longerich et al 1987, Ting and Janghorbani 1988). In the case of nebuliser flow, the effect on the ion levels appears to result from the change in the position of the plasma with respect to sampling cone, i.e. sampling depth (Vaughan and Horlick 1986). Less significant effects arise from the solution uptake rate and the auxiliary and coolant gas flows (Ting and Janghorbani 1988), changes in plasma sampling geometry again being the proposed explanation. The behaviour of doubly charged and hydroxide species is very similar but their levels are much lower than those of the oxides and the positions in terms of instrument settings are slightly different. The optimisation of the instrument parameters to give a maximum response for singly charged ions and minimum response for doubly charged species, oxides and hydroxides are complex and a compromise is usually required.

(v) polyatomic ion formation

It is possible for the analyte and matrix ions and atoms to undergo reactions with the plasma ions and form complex polyatomic species. However, MAr+ species are <10-5 of M+ and are the only significant species additional to those described above (Houk and Thompson 1988).

(vi) isobaric overlap

The existence of several isotopes of an element, both natural and synthetic, means that isobaric interferences between neighbouring elements can be a problem (Lichte et al 1987, Longerich et al 1987, Gray 1989, Jarvis et al 1992). It is often possible to view a mass region for the element free from interferences. A number of authors have produced algorithms for this process although instrument stability must still be accounted for using internal standards (Gaberino and Taylor 1987, Lichte et al 1987).

(vii) non-spectroscopic interferences

This category bulks together interferences encountered in the ICP-MS technique that cannot be accounted for by specific spectral observations. The presence of fairly high concentrations of matrix elements in the aspirated sample has generally been found to depress the element signal, although in some situations enhancement has been observed (Houke et al 1980, Gregoire 1988, Houk and Thompson 1988, Gray 1989). The more easily ionised elements (e.g.. Na, K, Cs, Ca) contribute most to matrix suppression (Houk et al 1980, Gray and Date 1983, Olivares and Houk 1986, Garbarino and Taylor 1987, Longerich et al 1987). The ionisation of argon can be depressed in some cases (Olivares and Houk 1986). At concentrations >0.1% the easily ionisable, heavy elements cause more suppression than the lighter elements and suffer less from suppression effects as analytes (Houk and Thompson 1988, Gray 1989). The explanation of these observations is unclear. It has been attributed in part to blockage of the apertures in the skimmer and sampler cones (Houke et al 1980, Olivares and Houk 1986, Williams and Gray 1988). More recently, a mechanism involving space charge effects and ion beam diffusion in the skimmer region has been modelled and found to fit experimental observations (Gillson et al 1988). These effects may be minimised by diluting the sample to reduce salt loading of the plasma or the technique of isotope dilution can be used as matrix effect will be the same for all isotopes of an element. Memory effects from traces of solution remaining trapped in part of the system or as oxides deposited on sample and skimmer cones may result in other non-spectroscopic interferences.

APPENDIX C

Data

Due to the large quantity of data, the results of the multi-element ICP-MS analysis used in this study are presented on the attached floppy disk. A copy and a printed data set may be obtained from the author. Summaries of this data are presented below. The disk is an Apple Mac formatted disk, however these files may be converted to an IBM format disk through the programme *Apple File Exchange*. The data is presented as both Excel files, that may be read by most spreadsheet packages, and text files that may be read into many data handling packages. All values are ppb.

The following files contain the relavent data:

ICP-MS sample data	(Excel 4.0)	134 rows 68 columns
ICP-MS sample data text	(text)	133 rows 68 columns
Control data	(Excel 4.0)	69 rows 11 columns
Control data text	(text)	69 rows 11 columns
Blank data	(Excel 4.0)	69 rows 10 columns
Blank data text	(text)	69 rows 10 columns

Table C.1 Mean Concentration (log ppb) and standard deviations for all replicates

Sample		Li	Be	B	Na	Mg	Al	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
ge-1	mean	4.867	2.460	5.637	5.880	6.363	6.775	6.364	4.057	5.792	4.874	6.647	5.995	7.963	5.368	6.581	5.043	4.672
	std deviation	0.013	0.124	0.084	0.034	0.033	0.034	0.014	0.035	0.015	0.012	0.021	0.012	0.014	0.029	0.031	0.089	0.011
eg-12	mean	4.135	1.890	5.738	5.499	6.993	6.041	5.936	3.995	5.251	3.657	5.773	5.620	7.394	5.216	6.045	3.132	4.061
	std deviation	0.024	0.521	0.046	0.034	0.032	0.012	0.019	0.023	0.032	0.029	0.025	0.007	0.012	0.008	0.011	0.055	0.030
lno-1	mean	4.815	2.547	5.241	5.305	6.835	6.083	6.058	4.216	5.532	3.408	5.065	5.815	7.839	5.134	6.195	3.065	3.920
	std deviation	0.247	0.169	0.295	0.087	0.030	0.020	0.049	0.039	0.055	0.025	0.055	0.013	0.016	0.012	0.017	0.281	0.058
ps-1	mean	4.751	1.577	5.606	6.380	6.235	5.665	8.086	4.370	5.667	3.451	5.160	6.021	7.312	4.593	6.284	3.966	3.689
	std deviation	0.020	0.420	0.087	0.024	0.014	0.026	0.021	0.036	0.021	0.026	0.019	0.018	0.018	0.019	0.020	0.236	0.024
msc-1	mean	4.197	1.960	5.390	5.250	6.802	6.570	6.834	4.008	4.846	4.321	6.349	6.092	7.752	5.077	6.363	4.702	4.321
	std deviation	0.026	0.223	0.096	0.121	0.021	0.008	0.018	0.014	0.038	0.019	0.058	0.007	0.006	0.008	0.010	0.017	0.253
t-1	mean	5.018	2.523	5.004	5.203	6.852	6.269	7.436	3.927	5.001	4.376	6.235	6.006	7.591	4.577	6.064	3.660	4.556
	std deviation	0.349	0.093	0.045	0.055	0.042	0.070	0.557	0.037	0.381	0.055	0.246	0.047	0.057	0.200	0.106	0.304	0.078
zmo-1	mean	4.650	1.926	5.406	5.545	6.830	6.764	8.334	4.178	5.881	4.472	6.630	6.419	7.562	5.256	6.468	3.957	4.750
	std deviation	0.013	0.348	0.120	0.167	0.013	0.007	0.008	0.015	0.007	0.011	0.007	0.007	0.004	0.003	0.004	0.028	0.015
zc-2	mean	4.439	2.070	5.537	5.481	6.901	6.314	6.286	4.185	4.648	4.663	6.840	6.258	7.976	5.237	6.394	3.267	4.575
	std deviation	0.015	0.198	0.059	0.055	0.033	0.011	0.023	0.028	0.018	0.041	0.047	0.012	0.021	0.018	0.013	0.052	0.067
zmc-5a	mean	4.448	1.876	5.285	5.581	6.789	6.580	6.676	4.269	4.403	4.387	6.404	6.081	7.772	5.145	6.387	3.055	4.323
	std deviation	0.023	0.352	0.136	0.021	0.043	0.020	0.026	0.024	0.050	0.012	0.021	0.013	0.011	0.010	0.014	0.071	0.014
zmc-5b	mean	4.499	2.264	5.753	5.823	6.936	6.693	6.406	4.369	4.499	4.681	6.754	6.460	7.927	5.186	6.511	3.784	4.554
	std deviation	0.032	0.299	0.073	0.014	0.017	0.014	0.014	0.017	0.027	0.011	0.013	0.011	0.010	0.010	0.010	0.170	0.020
zmc-5c	mean	4.424	2.116	5.605	5.519	6.917	6.586	6.684	4.276	4.436	4.594	6.626	6.209	7.846	5.171	6.475	3.288	4.484
	std deviation	0.021	0.049	0.033	0.035	0.016	0.017	0.019	0.020	0.023	0.022	0.016	0.017	0.018	0.021	0.021	0.074	0.033
zmc-5d	mean	4.395	1.809	5.343	5.371	6.590	6.594	6.633	4.255	4.551	4.596	6.545	6.027	7.833	5.135	6.442	2.896	4.473
	std deviation	0.020	0.380	0.110	0.040	0.025	0.015	0.034	0.010	0.011	0.017	0.013	0.018	0.014	0.010	0.014	0.290	0.009
zmc-5e	mean	4.474	2.182	5.101	5.265	6.764	6.639	6.278	4.086	4.305	4.561	6.751	5.997	7.760	5.112	6.378	3.230	4.677
	std deviation	0.026	0.129	0.056	0.215	0.039	0.010	0.026	0.028	0.011	0.015	0.012	0.018	0.025	0.035	0.032	0.382	0.024
zmc-5f	mean	4.575	2.365	4.700	5.485	6.633	6.660	6.289	4.204	4.288	4.532	6.583	6.112	7.771	5.080	6.394	3.337	4.542
	std deviation	0.010	0.148	0.301	0.095	0.032	0.014	0.019	0.029	0.157	0.007	0.016	0.013	0.013	0.016	0.014	0.083	0.022
zmf-1	mean	4.615	2.482	5.552	5.892	6.691	7.094	7.445	4.229	5.355	5.029	6.874	6.056	7.965	5.201	6.390	2.643	4.685
	std deviation	0.079	0.124	0.160	0.110	0.152	0.096	0.034	0.059	0.031	0.040	0.063	0.032	0.040	0.028	0.032	0.875	0.034
zmh-1	mean	5.008	2.348	5.627	5.903	6.574	6.843	8.274	4.063	5.837	4.604	6.658	6.336	7.952	5.253	6.565	4.609	4.460
	std deviation	0.010	0.201	0.089	0.061	0.032	0.012	0.008	0.019	0.008	0.015	0.022	0.005	0.004	0.006	0.007	0.040	0.035
zul-2	mean	4.458	2.127	5.332	5.378	6.766	6.184	6.518	3.930	4.366	4.291	6.616	5.983	7.724	4.940	6.272	3.297	4.443
	std deviation	0.352	0.391	0.152	0.163	0.049	0.098	0.569	0.078	0.397	0.095	0.252	0.032	0.068	0.208	0.113	0.562	0.104
zub-1	mean	5.111	3.553	5.267	6.273	6.891	7.087	7.959	4.920	5.717	4.995	6.705	6.059	7.687	4.913	6.042	5.340	4.422
	std deviation	0.024	0.048	0.033	0.026	0.016	0.012	0.022	0.024	0.023	0.024	0.022	0.025	0.027	0.023	0.025	0.020	0.046
zuc-4	mean	4.080	2.258	5.021	5.545	6.774	6.610	6.798	4.276	4.697	4.853	6.620	5.996	7.791	5.240	6.408	3.545	4.310
	std deviation	0.354	0.174	0.338	0.029	0.060	0.024	0.021	0.025	0.035	0.048	0.042	0.016	0.016	0.016	0.018	0.102	0.104
zfd-4	mean	4.174	1.803	5.767	5.803	7.230	6.881	8.112	4.362	5.597	4.705	6.596	6.290	7.820	5.172	6.481	4.271	4.451
	std deviation	0.042	0.331	0.022	0.021	0.026	0.016	0.019	0.021	0.019	0.011	0.016	0.019	0.019	0.018	0.017	0.034	0.020
eco-1	mean	5.213	1.723	5.690	6.947	6.793	6.971	6.168	3.986	5.064	4.913	5.235	6.070	7.225	4.829	6.243	4.379	3.973
	std deviation	0.026	0.476	0.164	0.014	0.010	0.014	0.028	0.037	0.011	0.010	0.014	0.012	0.009	0.016	0.013	0.019	0.025
wan-1	mean	4.618	2.487	5.766	6.304	6.915	6.758	5.891	4.190	4.652	4.517	5.876	5.573	7.624	5.124	6.247	4.264	4.235
	std deviation	0.018	0.137	0.049	0.010	0.024	0.012	0.049	0.030	0.045	0.047	0.042	0.011	0.019	0.009	0.009	0.020	0.023

Table C.1 Mean Concentration (log ppb) and standard deviations for all replicates

Sample		Ga	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	Ru	Rh	Pd	Ag	Cd	Sn
ge-1	mean	4.097	4.517	1.990	1.922	1.982	4.389	3.122	2.523	3.057	2.196	2.050	0.640	0.155	1.004	1.406	1.774	2.865
	std deviation	0.016	0.018	0.153	0.118	0.139	0.013	0.042	0.021	0.120	0.062	0.122	0.692	0.222	0.268	0.217	0.348	0.328
eg-12	mean	2.576	3.986	2.264	1.761	2.095	1.722	2.676	1.994	2.863	1.967	1.944	1.830	1.000	1.267	1.458	1.770	2.732
	std deviation	0.059	0.024	0.034	0.680	0.278	0.193	0.055	0.146	0.077	0.081	0.488	0.267	0.256	0.261	0.150	0.280	0.315
Ino-1	mean	3.144	4.688	2.073	0.000	2.284	1.882	3.031	3.224	3.202	2.369	1.299	0.961	0.771	1.098	0.912	2.243	2.735
	std deviation	0.039	0.012	0.064	0.000	0.111	0.188	0.035	0.033	0.087	0.070	0.334	0.580	0.133	0.000	0.205	0.080	0.313
ps-1	mean	2.490	3.798	2.064	1.817	2.665	1.997	4.704	2.592	3.096	0.000	2.726	1.410	0.582	0.890	1.009	1.672	2.788
	std deviation	0.114	0.044	0.032	0.433	0.084	0.119	0.015	0.013	0.092	0.000	0.027	0.117	0.178	0.375	0.708	0.271	0.468
msc-1	mean	2.904	4.071	2.344	2.507	2.011	1.600	3.723	1.949	2.890	0.885	1.679	0.000	0.143	0.425	1.120	1.657	2.311
	std deviation	0.021	0.012	0.068	0.000	0.494	0.542	0.016	0.062	0.212	0.379	0.487	0.000	0.126	0.866	0.326	0.168	0.311
t-1	mean	3.294	3.940	3.265	0.855	1.578	2.010	4.225	3.266	2.594	1.484	2.302	1.024	0.151	1.524	1.075	1.575	2.382
	std deviation	0.264	0.050	0.364	0.000	0.560	0.174	0.361	0.022	0.133	0.193	0.184	0.912	0.761	0.364	0.524	0.330	0.347
zmo-1	mean	3.369	4.017	3.253	1.700	1.480	2.198	5.149	3.577	3.143	2.780	2.064	1.867	1.089	1.469	1.841	2.204	2.536
	std deviation	0.021	0.018	0.094	0.000	0.373	0.035	0.002	0.009	0.245	0.032	0.324	0.343	0.466	0.325	0.120	0.257	0.227
zc-2	mean	3.123	4.476	2.598	2.310	0.000	2.165	3.574	1.125	2.911	1.142	1.941	1.438	0.981	2.050	1.432	1.995	2.447
	std deviation	0.053	0.066	0.046	0.205	0.000	0.134	0.013	0.302	0.126	0.276	0.128	0.187	0.410	0.189	0.132	0.000	0.462
zmc-5a	mean	2.823	4.339	2.624	1.889	1.626	1.955	3.424	0.528	2.984	1.311	2.043	1.170	0.853	1.634	1.330	0.000	2.867
	std deviation	0.043	0.042	0.069	0.573	0.795	0.132	0.024	0.861	0.099	0.136	0.238	0.000	0.169	0.230	0.000	0.000	0.097
zmc-5b	mean	3.083	4.433	2.910	1.735	1.037	2.196	3.419	1.644	2.869	1.284	1.988	1.422	0.822	1.469	1.376	0.000	2.844
	std deviation	0.039	0.023	0.028	1.028	1.303	0.077	0.018	0.162	0.352	0.185	0.174	0.413	0.230	0.257	0.174	0.000	0.196
zmc-5c	mean	2.878	4.310	3.041	2.065	0.000	2.048	3.377	0.771	2.587	1.181	1.730	1.199	0.832	1.462	1.084	0.911	2.665
	std deviation	0.061	0.033	0.038	0.000	0.000	0.193	0.024	0.548	0.102	0.217	0.562	0.559	0.252	0.185	0.251	0.000	0.486
zmc-5d	mean	3.018	4.447	3.030	0.000	2.165	2.200	3.451	1.712	3.081	1.390	1.786	0.000	0.584	1.259	0.916	1.976	2.473
	std deviation	0.025	0.013	0.023	0.000	0.309	0.099	0.047	0.146	0.115	0.233	0.647	0.000	0.371	0.399	0.247	0.236	0.298
zmc-5e	mean	3.013	4.045	2.854	1.991	2.743	1.809	3.144	1.144	2.682	1.086	1.750	1.542	-0.889	1.252	0.854	1.187	2.389
	std deviation	0.052	0.063	0.025	0.000	0.377	0.127	0.033	0.197	0.113	0.150	0.184	0.000	0.000	0.511	0.344	0.894	0.121
zmc-5f	mean	3.020	4.166	2.860	2.038	2.531	2.078	3.267	1.424	2.728	0.885	1.951	1.282	0.000	1.116	0.892	1.534	2.266
	std deviation	0.024	0.021	0.049	0.000	0.082	0.085	0.016	0.060	0.188	0.366	0.095	0.340	0.000	0.929	0.243	0.051	0.248
zmf-1	mean	3.882	4.358	3.223	1.545	1.858	2.024	3.697	3.225	3.163	1.177	2.053	1.210	0.742	1.669	1.200	2.138	2.330
	std deviation	0.022	0.035	0.041	0.997	0.415	0.519	0.043	0.034	0.256	0.561	0.333	0.428	0.592	0.140	0.438	0.173	0.535
zmh-1	mean	3.566	4.374	2.959	2.018	2.083	2.186	5.280	3.142	3.070	1.334	3.280	1.411	1.164	1.386	0.862	2.256	2.390
	std deviation	0.015	0.013	0.015	0.273	0.339	0.054	0.005	0.007	0.260	0.387	0.014	0.187	0.132	0.186	0.474	0.221	0.513
zul-2	mean	2.877	4.064	3.850	1.531	2.067	1.546	3.642	1.730	2.903	0.854	1.937	1.167	0.716	1.404	0.208	1.732	2.439
	std deviation	0.252	0.049	0.345	0.000	0.557	0.399	0.365	1.034	0.252	0.750	0.370	0.215	0.000	0.443	0.550	0.686	0.419
zub-1	mean	3.745	3.838	3.105	0.000	2.149	2.355	4.195	3.056	3.381	1.538	1.384	0.000	0.476	1.270	0.874	1.569	2.432
	std deviation	0.020	0.029	0.038	0.000	0.264	0.124	0.023	0.026	0.088	0.256	0.175	0.000	0.119	0.417	0.497	0.090	0.307
zuc-4	mean	3.071	4.488	4.443	2.358	2.261	1.989	4.076	1.652	3.066	1.167	1.092	1.365	0.559	0.721	1.479	2.103	2.616
	std deviation	0.038	0.041	0.056	0.375	0.100	0.134	0.024	0.193	0.177	0.156	0.622	0.188	0.290	0.227	0.388	0.319	0.319
zfd-4	mean	3.425	4.247	2.836	2.027	2.032	1.740	5.102	2.539	2.872	1.934	1.891	2.077	1.221	1.427	1.434	2.044	2.805
	std deviation	0.015	0.025	0.029	0.431	0.351	0.219	0.015	0.054	0.087	0.121	0.214	0.223	0.319	0.480	0.383	0.244	0.151
eco-1	mean	3.355	3.767	2.203	1.987	2.773	2.730	3.810	3.446	3.138	1.855	1.970	0.000	0.814	1.407	1.763	2.055	2.209
	std deviation	0.026	0.019	0.073	0.486	0.121	0.039	0.015	0.020	0.102	0.106	0.247	0.000	0.279	0.770	0.175	0.174	0.487
wan-1	mean	3.078	4.209	2.670	2.257	2.368	1.486	2.942	2.670	2.831	1.585	1.611	0.838	0.359	1.416	1.079	1.804	2.712
	std deviation	0.026	0.034	0.036	0.000	0.219	0.375	0.033	0.037	0.041	0.219	0.734	0.915	0.663	0.583	0.462	0.550	0.325

Table C.1 Mean Concentration (log ppb) and standard deviations for all replicates

Sample		Sb	I	Te	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm
ge-1	mean	1.218	1.194	1.567	3.047	4.401	1.145	1.846	0.923	1.730	1.637	1.454	1.485	0.800	1.539	0.813	1.289	0.481
	std deviation	0.238	0.203	0.226	0.015	0.069	0.146	0.053	0.248	0.069	0.063	0.085	0.201	0.110	0.090	0.265	0.110	0.182
eg-12	mean	1.617	1.000	1.809	0.593	2.537	1.985	2.329	1.246	2.081	1.192	0.821	0.684	0.788	1.391	-0.147	1.251	1.171
	std deviation	0.141	0.000	0.179	0.435	0.053	0.193	0.242	0.264	0.177	0.616	0.291	0.325	0.310	0.254	0.283	0.394	0.206
lno-1	mean	1.897	1.110	1.754	0.799	3.943	2.212	2.591	1.756	2.254	1.818	1.341	1.959	1.394	2.227	1.650	2.080	1.308
	std deviation	0.082	0.291	0.325	0.147	0.010	0.333	0.029	0.131	0.173	0.106	0.118	0.161	0.125	0.129	0.192	0.084	0.241
ps-1	mean	1.241	0.923	1.898	0.660	3.413	3.525	3.789	2.647	3.079	2.133	2.334	2.131	1.175	1.731	1.113	1.662	0.739
	std deviation	0.150	0.239	0.100	0.184	0.013	0.008	0.005	0.018	0.035	0.046	0.057	0.084	0.103	0.076	0.147	0.102	0.107
msc-1	mean	1.960	0.000	0.851	0.992	2.625	0.330	0.916	0.623	1.738	0.000	0.836	1.353	0.206	1.229	0.700	0.791	0.436
	std deviation	0.051	0.000	0.000	0.197	0.151	1.881	0.414	0.689	0.358	0.000	0.254	0.155	0.000	0.321	0.453	0.550	0.414
t-1	mean	2.728	-0.082	0.000	0.507	3.254	2.494	2.877	2.086	2.751	2.353	1.737	2.178	1.492	2.186	1.280	1.688	0.882
	std deviation	0.104	0.000	0.000	0.465	0.417	0.855	0.682	0.459	0.548	0.111	0.240	0.757	0.124	0.402	0.525	0.574	0.265
zmo-1	mean	2.109	1.574	1.830	1.644	3.452	4.213	4.478	3.454	3.984	3.104	2.427	3.096	2.135	2.656	2.008	2.369	1.325
	std deviation	0.076	0.221	0.189	0.131	0.035	0.009	0.005	0.010	0.018	0.033	0.061	0.036	0.037	0.064	0.047	0.065	0.144
zc-2	mean	2.203	0.940	1.498	0.716	3.157	1.411	1.494	0.283	1.363	0.161	1.159	1.124	0.526	0.758	0.749	0.037	0.612
	std deviation	0.102	0.531	0.327	0.336	0.036	0.221	0.193	0.790	0.661	0.000	0.292	0.170	0.361	0.972	0.358	0.003	0.381
zmc-5a	mean	2.364	0.070	1.256	0.682	2.930	1.196	1.292	0.792	1.528	0.000	0.959	0.052	0.223	0.000	0.986	0.010	0.482
	std deviation	0.066	1.492	0.504	0.476	0.037	0.428	0.559	0.401	0.383	0.000	0.380	0.014	0.578	0.000	0.247	0.001	0.556
zmc-5b	mean	2.333	1.355	1.299	1.282	3.188	1.192	1.500	0.889	1.541	1.427	0.778	1.360	0.417	1.127	0.771	0.002	0.432
	std deviation	0.069	0.000	0.304	0.173	0.027	0.188	0.156	0.106	0.406	0.000	0.796	0.235	0.236	0.328	0.326	0.001	0.077
zmc-5c	mean	2.563	0.000	1.468	0.901	2.863	1.157	0.641	0.212	1.285	0.000	1.025	0.928	0.604	0.854	0.656	0.003	0.258
	std deviation	0.063	0.000	0.293	0.485	0.075	0.247	0.526	0.399	0.456	0.000	0.300	0.543	0.278	0.000	0.270	0.050	0.513
zmc-5d	mean	2.505	0.799	1.742	0.745	3.154	1.599	2.092	1.026	1.553	1.296	0.712	1.338	0.504	0.000	0.536	1.165	0.716
	std deviation	0.048	0.000	0.242	0.354	0.049	0.095	0.059	0.238	0.261	0.550	0.627	0.293	0.317	0.000	0.469	0.172	0.294
zmc-5e	mean	2.443	0.000	1.575	0.816	2.864	0.000	0.924	0.797	1.557	1.315	0.900	1.419	0.000	0.500	0.292	1.159	0.664
	std deviation	0.083	0.000	0.000	0.154	0.054	0.000	0.000	0.171	0.308	0.000	0.527	0.144	0.000	1.127	0.968	0.421	0.117
zmc-5f	mean	2.476	1.214	1.776	0.703	3.033	1.017	1.134	0.066	1.482	0.000	0.860	1.279	0.000	1.131	0.549	0.418	-0.423
	std deviation	0.046	0.000	0.000	0.778	0.033	0.308	0.327	0.858	0.401	0.000	0.398	0.454	0.000	0.354	0.182	1.397	1.774
zmf-1	mean	1.767	0.870	0.000	0.964	2.876	1.640	2.274	1.526	2.360	2.163	1.167	2.158	1.432	2.296	1.642	2.104	0.918
	std deviation	0.056	0.391	0.000	0.482	0.447	0.554	0.472	0.426	0.340	0.103	0.269	0.125	0.150	0.078	0.176	0.094	0.351
zmh-1	mean	2.315	1.018	0.000	1.086	3.194	2.990	3.251	2.325	2.959	2.288	1.675	2.284	1.338	2.054	1.364	1.824	0.254
	std deviation	0.056	0.264	0.000	0.254	0.089	0.030	0.024	0.045	0.032	0.086	0.147	0.091	0.096	0.063	0.235	0.045	0.271
zul-2	mean	2.535	0.000	0.000	0.697	2.704	0.885	1.546	0.719	1.982	2.364	0.617	1.415	1.540	1.014	1.054	1.177	0.386
	std deviation	0.114	0.000	0.000	0.258	0.340	1.164	0.876	0.875	0.478	0.000	0.631	0.627	0.000	1.057	0.321	0.558	0.353
zub-1	mean	3.147	0.000	1.197	1.836	2.842	1.679	2.110	1.597	2.346	1.876	1.301	2.170	1.295	2.306	1.463	2.023	1.211
	std deviation	0.031	0.000	0.800	0.091	0.084	0.142	0.050	0.050	0.116	0.084	0.332	0.075	0.171	0.043	0.147	0.131	0.180
zuc-4	mean	2.310	1.308	1.007	0.977	2.749	1.359	1.489	0.916	1.333	0.812	-0.093	1.266	0.302	0.928	0.522	0.966	0.063
	std deviation	0.058	0.500	1.102	0.237	0.087	0.264	0.129	0.162	0.348	0.530	0.448	0.186	0.647	0.437	0.379	0.790	0.679
zfd-4	mean	2.565	1.337	1.783	1.706	2.772	2.419	2.777	1.772	2.397	1.920	1.709	1.794	1.178	1.027	1.127	1.431	0.979
	std deviation	0.067	0.566	0.142	0.107	0.075	0.054	0.051	0.052	0.150	0.154	0.150	0.263	0.242	0.834	0.425	0.739	0.280
eco-1	mean	1.612	0.862	2.011	2.368	2.828	1.862	2.210	1.488	2.276	2.141	1.704	2.327	1.633	2.399	1.805	2.271	1.554
	std deviation	0.116	0.143	0.121	0.032	0.045	0.151	0.049	0.263	0.134	0.135	0.188	0.066	0.127	0.085	0.034	0.091	0.142
wan-1	mean	2.044	1.053	1.895	0.821	2.834	1.420	1.128	0.666	1.691	1.122	0.998	1.595	0.770	1.507	0.763	1.603	1.003
	std deviation	0.085	0.000	0.321	0.457	0.059	0.123	0.203	0.257	0.274	0.300	0.311	0.318	0.263	0.329	0.448	0.167	0.113

Table C.1 Mean Concentration (log ppb) and standard deviations for all replicates

Sample		Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Th	U
ge-1	mean	1.242	0.564	1.434	2.075	0.000	0.000	0.334	0.528	0.909	0.393	0.000	2.179	2.784	0.462	1.883	1.268
	std deviation	0.133	0.368	0.114	0.384	0.000	0.000	0.384	0.128	0.122	0.202	0.000	0.022	0.021	0.137	0.028	0.063
eg-12	mean	1.111	0.753	1.316	1.453	2.391	-0.460	0.912	1.042	1.243	0.657	1.975	0.000	2.686	0.761	0.608	1.184
	std deviation	0.826	0.099	0.191	0.563	0.201	0.000	0.265	0.337	0.420	0.027	0.077	0.000	0.080	0.186	0.402	0.244
lno-1	mean	1.969	0.973	1.410	1.357	1.963	-0.321	0.955	0.412	0.937	0.000	0.000	0.835	2.917	1.170	1.283	0.000
	std deviation	0.202	0.265	0.088	0.364	0.121	0.554	0.000	0.000	0.203	0.000	0.000	0.262	0.113	0.650	0.209	0.000
ps-1	mean	1.745	1.114	1.452	0.819	0.000	0.950	-0.321	0.036	0.824	0.353	0.000	0.946	2.643	0.695	0.911	1.818
	std deviation	0.048	0.146	0.187	0.315	0.000	0.000	0.865	0.034	0.123	0.341	0.000	0.088	0.044	0.316	0.169	0.052
mec-1	mean	1.393	0.239	1.141	1.770	1.816	0.839	0.887	-0.029	0.630	0.817	0.000	1.464	2.470	1.285	0.969	0.248
	std deviation	0.253	0.287	0.577	0.696	0.118	0.445	0.377	0.730	0.580	0.233	0.000	0.224	0.080	0.153	0.000	0.445
t-1	mean	1.786	0.527	0.974	0.380	1.852	0.758	1.460	0.005	0.791	-0.069	0.000	0.911	3.159	1.504	0.000	2.295
	std deviation	0.244	0.526	0.435	0.431	0.284	0.530	0.392	0.371	0.283	0.126	0.000	0.314	0.365	0.336	0.000	1.070
zmo-1	mean	2.123	1.219	1.559	2.034	2.064	1.844	0.435	0.813	0.745	0.010	0.000	2.934	3.834	1.936	1.624	2.344
	std deviation	0.145	0.262	0.259	0.107	2.009	0.000	0.557	0.273	0.000	0.521	0.000	0.036	0.032	0.047	0.117	0.021
zc-2	mean	1.005	0.000	1.311	1.426	2.983	0.572	1.034	0.548	1.408	0.648	1.742	0.529	2.371	0.886	0.268	0.248
	std deviation	0.543	0.000	0.150	0.568	0.041	0.886	0.144	0.000	0.145	0.865	0.146	0.165	0.085	0.299	0.000	0.471
zmc-5a	mean	0.894	0.000	1.058	1.849	3.186	0.496	0.539	0.000	1.121	0.074	1.496	0.407	2.227	0.283	0.823	0.515
	std deviation	0.656	0.000	0.419	0.774	0.035	0.381	0.358	0.000	0.087	0.456	0.396	0.743	0.056	0.821	0.452	0.660
zmc-5b	mean	1.431	0.000	1.359	1.101	3.076	0.570	0.521	0.000	1.248	0.460	1.182	0.452	2.358	0.493	0.173	0.559
	std deviation	0.075	0.000	0.367	0.136	0.056	0.788	0.556	0.000	0.173	0.949	0.104	0.528	0.076	0.486	0.709	0.534
zmc-5c	mean	1.285	0.000	1.291	0.856	3.122	0.563	0.639	0.635	1.288	0.124	1.852	0.789	2.193	0.353	0.824	0.441
	std deviation	0.164	0.000	0.695	0.293	0.022	0.000	0.000	0.000	0.343	0.431	0.125	0.762	0.168	0.797	0.189	0.000
zmc-5d	mean	1.283	0.537	1.231	2.169	2.899	1.251	0.944	0.824	0.634	0.836	0.000	0.569	2.557	0.943	0.973	0.223
	std deviation	0.455	0.216	0.287	1.201	0.171	0.458	0.161	0.197	0.015	1.074	0.000	0.279	0.126	0.346	0.315	0.187
zmc-5e	mean	1.580	0.503	1.277	1.441	2.910	1.106	1.107	0.700	0.707	0.446	0.000	0.545	2.301	0.295	0.000	0.355
	std deviation	0.414	0.000	0.373	0.402	0.034	0.157	0.265	0.479	0.087	0.648	0.000	0.605	0.094	0.691	0.000	0.665
zmc-5f	mean	0.939	0.201	1.419	1.680	2.985	1.124	1.004	0.464	1.175	0.563	0.000	0.789	2.490	0.681	1.020	0.801
	std deviation	0.616	0.000	0.235	0.377	0.049	0.211	0.174	0.319	0.045	0.468	0.000	0.167	0.534	0.321	0.208	0.350
zmf-1	mean	2.017	1.034	1.386	1.931	3.228	1.087	0.000	0.725	0.942	0.639	0.000	0.653	3.319	0.825	1.585	0.741
	std deviation	0.166	0.197	0.463	0.850	0.000	0.887	0.000	0.287	0.510	0.453	0.000	0.139	0.033	0.594	1.324	0.577
zmh-1	mean	1.818	0.870	0.684	1.026	0.000	0.000	0.000	0.358	0.951	0.607	0.000	0.447	3.370	1.784	1.052	1.976
	std deviation	0.196	0.232	0.940	0.451	0.000	0.000	0.000	0.626	0.000	0.000	0.000	0.671	0.013	0.057	0.153	0.044
zul-2	mean	1.490	0.000	1.428	0.769	2.001	0.929	0.722	0.256	0.938	0.622	0.000	0.723	2.476	0.694	0.538	0.186
	std deviation	0.512	0.000	0.040	0.711	1.046	0.313	0.377	0.313	0.227	0.351	0.000	0.328	0.397	0.528	0.000	2.233
zub-1	mean	1.983	0.229	1.740	1.212	2.561	0.991	1.006	0.555	1.031	0.642	0.000	0.988	2.695	0.781	-0.886	1.707
	std deviation	0.140	0.472	0.120	0.449	0.064	0.426	0.409	0.057	0.000	0.204	0.000	0.150	0.106	0.337	0.000	0.098
zuc-4	mean	1.094	0.281	1.193	1.954	2.239	0.740	0.696	0.476	0.831	1.067	0.000	0.833	2.316	0.968	0.875	0.000
	std deviation	0.493	0.175	0.389	0.901	0.265	0.655	0.000	0.000	0.161	0.240	0.000	0.292	0.115	0.615	0.201	0.000
zfd-4	mean	1.273	0.947	1.267	1.038	2.581	1.335	1.035	1.258	1.396	0.453	1.921	0.000	2.501	0.776	0.777	0.963
	std deviation	0.662	0.260	0.241	0.432	0.063	0.912	0.552	0.068	0.327	0.644	0.166	0.000	0.048	0.309	0.505	0.323
eco-1	mean	2.275	1.618	1.380	1.010	2.614	0.591	0.613	1.166	0.848	0.394	1.663	-0.186	2.909	0.120	1.664	2.878
	std deviation	0.098	0.065	0.220	0.367	0.047	0.661	0.581	0.135	0.668	0.541	0.263	0.000	0.053	0.641	0.135	0.019
wan-1	mean	1.012	0.802	1.271	0.628	2.818	0.750	0.565	0.977	0.886	0.000	1.984	0.000	1.990	0.833	0.471	1.238
	std deviation	0.313	0.339	0.409	0.271	0.058	0.221	0.518	0.206	0.585	0.000	0.215	0.000	0.459	0.351	0.000	0.189

Table C.21 (cont).

		Sb	I	Te	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er
Lewisian	**Mean**	1.577	1.146	1.704	1.520	3.627	1.781	2.255	1.309	2.022	1.549	1.315	1.463	0.994	1.760	0.956	1.540
	Std Dev	0.317	0.223	0.247	1.158	0.794	0.512	0.335	0.399	0.265	0.428	0.248	0.533	0.339	0.399	0.699	0.443
Dalradian	**Mean**	2.263	0.995	1.588	0.887	3.085	1.989	2.143	1.317	2.044	2.213	1.341	1.700	0.928	1.519	0.915	1.377
	Std Dev	0.393	0.650	0.360	0.476	0.273	1.212	1.266	1.175	0.926	0.756	0.719	0.738	0.690	0.823	0.599	0.751
Basement	**Mean**	2.020	0.912	0.987	1.021	3.023	2.263	2.725	1.894	2.637	2.221	1.401	2.216	1.389	2.184	1.514	1.975
	Std Dev	0.278	0.319	0.654	0.368	0.347	0.771	0.584	0.493	0.378	0.108	0.325	0.120	0.126	0.138	0.234	0.156
Ophiolite	**Mean**	2.367	1.157	1.685	1.442	2.798	1.641	1.935	1.272	2.092	1.617	1.207	1.804	1.185	1.583	1.278	1.675
	Std Dev	0.475	0.402	0.549	0.643	0.158	0.685	0.667	0.585	0.444	0.583	0.626	0.477	0.433	0.819	0.480	0.569
All	**Mean**	2.174	1.049	1.641	1.139	3.072	1.871	2.152	1.358	2.109	1.846	1.302	1.753	1.068	1.658	1.067	1.575
	Std Dev	0.475	0.502	0.414	0.709	0.453	0.960	0.975	0.897	0.722	0.644	0.618	0.623	0.548	0.748	0.601	0.629

		Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Th	U
Lewisian	**Mean**	0.976	1.535	0.764	1.393	1.629	2.177	-0.356	0.685	0.858	1.041	0.459	1.975	1.507	2.796	0.805	1.296	1.226
	Std Dev	0.444	0.470	0.366	0.150	0.529	0.264	0.484	0.375	0.366	0.313	0.193	0.070	0.697	0.123	0.533	0.561	0.169
Dalradian	**Mean**	0.628	1.490	0.810	1.286	1.440	2.729	0.904	0.761	0.495	1.025	0.390	1.584	1.057	2.602	0.913	0.982	1.151
	Std Dev	0.520	0.480	0.442	0.391	0.735	0.591	0.483	0.575	0.465	0.346	0.602	0.327	0.861	0.503	0.653	0.453	1.011
Basement	**Mean**	0.616	1.926	0.958	1.093	1.513	3.228	1.087	0.540	0.541	0.943	0.634	1.025	0.550	3.342	1.267	1.230	1.311
	Std Dev	0.438	0.193	0.213	0.722	0.784	0.000	0.768	0.235	0.481	0.431	0.370	0.987	0.445	0.035	0.627	0.606	0.730
Ophiolite	**Mean**	0.975	1.674	0.818	1.399	1.118	2.469	0.876	0.766	0.953	1.002	0.620	1.856	0.780	2.505	0.732	0.989	1.543
	Std Dev	0.529	0.551	0.566	0.305	0.651	0.486	0.476	0.465	0.367	0.473	0.370	0.243	0.354	0.394	0.543	0.672	1.032
All	**Mean**	0.777	1.598	0.825	1.307	1.389	2.580	0.832	0.751	0.702	1.014	0.471	1.748	1.006	2.668	0.882	1.081	1.291
	Std Dev	0.535	0.497	0.456	0.412	0.717	0.560	0.584	0.513	0.476	0.392	0.516	0.312	0.774	0.472	0.624	0.570	0.936

Table C.2 Summary statistics of major and trace element concentrations (log ppb) for all the geological provinces used in this study and the total data set.

		Li	**Be**	**B**	**Na**	**Mg**	**Al**	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Lewisian	Mean	4.606	2.299	5.538	5.561	6.730	6.300	6.119	4.089	5.525	3.980	5.828	5.810	7.732	5.240	6.274	3.746	4.218
	Std Dev	0.363	0.416	0.278	0.246	0.269	0.337	0.183	0.103	0.224	0.641	0.648	0.153	0.244	0.099	0.227	0.933	0.329
Dalradian	Mean	4.533	2.056	5.349	5.538	6.752	6.482	6.913	4.193	4.783	4.420	6.441	6.153	7.736	5.051	6.378	3.562	4.448
	Std Dev	0.229	0.360	0.303	0.331	0.196	0.298	0.713	0.136	0.529	0.330	0.451	0.159	0.181	0.235	0.121	0.530	0.283
Basement	Mean	4.796	2.420	5.587	5.897	6.637	6.978	7.828	4.153	5.578	4.833	6.774	6.185	7.959	5.225	6.471	3.823	4.581
	Std Dev	0.204	0.164	0.128	0.084	0.120	0.142	0.414	0.093	0.241	0.214	0.116	0.141	0.028	0.032	0.090	1.076	0.117
Ophiolite	Mean	4.620	2.391	5.475	6.036	6.887	6.751	6.945	4.272	5.038	4.710	6.285	6.005	7.654	5.042	6.290	4.195	4.310
	Std Dev	0.467	0.654	0.319	0.528	0.168	0.293	0.890	0.324	0.530	0.244	0.547	0.219	0.204	0.171	0.152	0.685	0.178
All	Mean	4.590	2.215	5.432	5.714	6.777	6.579	6.894	4.198	5.026	4.480	6.345	6.067	7.733	5.090	6.347	3.781	4.391
	Std Dev	0.337	0.481	0.306	0.438	0.209	0.352	0.805	0.210	0.563	0.440	0.549	0.214	0.206	0.207	0.157	0.745	0.274

		Ga	**Ge**	**As**	**Se**	**Br**	**Rb**	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**Sn**
Lewisian	Mean	3.272	4.397	2.109	1.868	2.129	2.664	2.943	2.581	3.041	2.177	1.858	1.165	0.605	1.132	1.302	1.929	2.777
	Std Dev	0.629	0.299	0.147	0.352	0.236	1.230	0.196	0.510	0.170	0.178	0.433	0.698	0.435	0.265	0.295	0.325	0.303
Dalradian	Mean	3.001	4.186	2.803	1.884	2.143	2.022	3.777	1.846	2.872	1.355	2.004	1.395	0.721	1.360	1.214	1.692	2.554
	Std Dev	0.243	0.223	0.373	0.594	0.655	0.258	0.625	0.960	0.251	0.561	0.422	0.406	0.469	0.562	0.437	0.484	0.358
Basement	Mean	3.736	4.365	3.101	1.755	1.960	2.099	4.428	3.186	3.120	1.255	2.619	1.331	0.937	1.538	1.044	2.193	2.355
	Std Dev	0.159	0.026	0.135	0.723	0.364	0.364	0.790	0.048	0.242	0.447	0.652	0.287	0.461	0.206	0.451	0.190	0.482
Ophiolite	Mean	3.267	4.109	3.179	2.081	2.304	1.993	3.997	2.578	3.020	1.464	1.714	1.472	0.732	1.321	1.244	1.934	2.518
	Std Dev	0.301	0.249	0.753	0.393	0.362	0.492	0.689	0.711	0.238	0.508	0.566	0.561	0.483	0.500	0.563	0.363	0.386
All	Mean	3.181	4.210	2.842	1.904	2.167	2.109	3.777	2.286	2.963	1.504	1.969	1.359	0.733	1.346	1.216	1.885	2.562
	Std Dev	0.399	0.253	0.587	0.557	0.500	0.609	0.725	0.911	0.253	0.569	0.541	0.526	0.476	0.503	0.472	0.419	0.384

Table C.3 Pearson's product moment coeffecients

	Li	Be	B	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	Ru	Rh	Pd	Ag	Cd	Sn	Sb	Te	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu
Be	0.44																																		
B	-0.02	-0.21																																	
V	0.33	0.45	0.09																																
Cr	-0.24	0.17	-0.15	0.54																															
Co	-0.45	-0.23	0.24	0.20	0.45																														
Ni	-0.30	-0.38	0.21	0.20	0.50	0.69																													
Cu	0.47	0.87	-0.03	0.49	0.13	-0.03	-0.09																												
Zn	-0.15	-0.02	-0.23	0.35	0.79	0.45	0.51	0.05																											
Ga	0.33	0.30	0.14	0.65	0.36	0.41	0.34	0.57	0.45																										
Ge	-0.23	-0.19	-0.01	0.03	0.18	0.59	0.40	-0.16	0.03	0.21																									
As	-0.18	-0.03	-0.32	0.20	0.14	0.11	0.02	-0.12	-0.07	-0.11	0.17																								
Se	-0.32	-0.27	0.42	0.32	0.30	0.39	0.44	-0.13	0.01	0.21	0.26	0.28																							
Br	0.24	-0.04	-0.08	-0.03	-0.28	-0.41	-0.25	-0.04	-0.20	-0.16	-0.38	-0.16	-0.21																						
Rb	0.13	-0.01	0.15	0.26	0.01	0.47	0.43	0.40	0.29	0.80	0.28	-0.09	0.15	-0.09																					
Sr	0.13	-0.08	0.21	-0.06	0.09	0.18	0.41	0.03	0.17	0.06	-0.12	-0.06	0.16	-0.13	-0.11																				
Y	0.60	0.10	0.02	0.19	-0.13	-0.11	-0.12	0.08	0.16	0.21	-0.17	-0.13	-0.27	0.04	-0.08	0.44																			
Zr	0.42	0.62	-0.04	0.49	0.11	0.01	-0.09	0.58	-0.06	0.42	0.12	0.06	0.01	-0.10	0.06	0.18	0.50																		
Nb	0.06	-0.6	0.01	-0.12	-0.08	0.32	0.12	0.01	0.32	0.16	0.07	-0.10	-0.24	-0.18	0.15	0.42	0.71	0.32																	
Mo	0.28	-0.09	0.16	-0.10	0.04	0.09	0.35	0.02	-0.04	0.08	-0.01	-0.10	0.15	-0.03	-0.04	0.706	0.15	0.10	-0.01																
Ru	-0.31	-0.20	0.46	-0.13	-0.01	0.22	0.15	-0.18	-0.04	-0.09	-0.04	0.01	0.42	-0.16	-0.12	0.54	0.01	-0.13	0.24	0.07															
Rh	-0.14	-0.24	0.48	0.08	0.19	0.40	0.37	-0.21	0.15	0.03	0.10	-0.11	0.44	-0.31	-0.18	0.74	0.36	0.12	0.42	0.34	0.69														
Pd	-0.4	-0.05	0.12	0.22	0.49	0.11	0.09	-0.15	0.30	-0.03	0.03	-0.21	0.25	-0.25	-0.18	0.01	0.03	-0.08	-0.07	-0.04	0.06	0.44													
Ag	0.14	-0.20	0.40	0.29	-0.07	0.24	0.17	-0.07	0.12	0.16	-0.14	0.15	0.26	-0.24	0.12	0.33	0.62	0.25	0.63	-0.10	0.37	0.53	0.09												
Cd	0.21	-0.13	0.19	0.15	-0.13	0.30	0.15	-0.08	-0.05	0.24	0.25	0.25	0.18	-0.01	0.01	0.59	0.63	0.41	0.51	0.40	0.32	0.54	-0.23	0.52											
Sn	-0.26	-0.15	0.49	-0.22	-0.24	0.27	0.20	-0.04	-0.27	0.12	0.35	-0.06	0.36	-0.27	0.39	-0.06	-0.30	-0.07	0.06	-0.08	0.31	0.12	-0.16	0.05	-0.06										
Sb	0.34	0.87	-0.36	0.32	0.26	-0.34	-0.31	0.67	0.09	0.08	-0.28	0.03	-0.36	-0.10	-0.18	-0.01	-0.03	0.32	-0.17	-0.10	-0.09	-0.21	0.04	-0.32	-0.32	-0.24									
Te	0.16	-0.06	0.64	-0.09	-0.58	-0.11	-0.21	0.01	-0.44	-0.09	-0.16	-0.28	-0.08	0.23	0.03	0.07	0.31	0.16	0.35	-0.18	0.24	0.30	0.01	0.55	0.22	0.33	-0.22								
Cs	0.24	0.02	0.21	0.34	0.05	0.41	0.39	0.43	0.24	0.80	0.21	-0.11	0.14	-0.02	0.98	-0.09	0.03	0.12	0.17	-0.06	-0.12	-0.15	-0.15	0.23	0.05	0.34	-0.16	0.13							
Ba	0.17	-0.02	0.08	0.12	-0.01	0.44	0.36	0.32	0.22	0.74	0.45	-0.13	0.07	-0.11	0.94	-0.08	0.04	0.14	0.28	-0.03	-0.12	-0.17	-0.24	0.08	0.13	0.44	-0.23	0.06	0.92						
La	-0.01	-0.09	-0.06	-0.17	0.01	0.12	0.15	-0.08	0.36	-0.03	-0.23	-0.04	-0.18	-0.13	-0.06	0.54	0.66	0.25	0.87	0.06	0.19	0.43	0.01	0.60	0.38	-0.05	-0.13	0.28	-0.05	0.01					
Ce	-0.01	-0.01	-0.06	-0.16	0.01	0.12	0.15	-0.08	0.36	-0.03	-0.23	-0.04	-0.18	-0.13	-0.06	0.54	0.66	0.25	0.87	0.06	0.20	0.43	0.01	0.60	0.38	-0.05	-0.12	0.28	-0.05	0.01	1.00				
Pr	0.01	0.08	-0.07	-0.14	0.03	0.14	0.15	-0.07	0.39	-0.01	-0.22	-0.04	-0.19	-0.15	-0.06	0.54	0.68	0.25	0.88	0.07	0.20	0.44	0.02	0.60	0.40	-0.08	-0.11	0.26	-0.05	0.01	1.00	1.00			
Nd	0.03	-0.07	-0.08	-0.13	0.04	0.14	0.15	-0.07	0.40	0.01	-0.22	-0.04	-0.20	-0.16	-0.07	0.55	0.70	0.25	0.89	0.08	0.19	0.45	0.02	0.61	0.40	-0.10	-0.09	0.24	-0.05	0.01	0.99	0.99	1.00		
Sm	0.13	-0.05	-0.05	-0.05	0.04	0.12	0.13	-0.04	0.41	0.07	-0.23	-0.05	-0.20	-0.15	-0.05	0.59	0.79	0.30	0.89	0.11	0.20	0.48	0.04	0.61	0.48	-0.14	-0.08	0.25	-0.03	0.02	0.97	0.98	0.68	0.99	
Eu	0.17	-0.09	0.06	-0.21	-0.19	-0.18	0.06	-0.04	0.11	-0.02	-0.34	-0.13	-0.06	0.07	-0.04	0.56	0.60	0.26	0.66	0.20	0.24	0.37	-0.06	0.53	0.34	0.10	-0.14	0.41	-0.01	0.04	0.86	0.86	0.84	0.83	0.82
Gd	0.20	0.01	-0.08	-0.03	0.02	0.05	0.07	-0.01	0.39	0.07	-0.26	-0.06	-0.26	-0.12	-0.08	0.56	0.82	0.32	0.87	0.10	0.15	0.43	0.04	0.63	0.46	-0.19	-0.02	0.25	-0.04	-0.01	0.96	0.96	0.97	0.98	0.99	0.81
Tb	0.30	0.01	-0.01	0.04	-0.04	0.04	0.02	0.01	0.31	0.11	-0.22	-0.10	-0.23	-0.09	-0.08	0.54	0.90	0.40	0.89	0.07	0.18	0.48	0.05	0.70	0.54	-0.18	-0.05	0.34	-0.01	0.02	0.91	0.91	0.92	0.93	0.97	0.78
Dy	0.56	0.24	-0.08	0.21	-0.05	-0.13	-0.18	0.18	0.23	0.24	-0.22	-0.11	-0.30	-0.03	-0.08	0.39	0.97	0.56	0.74	0.07	-0.01	0.31	0.04	0.58	0.54	-0.31	0.11	0.24	0.01	0.03	0.71	0.71	0.73	0.75	0.82	0.63
Ho	0.48	0.10	-0.03	0.18	-0.07	-0.06	-0.07	0.06	0.20	0.19	-0.11	-0.14	-0.23	0.01	-0.10	0.40	0.97	0.56	0.77	0.07	0.01	0.38	0.06	0.62	0.58	-0.25	-0.04	0.29	-0.01	0.04	0.72	0.72	0.74	0.75	0.82	0.63
Er	0.57	0.20	0.05	0.25	-0.15	-0.15	-0.20	0.15	0.09	0.22	-0.20	-0.15	-0.26	0.12	-0.10	0.38	0.97	0.59	0.69	0.06	0.05	0.35	-0.01	0.62	0.62	-0.28	0.03	0.40	0.01	0.01	0.63	0.63	0.64	0.65	0.74	0.59
Tm	0.59	0.20	0.20	0.17	-0.44	-0.25	-0.44	0.16	-0.27	0.05	-0.19	-0.22	-0.28	0.29	-0.11	0.09	0.77	0.43	0.51	-0.19	0.10	0.21	-0.01	0.59	0.44	-0.15	0.01	0.63	0.04	-0.01	0.31	0.31	0.32	0.33	0.41	0.33
Yt	0.73	0.23	-0.05	0.30	-0.16	-0.33	-0.26	0.18	-0.01	0.21	-0.23	-0.14	-0.30	0.26	-0.12	0.23	0.90	0.61	0.45	0.12	-0.17	0.13	-0.02	0.47	0.50	-0.41	0.07	0.27	0.01	-0.02	0.40	0.41	0.42	0.43	0.53	0.45
Lu	0.55	-0.13	0.37	0.23	-0.39	-0.20	-0.01	-0.03	-0.25	0.12	-0.22	-0.16	0.01	0.38	-0.01	0.26	0.74	0.36	0.38	0.08	0.10	0.33	-0.01	0.71	0.55	-0.11	-0.31	0.64	0.16	0.04	0.32	0.32	0.32	0.32	0.40	0.46
Hf	0.20	0.66	-0.05	0.47	0.28	-0.03	-0.04	0.62	0.24	0.37	-0.20	-0.13	-0.15	-0.10	0.13	-0.04	0.29	0.65	0.31	-0.23	-0.20	-0.06	0.05	0.21	-0.10	0.01	0.47	0.15	0.17	0.11	0.37	0.37	0.36	0.35	0.34	0.35
Ta	-0.23	-0.10	-0.21	0.06	0.06	0.13	0.17	-0.11	0.05	-0.05	0.26	0.13	-0.13	-0.13	0.01	-0.13	-0.17	0.11	-0.06	-0.11	-0.17	-0.07	-0.08	-0.06	-0.08	-0.12	-0.01	0.10	-0.02	-0.01	-0.05	-0.05	-0.05	-0.05	-0.08	-0.14
W	-0.30	-0.11	-0.13	-0.16	0.27	-0.07	0.04	-0.26	0.11	-0.35	-0.07	0.06	-0.21	-0.15	-0.21	-0.27	-0.31	-0.28	-0.19	-0.24	-0.18	-0.15	0.33	-0.29	-0.52	-0.01	0.12	-0.22	-0.23	-0.28	-0.10	-0.10	-0.10	-0.10	-0.15	-0.25
Re	-0.06	0.20	-0.39	0.44	0.48	-0.11	-0.07	0.02	0.49	0.19	-0.18	0.01	-0.15	0.09	-0.20	-0.15	0.18	0.28	-0.02	-0.22	-0.24	-0.11	0.10	-0.07	-0.03	-0.59	0.22	-0.30	-0.21	-0.25	0.09	0.09	0.11	0.12	0.15	-0.04
Os	0.28	0.32	-0.22	-0.03	-0.06	-0.47	-0.51	0.19	0.09	-0.12	-0.47	-0.16	-0.33	0.26	-0.16	-0.16	-0.05	-0.31	-0.19	-0.26	0.11	-0.26	0.08	-0.20	-0.37	-0.31	0.52	-0.10	-0.13	-0.21	-0.21	-0.21	-0.19	-0.17	-0.14	-0.17
Ir	0.05	-0.17	0.58	0.11	-0.28	0.03	-0.10	-0.11	-0.19	-0.03	-0.31	-0.20	0.08	0.25	-0.12	0.28	0.25	-0.07	0.17	-0.05	0.60	0.51	0.04	0.52	0.36	-0.04	-0.17	0.62	-0.02	-0.20	0.06	0.06	0.07	0.07	0.13	0.06
Pt	-0.27	-0.22	0.59	0.04	0.03	0.20	-0.02	-0.20	-0.14	-0.03	0.06	-0.17	0.47	-0.12	-0.01	-0.01	-0.22	-0.30	-0.11	-0.21	0.65	0.48	0.50	0.24	-0.03	0.29	-0.21	0.33	0.02	-0.07	-0.23	-0.23	-0.24	-0.24	-0.23	-0.16
Au	-0.25	0.02	-0.27	0.13	0.21	-0.01	0.13	0.01	0.11	-0.05	0.09	0.09	-0.12	-0.01	-0.03	-0.24	-0.30	0.12	-0.23	-0.17	-0.25	-0.26	-0.04	-0.19	-0.28	-0.31	0.10	-0.08	-0.05	-0.09	-0.15	-0.15	-0.16	-0.17	-0.20	-0.21
Tl	-0.03	-0.08	-0.7	-0.06	0.09	0.29	0.24	0.01	0.49	0.13	-0.13	-0.01	-0.19	-0.20	0.12	0.45	0.64	0.24	0.92	-0.04	0.14	0.38	0.01	0.63	0.56	-0.05	-0.12	0.23	0.14	0.17	0.96	0.96	0.97	0.97	0.95	0.74
Pb	0.18	-0.06	-0.09	0.01	0.13	0.18	0.17	-0.06	0.48	0.16	-0.15	-0.07	-0.19	-0.21	-0.05	0.61	0.81	0.31	0.83	0.24	0.14	0.48	0.05	0.56	0.54	-0.24	-0.10	0.09	-0.03	0.03	0.90	0.90	0.92	0.93	0.96	0.72
Bi	0.19	-0.09	-0.19	-0.22	0.01	0.16	0.18	-0.09	0.30	-0.01	0.05	0.03	-0.23	-0.28	-0.13	0.71	0.69	0.23	0.71	0.47	0.12	0.44	-0.07	0.32	0.61	-0.26	-0.08	-0.06	-0.15	0.01	0.75	0.75	0.77	0.78	0.81	0.59
Th	0.31	-0.12	0.20	0.44	0.04	0.37	0.32	0.16	0.30	0.75	0.19	-0.11	0.13	0.01	0.68	0.06	0.53	0.39	0.50	-0.04	-0.10	0.14	-0.07	0.57	0.44	0.12	-0.38	0.26	0.74	0.70	0.30	0.30	0.31	0.31	0.38	0.28
U	0.76	-0.05	0.06	0.16	-0.36	-0.49	-0.29	-0.02	-0.13	0.01	-0.44	-0.07	-0.25	0.28	-0.07	0.10	0.66	0.07	0.17	0.05	-0.13	0.02	0.09	0.49	0.19	-0.34	-0.01	0.33	0.09	-0.08	0.18	0.18	0.19	0.21	0.30	0.29

	Gd	Tb	Dy	Ho	Er	Tm	Yt	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Tl	Pb	Bi	Th
Tb	0.98																			
Dy	0.86	0.92																		
Ho	0.85	0.93	0.97																	
Er	0.78	0.87	0.96	0.97																
Tm	0.45	0.61	0.72	0.74	0.83															
Yt	0.58	0.70	0.88	0.88	0.93	0.80														
Lu	0.43	0.57	0.62	0.70	0.77	0.83	0.80													
Hf	0.36	0.37	0.43	0.39	0.39	0.25	0.36	0.12												
Ta	-0.09	-0.10	-0.18	-0.14	-0.16	-0.21	-0.13	-0.12	-0.05											
W	-0.15	-0.21	-0.29	-0.25	-0.32	-0.32	-0.27	-0.33	-0.04	0.03										
Re	0.16	0.20	0.26	0.23	0.25	-0.04	0.29	-0.03	0.33	0.33	0.09									
Os	-0.09	-0.11	0.01	-0.14	-0.05	0.13	-0.03	-0.17	-0.17	-0.18	-0.04	0.07								
Ir	0.12	0.23	0.14	0.18	0.33	0.52	0.20	0.56	-0.20	0.02	-0.19	-0.02	0.18							
Pt	-0.26	-0.18	-0.26	-0.22	-0.16	0.12	-0.27	0.11	-0.18	-0.25	-0.02	-0.27	0.11	0.55						
Au	-0.19	-0.24	-0.27	-0.26	-0.25	-0.31	-0.15	-0.21	0.08	0.89	0.14	0.53	-0.10	-0.08	-0.24					
Tl	0.94	0.89	0.69	0.70	0.60	0.30	0.36	0.27	0.39	-0.02	-0.08	0.10	-0.20	0.05	-0.23	-0.13				
Pb	0.96	0.94	0.84	0.83	0.74	0.34	0.56	0.36	0.28	-0.07	-0.20	0.24	-0.17	0.08	-0.27	-0.19	0.89			
Bi	0.81	0.76	0.68	0.67	0.57	0.21	0.43	0.19	0.01	-0.04	-0.26	0.01	-0.16	-0.07	-0.37	-0.20	0.71	0.87		
Th	0.37	0.46	0.48	0.54	0.53	0.40	0.50	0.58	0.30	0.02	-0.33	0.14	-0.39	0.15	-0.04	-0.07	0.43	0.41	0.17	
U	0.37	0.45	0.58	0.55	0.60	0.67	0.71	0.74	-0.06	-0.16	-0.14	-0.05	0.31	0.33	-0.07	-0.21	0.15	0.29	0.21	0.31

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Cluster Analysis

In this study the distance between the points has been measured in terms of Euclidean distance (for a detailed mathematical discussion see Everitt 1977). Cluster analysis is essentially an exploratory tool for helping to resolve classification problems, especially when little or nothing is known. Thus it is useful in initial stages of a problem, although there are some points that must be born in mind.

1. It is a tool of discovery that can simplify a data set and give an insight into any underlying structure present. It does not and cannot give an "answer" or "correct solution" to the problems posed.
2. There are a number of algorithms available for hierarchical cluster analysis, but no explicit rules as to which method is most applicable in a given situation. As these different algorithms do not necessary produce the same results on a given data set it difficult to establish the exact method to utilise.
3. Although the clusters obtained are formed by an explicit and objective procedure there is a large subjective component in the actual choice of the numbers of clusters.
4. The clusters obtained may be sensitive to the particular choice of variables made, different combinations sometimes giving very different results.
5. The output presentation, the dendrogram, it by its nature merely a two dimensional simplification of a hugely complex multidimensional situation (Christie & Brenna 1979).

Visual inspection of dendrograms, figures C.1 - C.4, is the most commonly used method of identification of groups. The main points of the visual inspection are:

1. Replicates generally tend to cluster
2. Geological regions are mixed, at best they form poor cluster with odd samples from other groupings. The Lewisian and Dalradian samples never form good groupings, thus differing from the Principal Components and Discriminant Analysis.
3. The samples from the single source (Cunningsburgh) do not form a cluster.
4. Dendrograms formed from the soluble and insoluble elements tend to form the best cluster. Thus agreeing with the Principal Component and Discriminant Analysis.

The fact that cluster analysis proved to be the least useful technique maybe a result of the tendency of compositional groups to elongate due to inter-elemental correlation.

The following figures, C. 1-C.4, are the dendrograms formed from the cluster analysis utilising the separate elemental groups. The sample numbers represent the following geological groups:

1 - 18	Lewisian
19 - 42	Dalradian
43 - 83	Cunningsburgh/Dalradian
84 - 96	Basement
97 - 132	Ophiolite

The elemental groups used in these analysis are:

Figure C.1	Elements considered to be well analysed (Group B)
Figure C.2	Elements showing discriminating potential from univariate analysis (Group D)
Figure C.3	Soluble cations (Group G)
Figure C.4	immobile hydrolysates (Group J)

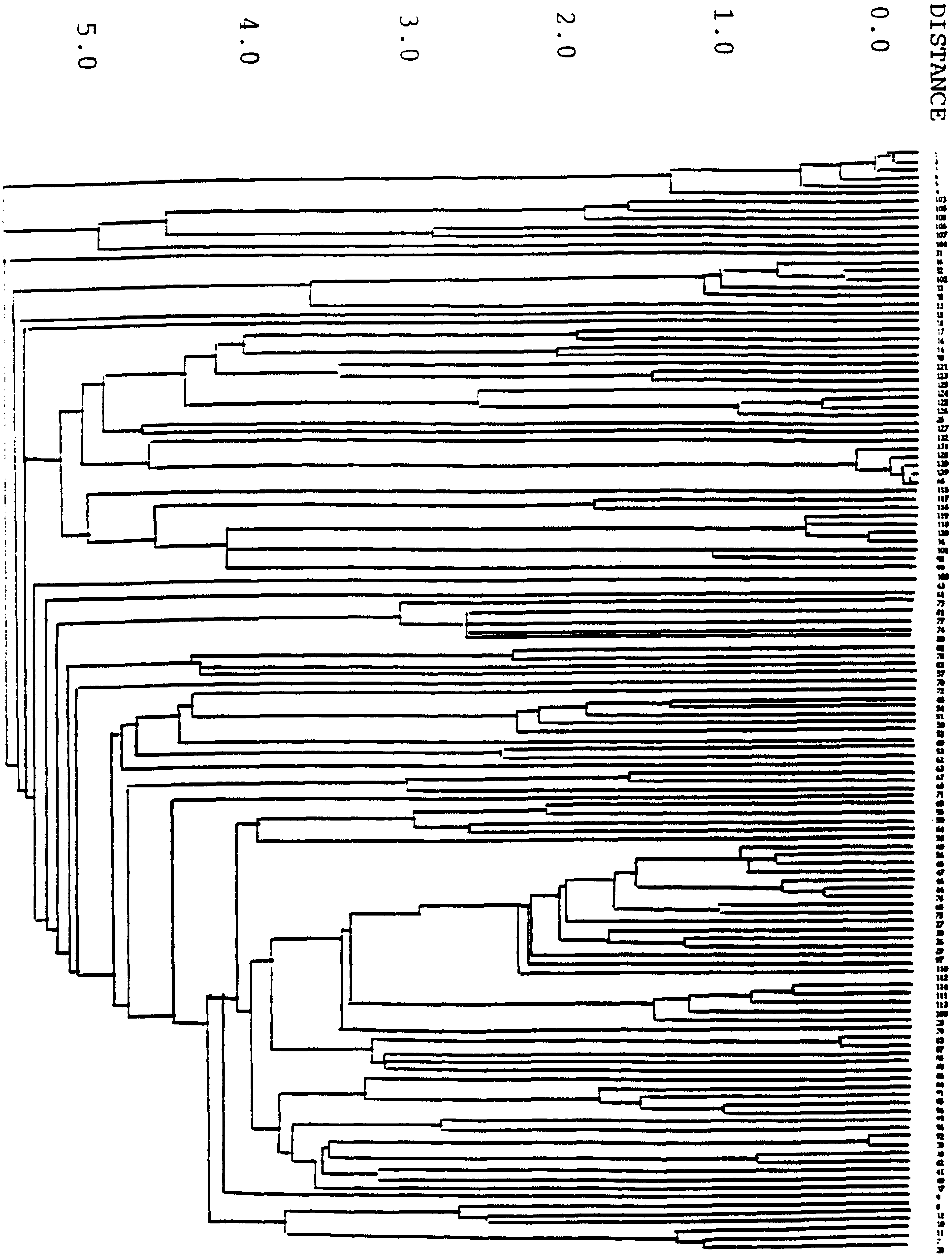

Figure C.1

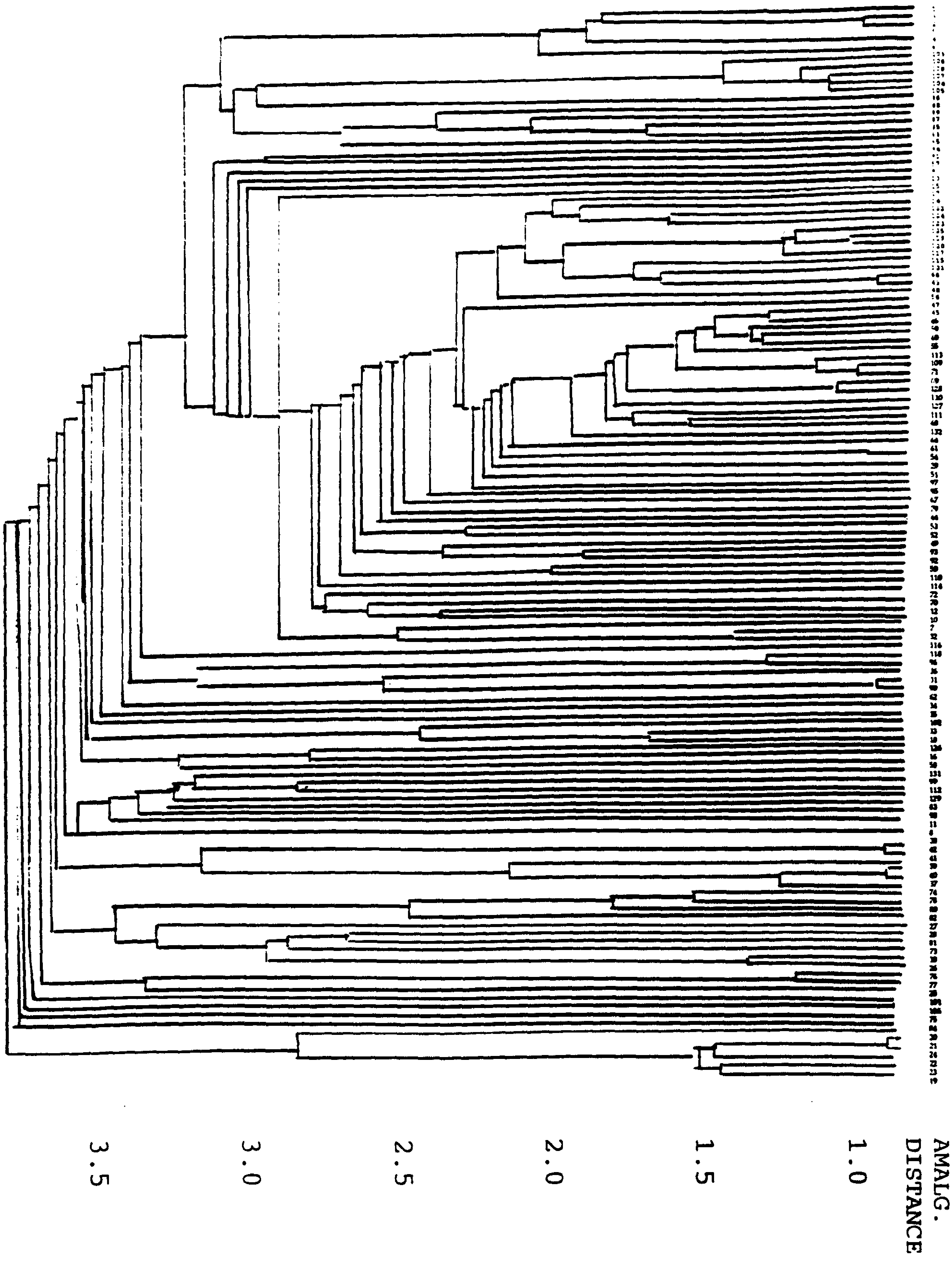

Figure C.2

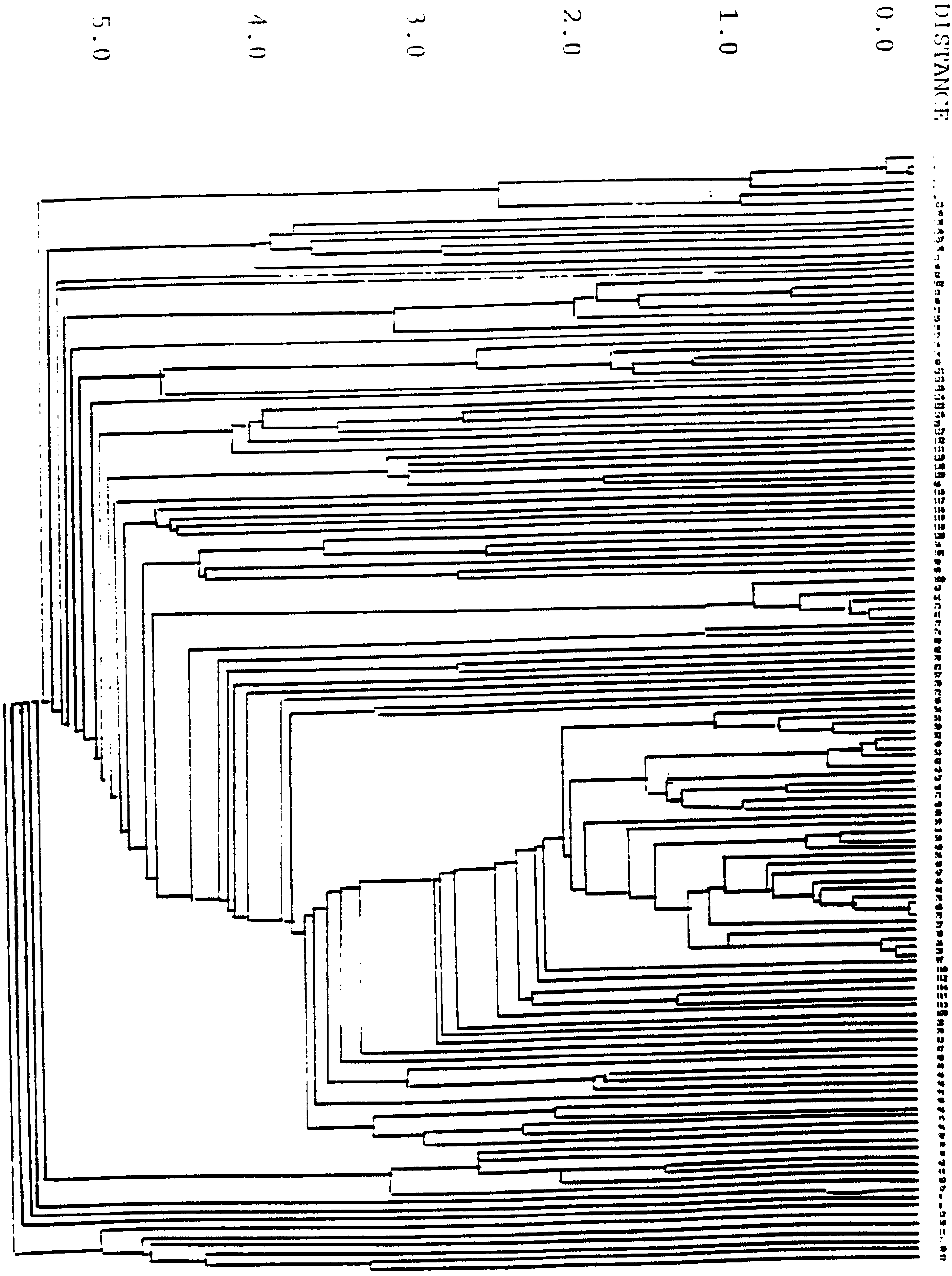

Figure C.3

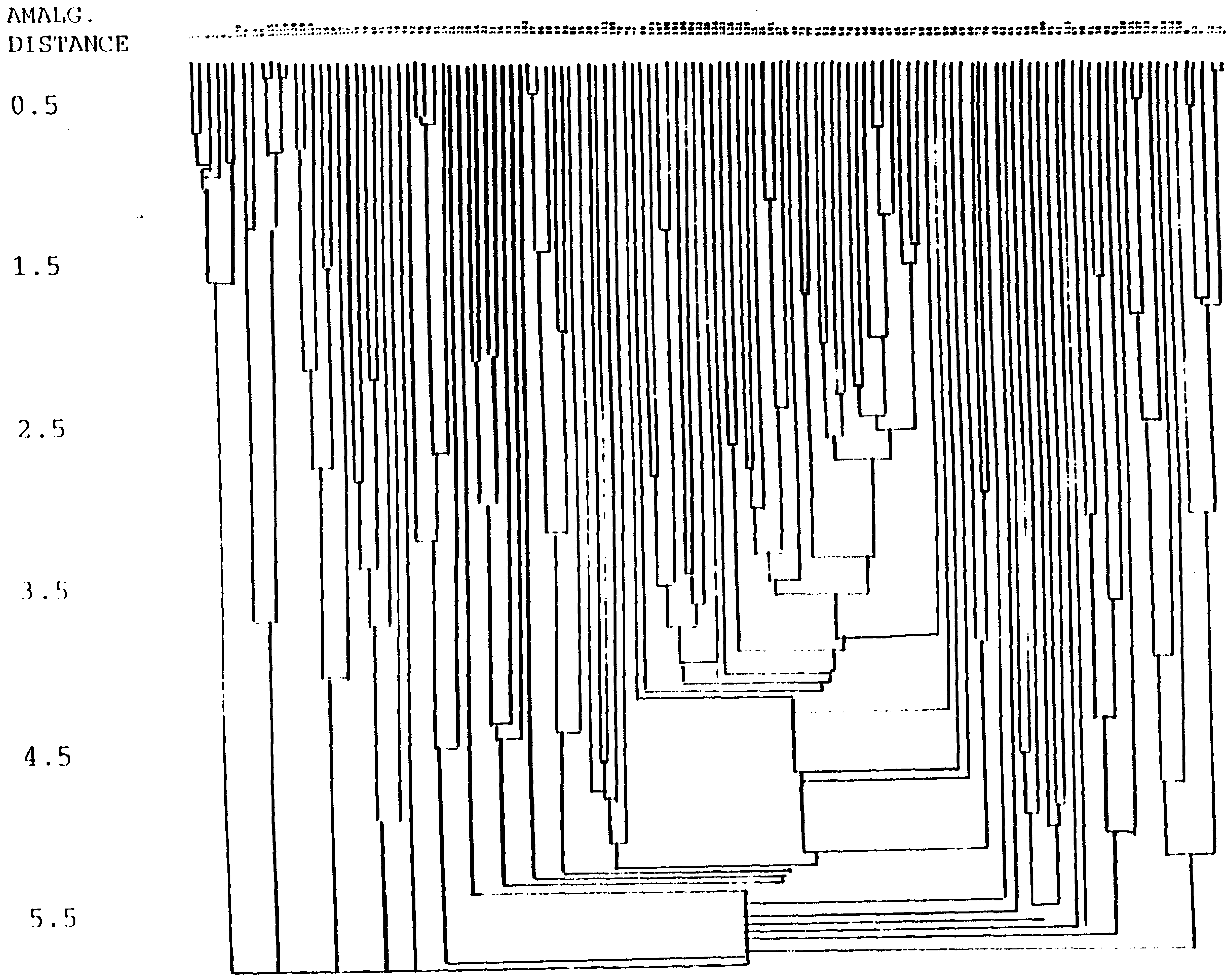

Figure C.4

Appendix D Rare Earth Element results from British sources (ppb).

REE	ZFD-4	error	ZFD-2	error	ZFD-6	error	WAN-1	error	WAN-4	error	WAN-5	error	ECO-1	error	ECO-2	error
La	264.00	20.27	295.74	20.92	372.31	31.90	27.20	2.85	34.10	3.12	30.60	2.90	76.80	5.22	155.65	13.29
Ce	602.00	35.65	642.36	32.66	653.67	45.00	69.20	6.90	101.00	7.59	93.49	6.33	253.00	14.50	448.44	33.65
Pr	59.50	4.77	72.71	5.42	85.52	7.61	12.54	1.43	19.40	1.88	13.48	1.41	44.90	3.20	75.52	6.50
Nd	262.00	15.96	301.80	23.65	367.20	25.63	58.20	5.84	100.20	7.12	83.04	5.48	266.00	17.18	418.20	30.20
Sm	87.90	9.95	97.70	9.66	105.89	9.33	18.50	1.85	30.81	2.85	27.20	2.60	144.00	9.47	176.28	14.56
Eu	53.90	4.34	53.80	4.10	70.78	6.36	10.40	1.00	14.63	1.48	11.61	1.25	54.10	3.78	70.34	6.06
Gd	97.90	7.68	127.17	9.20	169.13	14.69	46.50	4.71	56.46	5.57	51.80	4.52	215.00	15.60	281.79	23.97
Tb	16.90	1.54	21.90	1.89	26.92	2.65	10.30	1.22	10.90	1.16	10.76	1.18	44.50	3.18	55.27	5.92
Dy	106.10	8.30	140.39	10.12	174.81	15.17	49.60	5.01	77.60	6.81	75.67	6.80	305.00	19.64	371.59	31.58
Ho	25.43	2.19	33.60	2.70	40.42	3.79	14.47	1.62	18.26	1.78	16.87	1.71	79.00	5.36	85.30	7.33
Er	72.50	5.75	81.06	6.00	104.58	9.22	38.80	3.97	49.98	4.47	52.08	4.75	240.00	15.53	251.37	21.40
Tm	11.30	1.11	12.12	1.21	15.68	1.69	7.30	0.93	8.78	0.98	8.13	0.95	37.20	2.72	39.92	3.49
Yb	66.20	5.28	76.49	5.68	84.02	7.48	36.20	3.72	58.31	5.17	53.92	4.91	242.00	15.66	273.79	23.30
Lu	10.20	1.03	11.56	1.17	13.07	1.47	6.72	0.87	8.37	0.94	10.69	1.17	41.80	4.21	42.92	4.37

REE	ECO-9	error	MST-1	error	MST-2	error	MST-3	error	MSC-1	error	MSC-2	error	PS-1	error
La	98.27	6.94	582.00	45.88	881.95	69.40	754.85	42.91	0.80	0.15	43.71	2.98	3350.00	227.95
Ce	307.85	15.45	1200.00	75.35	1903.65	149.51	1604.52	90.83	12.70	0.93	157.88	10.11	6150.00	345.22
Pr	53.56	3.97	159.00	11.47	247.95	19.70	180.32	10.51	6.59	0.60	30.61	2.17	444.00	30.80
Nd	330.00	17.78	794.00	55.84	1047.00	82.34	837.00	47.54	70.50	4.09	148.68	9.53	1200.00	82.09
Sm	146.64	10.17	192.00	13.78	309.47	24.52	207.81	12.06	20.14	1.34	55.85	3.74	137.00	9.98
Eu	57.70	4.24	60.00	4.56	95.11	7.72	71.74	4.38	5.11	0.52	17.24	1.33	217.00	15.41
Gd	233.10	15.92	199.43	14.30	255.63	18.62	227.66	13.18	19.70	1.31	54.34	3.65	137.00	10.27
Tb	47.83	3.58	26.70	2.23	35.74	3.06	33.23	2.65	3.26	0.41	10.11	0.90	15.30	1.72
Dy	328.44	25.66	160.36	11.57	235.74	18.74	203.18	11.80	18.30	1.24	67.62	4.64	54.50	4.38
Ho	75.39	5.42	26.40	2.21	36.07	3.09	36.91	2.42	6.04	0.57	18.31	1.40	13.50	1.60
Er	243.18	16.59	71.40	5.35	122.64	9.87	104.73	6.24	16.80	1.15	56.45	3.78	46.90	3.87
Tm	38.43	2.96	8.85	0.98	18.37	1.70	16.14	1.25	3.88	0.45	7.88	0.75	5.63	1.07
Yb	283.61	19.29	62.50	4.73	117.46	9.47	105.13	6.27	28.70	1.81	45.35	3.09	55.80	4.47
Lu	47.88	4.57	9.02	1.00	17.13	1.78	16.00	2.36	3.90	0.45	7.89	0.75	13.60	1.61

Appendix D Rare Earth Element results from British sources (ppb).

REE	ZMF-1	error	ZMF-2	error	ZMF-7	error	ZC-2	error	ZMC-1	error	ZMC-12	error	ZMC-19	error	ZMC-44	error
La	133.00	10.23	195.96	15.96	80.63	6.99	28.80	2.14	25.50	1.96	16.10	1.43	16.10	1.78	40.50	3.76
Ce	417.00	23.18	582.57	32.52	252.10	14.87	33.90	2.48	48.90	3.54	33.40	2.74	33.10	2.78	81.13	7.40
Pr	59.30	5.70	92.60	5.72	61.49	6.32	2.97	0.41	5.53	0.61	5.28	0.61	4.38	0.47	11.90	1.20
Nd	327.00	18.25	471.60	26.45	334.45	19.52	15.70	1.26	30.80	2.31	30.50	2.52	17.50	1.53	41.20	3.82
Sm	150.00	8.57	164.21	9.64	119.77	7.41	5.24	0.57	4.51	0.54	4.45	0.55	4.40	0.48	4.13	0.50
Eu	17.40	1.32	29.47	2.27	14.48	1.48	14.20	1.16	7.97	0.77	10.60	1.01	10.40	1.13	5.15	0.59
Gd	150.00	14.95	210.83	12.19	148.69	9.04	9.39	0.84	8.56	0.81	8.21	0.83	12.70	1.14	10.81	1.10
Tb	28.50	3.37	38.63	2.77	26.69	2.16	1.66	0.23	2.25	0.30	1.44	0.23	2.27	0.31	2.11	0.23
Dy	200.00	11.31	265.40	26.96	188.05	15.96	13.30	1.10	14.20	1.19	13.40	1.23	14.40	1.28	12.00	1.21
Ho	46.50	2.91	59.67	3.92	32.51	2.49	2.57	0.39	2.71	0.42	3.13	0.45	3.45	0.40	3.80	0.47
Er	129.00	7.42	168.84	9.89	119.28	7.39	9.18	0.83	10.10	0.92	10.12	0.98	10.28	0.95	16.10	1.57
Tm	18.60	1.38	25.08	2.03	17.04	1.62	1.10	0.29	1.29	0.26	1.41	0.32	1.52	0.24	1.94	0.31
Yb	111.00	6.44	151.53	8.95	107.22	6.71	4.77	0.53	9.29	0.86	9.05	0.90	10.10	0.93	15.25	1.50
Lu	11.80	1.55	22.12	1.87	17.61	2.35	0.51	0.13	1.03	0.12	1.36	0.16	1.35	0.23	2.50	0.36

REE	PS-10	error	PS-6	error	GE-1	error	GE-3	error	GE-4	error	EG-12	error	EG-3	error	EG-6	error
La	4927.14	338.85	1787.15	135.26	21.08	1.71	63.86	4.93	106.64	7.65	105.00	5.98	110.00	8.77	173.29	12.39
Ce	7371.38	455.67	4931.39	303.96	70.50	3.95	174.53	10.22	281.99	19.82	242.00	13.27	249.00	15.47	407.23	21.55
Pr	549.37	38.10	334.40	25.61	9.35	1.13	26.96	2.14	42.82	3.23	32.10	2.10	35.10	2.90	54.17	4.08
Nd	1510.51	104.13	893.40	67.80	55.50	3.44	142.80	7.40	224.40	15.83	130.00	7.31	160.20	10.62	253.20	14.93
Sm	219.06	15.41	139.23	10.88	23.00	1.81	49.53	3.85	74.88	5.45	27.80	1.87	35.20	2.91	89.90	6.57
Eu	178.80	12.64	253.13	19.48	29.40	2.13	40.79	3.19	51.38	3.82	2.46	0.24	3.90	0.45	9.78	0.98
Gd	171.20	15.48	96.87	7.68	32.60	2.29	69.15	5.32	92.98	6.71	24.79	1.71	26.30	2.21	77.18	5.68
Tb	19.39	1.69	11.09	1.21	6.46	0.69	12.28	1.04	17.59	1.47	4.42	0.63	5.40	0.57	14.46	1.31
Dy	85.01	6.20	57.32	4.70	36.10	2.47	76.96	5.91	117.21	8.39	32.30	2.11	35.30	2.91	98.05	7.14
Ho	19.67	2.37	14.14	1.44	7.31	1.02	17.30	1.42	25.78	2.04	7.51	0.79	7.95	0.77	21.87	1.82
Er	37.59	2.94	58.38	4.78	20.20	1.67	49.35	3.83	76.02	5.53	22.90	1.61	25.30	2.13	64.90	4.83
Tm	7.09	0.85	5.80	0.81	3.62	0.84	8.20	0.73	12.15	1.10	4.40	0.42	3.90	0.45	10.04	1.00
Yb	39.29	3.06	50.37	4.17	26.70	2.00	53.92	4.18	77.54	5.64	25.83	1.77	23.20	1.97	62.07	4.63
Lu	6.47	0.80	8.18	0.99	3.99	0.37	8.08	0.89	12.14	1.10	4.81	0.65	4.12	0.47	9.69	0.97

Appendix D Rare Earth Element results from British sources (ppb).

REE	ZUB-3	error	ZMO-1	error	ZMO-2	error	ZMO-3	error	ZMH-1	error	ZMH-2	error	ZMH-3	error
La	185.69	18.10	16300.00	1495.18	22134.00	1328.58	13292.49	602.33	979.00	53.92	1269.45	123.21	1593.40	157.67
Ce	448.44	38.65	30100.00	2477.27	42339.20	2201.24	19115.99	955.68	1790.00	98.28	2558.13	202.00	2965.36	315.95
Pr	65.76	5.53	2840.00	206.70	4142.39	183.67	1471.03	55.69	212.00	15.49	334.28	32.62	358.68	37.71
Nd	282.00	27.33	9630.00	625.61	9291.60	555.90	6328.20	340.05	912.00	50.25	1384.20	104.96	1326.00	139.06
Sm	87.95	8.73	1270.00	118.21	1746.62	105.04	793.39	42.84	197.00	14.96	350.03	34.14	347.10	36.50
Eu	30.06	3.18	270.00	17.86	260.79	15.87	237.33	12.98	49.40	3.07	99.23	9.85	84.53	8.98
Gd	103.08	10.18	1250.00	98.69	1352.76	87.70	1012.17	54.59	181.00	11.46	325.56	23.66	286.20	30.15
Tb	18.06	2.70	137.00	10.22	147.79	9.08	121.77	6.78	22.30	2.24	54.37	5.50	44.89	4.83
Dy	117.85	11.59	457.00	58.05	855.88	51.58	457.88	22.99	114.00	6.60	382.86	37.32	300.23	25.40
Ho	25.85	2.77	102.00	8.91	128.38	7.92	119.62	6.66	25.60	1.77	81.28	8.11	64.69	6.90
Er	73.50	7.34	236.00	25.32	304.71	22.50	167.29	9.22	67.00	4.03	233.73	22.88	181.80	22.70
Tm	10.11	1.26	22.10	2.99	40.63	2.65	22.19	1.43	10.80	0.96	34.51	4.16	27.59	3.02
Yb	64.37	6.47	138.00	10.17	147.03	9.04	128.97	7.16	71.10	4.25	213.39	20.91	178.70	18.85
Lu	9.69	1.22	18.60	1.82	23.41	1.62	13.79	0.98	9.19	0.96	32.39	3.37	27.47	3.25

REE	ZUL-1	error	ZUL-2	error	ZUL-5	error	ZUC-4	error	ZUC-2	error	ZUC-1	error	ZUB-1	error	ZUB-4	error
La	115.11	11.45	212.04	18.77	182.28	20.76	50.10	4.96	89.59	7.94	68.20	5.89	115.00	10.31	228.04	18.14
Ce	250.00	25.00	492.40	45.00	406.42	41.36	170.00	12.55	348.25	21.03	298.96	15.48	250.00	18.96	550.25	35.70
Pr	35.30	4.57	63.56	6.30	51.12	6.01	39.70	3.96	65.03	5.82	59.78	5.18	35.30	1.99	80.40	6.55
Nd	124.50	15.70	302.40	22.40	243.00	27.59	228.00	15.99	359.40	20.91	354.00	17.32	190.00	16.95	390.00	30.85
Sm	38.50	3.02	94.77	9.38	73.91	8.57	76.40	6.69	117.92	10.38	120.90	10.33	68.50	3.53	112.91	9.10
Eu	11.70	1.63	33.96	4.57	26.24	3.21	25.00	2.55	30.94	2.88	28.67	2.56	11.70	1.16	39.03	3.30
Gd	40.10	5.17	113.18	11.20	86.25	9.96	110.00	10.70	164.98	14.44	152.81	17.96	39.10	3.59	135.72	10.89
Tb	5.77	0.66	20.33	2.03	15.50	2.00	21.10	2.18	33.13	2.69	29.39	2.62	6.77	0.72	24.27	2.14
Dy	42.00	5.41	138.60	15.83	104.65	5.69	163.00	15.78	239.89	20.90	218.96	18.58	42.00	3.84	160.03	12.80
Ho	7.86	1.15	30.80	3.07	23.05	2.85	35.40	3.55	52.13	6.66	49.54	6.67	9.36	0.95	35.61	3.59
Er	24.70	2.98	89.67	8.88	67.20	7.82	110.00	10.70	150.78	13.22	144.90	12.35	24.70	2.31	102.06	8.25
Tm	3.95	0.59	13.77	1.38	10.17	1.40	17.40	2.37	23.72	2.26	22.68	2.06	3.99	0.48	15.81	1.48
Yb	26.70	1.37	87.99	8.71	64.37	7.50	109.00	10.60	150.69	14.99	150.48	12.82	26.70	2.49	103.46	8.36
Lu	3.90	0.46	13.43	1.35	9.69	1.56	17.10	1.79	23.70	2.26	23.83	2.15	3.93	0.52	15.46	1.88

Appendix D Concentration in ppm of GSP-1 reference rock material. Ref 1 Data from Govindaraja 1989.

REE	Ref 1	A		B		C		D		E		F	
La	184	183.81	±9.16	175.62	±7.06	175.02	±5.94	165.60	±8.54	173.56	±9.21	182.54	±11.45
Ce	399	411.02	±19.28	419.91	±17.19	385.15	±16.15	378.69	±15.24	379.65	±14.14	399.88	±15.65
Pr	52	50.47	±3.46	53.62	±4.05	48.93	±3.04	46.97	±2.25	44.87	±2.65	54.77	±2.65
Nd	196	188.33	±9.08	200.64	±8.21	198.06	±9.12	179.22	±8.58	189.57	±7.84	199.07	±8.01
Sm	26.2	23.17	±1.73	25.31	±2.02	24.89	±2.01	23.47	±1.95	25.75	±1.65	25.79	±1.99
Eu	2.3	2.21	±0.21	2.33	±0.19	2.10	±0.21	2.26	±0.15	2.27	±0.16	2.37	±0.15
Gd	12.1	11.20	±0.83	16.31	±1.05	11.93	±0.72	11.23	±0.95	11.58	±0.87	12.58	±0.07
Tb	1.34	1.49	±0.06	1.52	±0.07	1.25	±0.07	1.17	±0.08	1.25	±0.07	1.25	±0.08
Dy	5.5	5.32	±0.04	6.00	±0.03	5.22	±0.03	4.28	±0.02	5.14	±0.03	5.44	±0.14
Ho	1.01	0.89	±0.07	0.89	±0.06	0.92	±0.06	0.92	±0.05	1.00	±0.04	0.95	±0.04
Er	2.7	2.26	±0.07	2.29	±0.09	0.32	±0.11	2.22	±0.10	2.58	±0.12	2.61	±0.15
Tm	0.38	0.31	±0.01	0.32	±0.02	0.32	±0.01	0.32	±0.01	0.31	±0.03	0.32	±0.02
Yb	1.7	1.55	±0.08	1.49	±0.07	1.47	±0.09	1.62	±0.08	1.58	±0.14	1.65	±0.11
Lu	0.21	0.18	±0.01	0.19	±0.01	0.18	±0.01	0.20	±0.01	0.19	±0.01	0.19	±0.01

Appendix D Concentration in ppm of GSP-1 reference rock material.
Ref 1 Data from A & B Standard disolution no preconcentration. C Preconcentration method 2. D Preconcenreation method 1

REE	**Ref 1**	**A**		**B**		**C**		**D**	
La	184	183.81	±9.16	175.62	±7.06	175.02	±5.94	138.60	±8.09
Ce	399	411.02	±19.28	419.91	±17.19	385.15	±16.15	308.69	±14.25
Pr	52	50.47	±3.46	53.62	±4.05	48.93	±3.04	33.97	±3.04
Nd	196	188.33	±9.08	200.64	±8.21	198.06	±9.12	159.22	±9.31
Sm	26.2	23.17	±1.73	25.31	±2.02	24.89	±2.01	19.47	±2.05
Eu	2.3	2.21	±0.21	2.33	±0.19	2.10	±0.21	1.46	±0.22
Gd	12.1	11.20	±0.83	16.31	±1.05	11.93	±0.72	8.23	±0.066
Tb	1.34	1.49	±0.06	1.52	±0.07	1.25	±0.07	0.77	±0.06
Dy	5.5	5.32	±0.04	6.00	±0.03	5.22	±0.03	3.28	±0.05
Ho	1.01	0.89	±0.07	0.89	±0.06	0.92	±0.06	0.62	±0.09
Er	2.7	2.26	±0.07	2.29	±0.09	0.32	±0.11	0.22	±0.08
Tm	0.38	0.31	±0.01	0.32	±0.02	0.32	±0.01	0.22	±0.01
Yb	1.7	1.55	±0.08	1.49	±0.07	1.47	±0.09	1.12	±0.09
Lu	0.21	0.18	±0.01	0.19	±0.01	0.18	±0.01	0.11	±0.03

Appendix E Elemental concentrations (ppb) fot artifact samples

Element	GA 1133	error	GA 1134	error	GA 1136	error	AQ 14	error	AQ 114	error	AQ 116	error	BD 35	error
B	3464.21	367.79	7626.25	662.50	3934.91	380.99	1172.87	268.49	1499.07	537.32	5.03	0.50	2482.68	666.23
Ga	79329.03	576.54	270.83	75.00	90107.86	597.22	4126.24	155.44	11850.71	363.97	40734.02	1669.18	36073.56	2831.17
As	1058.65	218.69	600.00	161.67	1202.49	226.53	673.58	98.92	3146.21	74.03	59994.95	980.39	30138.50	1428.57
Rb	188.72	14.91	108.33	8.33	214.36	15.45	375.37	14.13	882.17	55.52	266.47	40.22	73.59	8.66
Sr	79801.19	899.60	687.50	45.83	90644.18	931.87	489.87	146.02	44750.15	314.62	35701.34	1181.50	10290.03	220.78
Y	2027.83	39.76	1187.92	10.42	2303.36	41.19	75.37	4.71	8161.63	43.18	7838.11	489.19	138.53	0.43
Zr	1878.73	113.67	1137.50	18.33	2134.00	117.75	197.83	9.42	12251.70	191.24	402.21	100.55	268.40	12.99
Nb	1766.70	64.61	1165.83	8.33	2006.75	66.93	1339.14	193.12	4120.91	234.42	734.04	95.53	82.25	3.03
Sb	29.82	4.97	24.13	12.50	33.87	5.15	51.81	18.84	74.03	24.68	85.47	7.04	813.85	64.94
Cs	4.23	0.57	8.33	0.42	5.03	0.56	1.41	0.47	25.10	6.17	5.94	0.50	183.98	7.79
Ba	1948339.99	25616.30	13870.83	358.33	2213070.69	26535.16	1705.13	395.67	6674.89	234.42	346525.75	6636.50	492432.41	10125.53
La	840.06	39.76	109.83	4.42	211.62	14.19	73.05	11.30	1175.39	67.86	2433.88	50.28	424.68	17.32
Ce	2379.52	139.17	249.00	14.17	530.02	44.16	196.67	32.97	4317.70	349.35	8150.32	181.00	908.66	60.61
Sm	597.22	124.25	52.50	3.75	117.48	12.71	42.39	14.13	1454.90	143.18	2490.95	175.97	42.16	30.30
Hf	89.46	54.67	1.67	0.17	101.62	56.63	14.13	4.71	407.16	18.51	15.08	2.51	4.33	0.43
Ta	131.01	29.82	17.50	0.83	148.82	30.89	489.87	296.75	425.66	43.18	120.66	25.14	147.19	9.96
Pb	1542.74	74.55	1112.50	44.17	1520.30	77.23	5699.01	70.65	1671.81	209.75	5233.78	303.32	3683.98	277.06

Element	GA 989	error	GA 1047	error	GA 986	error	GA 979	error	GA 984	error	GA 985	error	GA 1132	error
B	1609.43	1021.40	3970.30	451.12	1127.74	224.55	1592.11	322.27	553.38	274.24	1614.56	746.62	2920.89	545.76
Ga	10583.63	189.20	6626.26	166.75	8353.26	114.77	14915.81	331.89	7551.42	215.48	10116.66	220.72	2197.73	39.55
As	19968.82	734.43	3053.67	604.48	1207.58	104.79	2414.62	115.44	1116.55	73.46	1147.92	153.99	598.87	96.04
Rb	549.61	58.37	3720.69	39.08	129.74	1.00	317.46	14.43	378.35	4.90	397.99	9.33	135.59	11.30
Sr	22003.83	312.26	25486.34	2251.17	8652.66	224.55	27599.78	129.87	6469.15	241.43	14025.20	405.97	22135.52	163.84
Y	3176.06	29.18	2423.14	238.67	3403.18	54.89	6936.02	52.91	1880.51	48.97	2966.87	28.00	1112.99	11.30
Zr	627.43	77.82	2420.53	52.11	3627.73	219.56	18917.73	476.19	1498.53	53.87	2837.14	74.66	1412.99	16.95
Nb	904.18	24.32	927.57	5.21	1808.38	24.95	14660.88	259.74	1150.83	83.25	1157.26	56.00	1124.29	16.95
Sb	63.23	38.91	99.01	8.86	19.96	9.98	38.48	3.85	51.42	4.90	4.67	0.47	43.50	27.12
Cs	6.23	0.49	2.18	0.52	9.98	3.99	3.67	0.48	4.90	0.49	1.67	0.47	9.04	2.82
Ba	191098.70	3696.49	39566.44	958.83	26292.31	184.63	99769.02	1346.80	9211.56	318.32	56257.59	1194.59	20011.24	1389.83
La	1480.15	82.68	175.70	19.90	2453.08	95.06	2422.70	120.25	278.45	32.32	265.97	28.00	84.75	11.30
Ce	5921.19	191.63	888.32	57.32	12528.89	250.70	11736.88	303.03	1764.54	14.69	1909.19	79.33	150.40	22.60
Sm	1331.13	89.18	762.79	56.06	1747.30	129.74	2933.86	67.34	644.66	36.24	841.95	14.00	33.90	1.13
Hf	35.51	0.49	161.54	78.17	129.74	9.98	582.01	52.91	68.56	29.38	106.58	4.67	2.82	0.56
Ta	240.27	34.05	156.33	89.63	109.78	4.99	841.75	52.91	221.60	39.86	82.22	18.67	57.63	5.65
Pb	5550.08	196.98	3335.07	177.18	3327.34	119.96	4136.60	110.63	2815.87	53.87	3271.12	111.99	1698.86	101.69

Appendix E Elemental concentrations (ppb) for artifact samples

Element	HD 1748	error	HTA 71	error	HSA 726	error	HSA 182	error	HSA 672	error	HSA 722	error	HSA 688	error
B	536.74	222.43	1755.95	540.67	376.66	163.10	2401.63	173.74	2514.30	745.66	1619.85	480.98	8462.27	852.46
Ga	31559.37	372.33	19885.91	64.48	3965.34	178.39	1134.39	10.22	602.66	61.29	5388.54	204.05	878.69	36.07
As	2398.41	43.52	2068.45	158.73	657.49	124.87	2437.40	204.39	1915.22	107.25	2534.84	258.71	3937.69	157.38
Rb	1160.52	87.04	523.81	51.69	85.63	1.53	45.99	5.11	85.29	3.06	44.51	14.58	45.90	3.28
Sr	140103.78	1347.17	24438.99	398.66	105229.36	876.66	7424.63	178.85	13615.93	311.54	16767.60	40.08	24527.15	429.18
Y	9951.46	174.08	2708.33	34.72	1167.18	54.54	71.54	35.77	122.57	153.22	342.21	18.22	149.90	33.44
Zr	50443.94	585.10	1125.99	138.89	586.14	56.07	127.75	5.11	372.83	5.11	2134.26	222.27	353.90	19.67
Nb	5849.99	245.64	5426.09	31.60	472.48	400.31	76.65	35.77	86.82	2.55	342.94	36.44	51.48	13.11
Sb	225.33	28.48	108.63	59.52	252.80	285.42	102.20	15.33	183.86	36.77	72.97	47.37	318.03	62.29
Cs	2.94	0.38	7.33	0.76	188.58	35.68	215.33	2.04	125.13	86.31	214.59	0.36	213.77	3.28
Ba	253568.78	570.59	151279.75	3452.38	1620.80	244.65	2943.28	526.32	2727.27	61.29	3433.05	448.19	5045.89	236.06
La	11528.69	159.57	520.44	29.76	291.23	30.58	95.77	8.69	127.25	15.32	191.11	65.59	208.69	16.56
Ce	36546.62	483.55	1326.19	29.76	1099.69	45.87	256.21	20.44	244.50	25.54	605.46	46.44	484.92	26.56
Sm	4568.60	149.90	339.19	49.60	193.29	45.87	58.70	15.33	80.43	0.51	123.91	13.64	119.84	9.98
Hf	1025.13	83.51	59.52	29.76	28.54	16.31	5.11	0.51	16.04	5.11	73.95	43.73	9.84	2.95
Ta	1039.63	38.68	497.22	9.92	953.11	152.91	157.38	20.44	715.02	25.54	80.52	10.93	99.67	25.25
Pb	21631.04	1130.56	5669.64	306.75	815.49	158.00	197.44	14.19	212.77	18.75	426.85	98.38	580.33	19.67

Appendix E Elemental concentrations (ppb) for source samples

Element	GE-1	error	EG-1	error	LNO-1	error	MPS-1	error	MSC-1	error	ZUL-1	error	ZMO-1	error
B	1632.35	145.32	5465.82	140.38	1741.14	65.82	4988.26	178.78	2618.59	85.49	10057.47	333.47	25608.89	1021.03
Ga	23457.87	563.32	376.48	541.37	1392.88	100.23	382.17	14.70	854.87	26.91	1958.39	89.98	2353.97	99.85
As	150.47	15.97	183.74	14.25	118.20	6.25	143.24	4.13	235.24	6.68	1832.04	56.66	1801.91	77.84
Rb	278.01	19.55	52.67	19.22	76.28	4.32	122.72	5.40	42.47	1.38	101.81	3.45	158.64	7.33
Sr	2485.97	259.61	474.76	24.75	1073.98	54.95	62434.73	2222.66	5637.40	147.04	16704.56	555.62	141789.44	5653.15
Y	2568.33	197.44	98.72	5.26	1674.99	80.74	482.70	15.30	94.73	3.01	1836.83	62.83	3799.48	159.49
Zr	5603.74	432.73	729.66	35.35	1593.80	54.66	1541.51	54.25	827.99	26.03	390.74	14.15	1399.60	60.80
Nb	1854.92	10.58	902.60	10.59	2333.65	147.19	1.24	0.04	8.17	0.25	30.35	1.03	607.12	30.21
Sb	44.88	4.12	41.40	3.93	58.94	3.39	21.55	0.78	97.24	3.10	532.90	19.94	129.37	6.16
Cs	2.27	1.36	3.92	0.32	6.29	0.54	5.65	0.21	10.46	0.33	3.20	0.12	44.32	2.77
Ba	98722.12	1875.09	23484.24	1792.15	87079.40	1478.65	3195.84	115.54	449.06	15.66	1785.82	80.11	2852.83	121.74
La	478.54	32.32	96.51	6.65	162.85	11.44	4134.88	147.19	2.28	0.07	310.28	10.87	16434.31	684.55
Ce	2164.85	187.55	213.08	11.54	389.89	20.98	7601.18	272.45	8.79	0.33	750.72	25.27	30248.79	1206.32
Sm	404.98	23.65	15.57	0.95	65.71	4.08	167.99	6.02	1.07	0.03	224.23	7.98	1279.56	54.02
Hf	87.54	8.65	20.69	1.65	25.70	1.36	34.95	1.05	14.75	0.50	9.38	0.42	36.46	1.25
Ta	223.60	4.89	78.40	4.67	62.75	5.98	8.14	0.26	62.83	1.99	2.39	0.06	108.81	4.65
Pb	3299.14	19.99	4840.89	196.08	2825.65	157.74	542.90	19.47	314.42	12.60	1435.59	48.32	6867.37	289.65

Appendix E Elemental concentrations (ppb) for source samples

Element	ZC-2	error	ZMC-5A	error	ZMC-5C	error	ZMC-5E	error	ZMC-5F	error	ZMF-1	error	ZMH-1	error
B	43863.61	628.65	192616.73	776.63	13588.34	1825.86	937.21	57.04	19789.00	1250.29	4007.44	144.15	4376.97	137.96
Ga	789.04	53.61	665.24	66.22	593.40	45.02	947.28	97.72	845.02	79.70	8578.52	308.57	3798.15	119.72
As	2326.14	219.30	421.20	25.89	4986.55	650.31	3940.29	82.29	3777.90	388.54	1880.92	67.66	938.95	29.60
Rb	92.23	4.87	90.22	6.02	129.65	45.02	60.46	5.14	35.31	19.93	118.94	4.28	158.43	4.99
Sr	978.62	92.59	2657.23	114.39	2536.16	325.15	1133.72	56.58	1721.90	199.25	5606.24	201.66	196852.45	6204.76
Y	420.14	63.35	3.37	0.32	54.85	5.00	25.19	2.57	25.70	4.98	1888.47	67.93	1430.33	45.08
Zr	584.10	233.92	963.98	288.98	179.52	47.52	156.20	15.43	657.92	44.83	1639.64	58.98	1213.47	38.25
Nb	24.56	1.65	20.47	2.04	24.99	0.51	15.25	1.03	7.50	0.35	16.92	0.61	22.26	0.70
Sb	0.00	0.00	231.04	14.25	393.94	45.02	372.87	128.58	474.94	154.92	65.75	2.37	213.40	6.73
Cs	194.70	14.62	4.81	0.89	199.46	10.00	251.94	5.14	257.00	4.98	10.36	0.37	12.60	0.40
Ba	1440.00	81.38	850.70	55.56	2149.20	210.10	1103.48	5.43	1567.70	174.34	846.44	30.45	1612.32	50.82
La	30.74	0.49	15.70	0.60	44.88	5.23	5.04	2.52	10.28	0.58	49.18	1.77	1008.43	31.79
Ce	51.24	4.87	19.58	1.98	64.83	5.12	10.08	2.87	20.56	0.56	211.45	7.61	1841.77	58.05
Sm	15.37	1.46	1.00	0.24	39.89	5.01	5.04	2.57	10.28	0.54	163.86	5.89	200.49	6.32
Hf	2.70	0.25	11.42	0.31	0.00	0.00	0.00	0.00	0.00	0.00	27.38	0.98	4.98	0.16
Ta	7.80	0.74	70.63	0.91	558.49	115.05	50.39	25.72	0.00	0.00	95.93	3.45	10.96	0.35
Pb	2397.87	136.45	168.76	8.95	1770.22	120.06	1708.13	15.43	2734.48	268.99	2343.21	84.29	2418.17	76.22

Element	ZUC-2	error	ZUQ-4	error	ZUB-1	error	ZUC-4	error	ZFD-4	error	ECO-1	error	WAN-1	error
B	22583.33	795.21	12900.75	234.59	185403.63	6543.53	10497.38	343.01	4128.08	163.53	4892.60	179.98	5842.93	176.78
Ga	781.80	27.53	515.00	5.21	5576.61	197.06	1179.39	38.71	2660.16	105.43	2266.96	83.36	1199.30	36.49
As	7346.19	258.68	43405.00	344.06	1277.48	45.33	27714.18	905.26	686.20	27.32	162.00	5.90	471.39	14.50
Rb	36.44	1.28	15.00	1.56	227.27	8.27	98.64	3.42	56.23	2.39	539.59	19.79	33.98	1.29
Sr	4550.13	160.22	2685.00	140.75	15705.74	554.54	11911.36	389.19	126462.69	5004.80	6452.91	237.40	877.40	26.77
Y	55.72	1.96	10.00	2.09	1140.42	40.50	46.15	1.70	347.53	13.91	2792.49	102.70	470.62	14.48
Zr	829.17	29.20	550.00	62.56	2413.12	85.41	1164.60	38.23	745.58	29.67	1374.84	50.53	680.85	20.83
Nb	7.40	0.26	125.00	10.43	34.67	1.47	15.94	0.72	87.21	3.61	73.93	2.66	41.81	1.53
Sb	355.64	12.52	380.00	11.99	1407.59	49.93	205.61	6.91	368.17	14.73	43.29	1.53	113.99	3.71
Cs	5.16	0.18	15.00	1.56	68.80	2.68	10.73	0.55	52.10	2.22	235.96	8.62	9.99	0.57
Ba	523.92	18.45	595.00	245.01	696.89	24.84	562.56	18.57	593.37	23.64	675.12	24.78	685.54	20.97
La	7.96	0.28	20.00	2.09	47.92	1.94	24.07	0.98	263.46	10.59	75.08	2.70	29.67	1.16
Ce	36.48	1.28	370.00	3.65	129.21	4.81	32.04	1.24	600.04	23.91	164.71	6.00	16.79	0.77
Sm	239.63	8.44	10.00	1.04	75.43	2.91	7.73	0.45	84.51	3.51	140.68	5.11	16.61	0.77
Hf	27.78	0.98	0.00	0.00	55.10	2.19	16.81	0.75	19.72	0.94	26.35	0.91	22.02	0.93
Ta	6.09	0.21	385.00	12.51	16.36	0.83	91.09	3.17	12.15	0.64	12.59	0.40	7.61	0.49
Pb	310.35	10.93	455.00	12.51	497.25	17.80	208.19	7.00	318.35	12.76	812.64	29.84	100.99	3.31

Appendix E Artifact Sample REE results (ppb).

REE	GA 979	error	GA 984	error	GA 985	error	GA 986	error	GA 989	error	GA 1132	error	GA 1133	error
La	2432.42	72.91	253.18	78.12	254.78	10.18	2431.14	44.15	1450.88	78.95	90.4	3.33	839.46	42.14
Ce	11765.27	302.95	1744.37	295.52	1897.34	74.89	12687.62	185.65	6062.26	204.21	159.98	6.61	2319.58	144.02
Pr	2022.61	50.67	419.69	49.43	487.17	19.44	1968.56	34.43	861.38	44.32	19.15	0.67	364.81	14.88
Nd	10125.54	313.76	2442.21	300.06	2818.01	111.55	9397.21	205.81	4376.46	154.55	89.4	3.11	1779.32	100.54
Sm	2942.28	84.26	606.27	82.19	846.01	30.2	1711.08	56.2	1367.7	65.89	28.25	1.02	574.28	24.97
Eu	757.09	20.71	113.12	20.2	230.05	9.01	241.02	14.61	286.96	22.45	43.14	1.55	974.65	48.99
Gd	3362.19	100.81	753.67	98.34	926.27	35.09	1992.51	66.71	1213.03	65.01	32.48	1.2	433.9	28.69
Tb	380.95	14.42	77.86	14.07	125.99	5.07	189.12	9.57	144.94	10.45	5.8	0.25	64.61	6.32
Dy	2177.01	60.31	524.98	58.83	653.76	25.14	896.21	41.99	902.72	52.1	39.09	1.45	462.72	22.76
Ho	349.21	15.47	106.76	15.09	146.06	6.87	175.15	10.98	188.72	11.67	9.08	0.39	127.73	11.41
Er	948.53	21.45	241.43	20.92	460.57	17.45	566.37	19.19	535.99	41.99	26.55	1.11	323.56	16.21
Tm	105.34	2.16	36.73	2.11	56.93	1.65	74.35	1.88	76.85	5.33	3.86	0.18	55.17	4.65
Yb	716.21	22.48	237.51	21.93	452.17	17.5	589.82	19.71	455.74	20.03	24.66	0.9	429.29	18.74
Lu	85.14	2.25	29.38	2.19	69.53	2.78	83.33	2.49	77.33	5.98	3.82	0.17	68.09	6.62

REE	GA 1134	error	GA 1136	error	GA 1047	error	AQ 14	error	AQ 116	error	AQ 114	error	BD 35	error
La	109.74	5.32	219.19	14.77	176.08	10.26	78.74	5.57	2338.86	77.84	1192.47	54.35	420.67	22.47
Ce	238.36	11.88	593.88	42.12	878.3	27.59	197.15	11.61	7889.39	262.72	4294.88	201.95	897.69	41.8
Pr	34.65	2.22	96.99	6.33	262.3	14.58	27.21	1.27	1565.11	53.11	782.85	32.84	60.63	2.89
Nd	176.4	11.82	347.3	21.59	1948.2	100.23	143.4	9.93	8395.68	275.58	3959.4	177.72	149.35	3.25
Sm	58.11	5.65	127.53	5.84	737.88	58.87	48.17	2.22	2517.35	83.83	1354.67	74.84	41.73	2.15
Eu	57.84	4.41	343.89	15.5	137.57	10.17	41.45	2.03	574.66	18.31	616.9	30.01	156.17	7.45
Gd	74.33	4.14	222.6	11.63	765.86	17.05	69.15	3.65	2671.19	87.85	1682.29	102.31	83.14	3.99
Tb	13.46	2.29	37.16	2.14	121.82	2.26	11.71	0.54	433.57	16.63	254.16	14.97	12.04	0.89
Dy	88.87	4.99	273.75	13.32	959.56	45.35	82.11	4.98	2990.41	99.58	1616.29	99.11	75.03	2.75
Ho	20.03	1.54	60.46	3.01	177.92	9.32	17.73	0.65	728.34	24.25	414.56	19.58	15.37	0.66
Er	51.45	4.66	182.07	8.87	538.44	25.91	50.82	3.61	2010.54	60.95	1167.8	55.35	41.79	1.78
Tm	8.94	0.95	28.35	1.65	85.02	4.32	8.33	0.84	345.74	10.51	181.02	8.88	8.88	0.51
Yb	58.31	5.21	188.73	8.98	550.72	47.07	54.13	2.41	2079.76	69.25	1120.3	51.14	41.38	2.25
Lu	8.47	0.74	27.11	1.36	78.17	7.1	7.76	0.35	304.52	11.51	170.27	5.69	6.28	0.49

Appendix E Artifact Sample REE results (ppb).

REE	HD 1748	error	HTA 71	error	HSA 726	error	HSA 182	error	HSA 672	error	HSA 722	error	HSA 688	error
La	11727.27	381.98	525.57	17.12	316.51	129.19	95.79	3.08	127.1	5.06	189.35	56.55	203.48	7.27
Ce	36380.56	12.81.9	1337.8	44.59	1029.56	400.49	253.71	8.14	358.75	15.03	601.97	177.81	482.38	18.15
Pr	4884.43	147.14	201.39	5.56	153.41	60.61	37.09	1.21	52.34	2.09	88.08	23.3	73.61	2.66
Nd	20288.2	649	1028.77	36.32	709.99	293.94	180.6	6.81	251.4	11.02	419.92	124.4	365.4	17.93
Sm	4938.18	147.43	387.47	11.62	194.42	78.51	58.89	1.48	80.93	2.22	128.29	39.34	111.93	3.91
Eu	974.98	32.67	257.44	7.38	62.18	22.79	22.86	0.74	30.72	1.27	40.5	11.09	40.28	1.23
Gd	4760.15	154.64	491.32	15.01	255.89	101.02	78.74	1.53	106.45	3.24	160.32	47.88	151.26	4.37
Tb	534.33	14.35	87.3	2.84	46.89	14.69	14.17	0.46	19.72	0.78	28.91	7.63	24.27	0.76
Dy	2503.87	87.34	616.07	22.07	317.02	114.4	95.96	2.08	131.7	5.24	194.17	58.99	173.56	5.17
Ho	495.16	12.08	124.93	3.07	70.01	31.91	21.11	0.63	28.72	1.24	42.29	11.63	37.12	1.21
Er	1203.58	45.1	395.34	14.88	200.76	77.04	60.27	1.43	81.27	2.24	120.54	33	107.31	3.41
Tm	170.7	5.24	47.12	1.55	31.59	12.59	9.62	0.34	13.15	0.55	18.5	5.52	16.1	0.89
Yb	1388.3	48.1	275.79	14.89	197.3	54.79	61.45	1.94	84.65	3.57	118.29	39.33	106.59	3.57
Lu	160.06	4.19	53.08	1.22	29.98	9.95	9.37	0.31	13.17	0.42	18.06	4.39	15.84	1.54

Appendix E Concentrations in ppm of the trace elements used in this study in standard reference material GSP-1. Rec = recommended values (Govindaraja 1989), A-G are standards analysed during sample analysis.

	GSP-1								
	Rec	A		B		C		D	
B	1.3	1.551	±0.102	1.554	±0.091	1.420	±0.052	1.566	±0.154
Ga	23	20.55	±1.654	20.32	±2.336	19.95	±1.989	20.65	±2.657
Rb	254	267	±15.1	269	±14.3	259	±19.3	269	±18.8
Sr	234	229	±21.6	215	±15.5	219	±10.4	213	±11.6
Y	26	29.5	±1.92	24.3	±2.13	25.6	±2.23	26.8	±2.87
Zr	530	471	±15.1	508	±11.2	475	±14.9	476	17.1
Nb	27.9	25.98	±0.895	24.234	±0.844	23.97	±0.971	23.18	±0.775
Sb	3.2	3.40	±0.124	3.35	±0.208	3.36	±0.106	3.34	±0.109
Cs	1.02	0.991	±0.031	1.08	±0.022	0.999	±0.036	1.001	±0.035
Ba	1310	1355	±32	1398	±26	1401	±21	1410	±34
La	184	189	±5.20	194	±6.53	194	±9.86	195	±15.84
Ce	399	416	±20.89	415	±15.74	416	±16.99	411	±21.66
Sm	26.3	32.33	±1.89	29.45	±1.74	29.89	±2.26	29.71	±1.65
Hf	15.5	10.42	±1.47	13.66	±1.61	13.21	±1.80	12.62	±1.56
Ta	0.97	0.99	±0.094	0.97	±0.042	0.98	±0.085	0.99	±0.041
Pb	55	59.2	±4.21	59.7	±2.34	59.7	3.31	60.1	±3.32

	GSP-1								
	Rec	D		E		F		G	
B	1.3	15.35	±0.555	1.420	±0.109	1.433	±2.654	1.415	±0.339
Ga	23	20.01	±2.84	21.65	±2.61	20.48	±2.84	20.07	±1.56
Rb	254	266	±14.6	245	±16.8	266	±17.8	278	±16.3
Sr	234	219	±11.8	213	±18.9	219	±16.1	211	±14.0
Y	26	25.5	±1.65	27.1	±1.62	24.6	±2.65	24.0	±4.61
Zr	530	479	±20.2	451	±21.6	435	±19.9	483	±16.0
Nb	27.9	23.88	±0.974	23.54	±0.805	23.42	±0.911	23.84	±1.01
Sb	3.2	3.42	±0.214	3.35	±0.254	3.35	±0.297	3.31	±0.300
Cs	1.02	1.05	±0.033	0.983	±0.041	0.996	±0.029	0.991	±0.030
Ba	1310	1412	±54	1483	±29	1347	±33	1375	±32
La	184	189	±4.8	191	±6.9	198	±6.5	191	±7.1
Ce	399	416	±12.3	416	±15.6	411	±16.4	411	±9.9
Sm	26.3	29.9	±2.65	29.6	±1.23	29.4	±1.28	31.9	±1.06
Hf	15.5	12.3	±0.87	13.9	±0.78	13.1	±0.88	12.6	±0.90
Ta	0.97	0.98	±0.097	0.97	±0.084	0.098	±0.091	0.98	±0.095
Pb	55	60.1	±3.22	59.3	±2.91	59.4	±4.62	59.1	±6.33

APPENDIX F

Subject: Dissolution Procedure of Steatite using Savillex™ Beakers

Objective:

To provide a routine method for the total dissolution of steatite thus enabling elemental analysis of the sample through Inductively Coupled Plasma techniques.

Introduction:

ICP-MS offers the possible analysis of a wide range of elements with very low detection limits. Analysis time is relatively short is comparison with other methods with similar detection limits. Currently nebulisation of aqueous solutions is the most reliable and well characterised sample introduction technique. This requires the total dissolution of the sample before analysis.

Reagents:

Aristar or better grade reagents are used throughout this procedure. Double distilled analytical grade reagents are preferable. These should be distilled and stored in clean laboratory conditions. Reagents should be stored in PFA vessels.

1. Hydrofluoric acid (HF) 40%
2. Nitric acid (HNO_3) 14M
3. Hydrochloric acid (HCl) 6M
4. Ultrapure water

Apparatus:

1. Savillex™ 50 ml PTFE screw-top beaker
2. Laboratory hot-plate, set at 180°C
3. Analytical balance, five figure
4. 100 ml graduated flask
5. 125 ml PFA bottles
6. Laboratory heat lamps

Method:

1. Sample is ground to 53 µm sing an agate mortar and pesile.

2. 200 mg sample is weighted out into PTFE (Savillex™) screw-top beaker. A balance with five figure is sufficient to enable suitable precision to be obtained.

3, Samples should be handled with care to avoid cross-contamination while weighing out. It is therefore recommended that:
a) samples are dispensed within an enclosed balance under still air conditions.
b) each sample is dispensed individually, ie. only one beaker is open at any one time.

4. To ensure low procedural blank levels all stages should be conducted under clean laboratory conditions.

5. 1 ml HNO_3 is added to beaker containing sample to allow reaction of carbonates. Any reaction should be allowed to take place before HF is added. 8 ml HF is added to the beaker. The beaker is sealed and placed on a hot-plate for 72 hours.

6. The beaker is removed from the hot-plate and allowed to cool for 10 minutes. It is then placed under heat lamps with a clean-air flow across the top. The sample is left until all the reagents have evaporated. To minimise fluorite formation a single drop of HNO_3 is added to the sample just before it reaches dryness, then the sample is taken to dryness. Care must be taken not to *bake* the sample.

7. The residue is then redisolved in 5 ml HCl and replaced on the hot-plate for 12 hours. The sample is then dried down again under the heat lamps.

8. The residue is then redisolved in 5 ml HNO_3 and replaced on the hot-plate for 24 hours. The sample is then dried down again under the heat lamps.

9. The sample is then redisolved in 50 ml of 5% HNO_3 and placed on the hot-plate for 5 minutes shaking regularly. The sample is then made up to 100 ml in a graduated flask and transferred to PFA bottles for storage before analysis.

Quality Assurance

1. Standard Reference materials should be included in each sample dissolution run and subsequent analysis. These should be compared to reference values and accuracy quoted with reported values.

2, In order to minimise blank values all apparatus should be cleaned in 1.5 M HNO_3, 1.5 M HCl and ultrapure each for 24 hours.

Subject: Dissolution Procedure of Steatite using Steal Bombs

Objective:

To provide a routine method for the total dissolution of steatite thus enabling elemental analysis of the sample through Inductively Coupled Plasma techniques.

Introduction:

ICP-MS offers the possible analysis of a wide range of elements with very low detection limits. Analysis time is relatively short is comparison with other methods with similar detection limits. Currently nebulisation of aqueous solutions is the most reliable and well characterised sample introduction technique. This requires the total dissolution of the sample before analysis.

Reagents:

Aristar or better grade reagents are used throughout this procedure. Double distilled analytical grade reagents are preferable. These should be distilled and stored in clean laboratory conditions. Reagents should be stored in PFA vessels.

1. Hydrofluoric acid (HF) 40%

2. Nitric acid (HNO_3) 14M

3. Hydrochloric acid (HCl) 6M

4. Ultrapure water

Apparatus:

1. Steel pressure bombs with PTFE inner liners

2. Laboratory oven, set at 220°C

3. Analytical balance, five figure

4. 100 ml graduated flask

5. 125 ml PFA bottles

6. Laboratory heat lamps

Method:

1. To ensure low procedural blank levels all stages should be conducted under clean laboratory conditions.

2. Samples are ground to 53 µm using an agate mortar and pesile.

3. 200 mg sample is weighted out into PTFE inners liner. A balance with five figure is sufficient to enable suitable precision to be obtained.

4, Samples should be handled with care to avoid cross-contamination while weighing out. It is therefore recommended that:
a) samples are dispensed within an enclosed balance under still air conditions.
b) each sample is dispensed individually, ie. only one inner is open at any one time.

5. 1 ml HNO_3 is added to inner containing sample to allow reaction of carbonates. Any reaction should be allowed to take place before HF is added. 5 ml HF is added to the inner. This is approximately 20% of the total vessel volume. It is hazardous to over-fill these vessels. The inner is sealed, skrink tubing placed over inner and placed in steal bomb which is tightened to hand-tightness. The bomb is placed in an oven at 220°C for 72 hours.

6. The bomb is removed from the oven and allowed to cool for 1 hour. The inner is removed and then placed under heat lamps with a clean-air flow across the top. The sample is left until all the reagents have evaporated. To minimise fluorite formation a single drop of HNO_3 is added to the sample just before it reaches dryness, then the sample is taken to dryness. Care must be taken not to *bake* the sample.

7. The residue is then redisolved in 5 ml HNO_3 and the inner replaced in the bomb which is replaced in the oven for 24 hours. After cooling again the sample is then dried down again under the heat lamps.

9. The sample is then redisolved in 50 ml of 5% HNO_3 and placed on the hot-plate for 5 minutes shaking regularly. The sample is then made up to 100 ml in a graduated flask and transferred to PFA bottles for storage before analysis.

Quality Assurance

1. Standard Reference materials should be included in each sample dissolution run and subsequent analysis. These should be compared to reference values and accuracy quoted with reported values.

2, In order to minimise blank values all apparatus should be cleaned in 1.5 M HNO_3, 1.5 M HCl and ultrapure each for 24 hours.

Subject: Rare Earth Element Pre-Concentration Method for Steatite Analysis

Objective:

To provide a routine method for the pre-concentration of REE thus enabling elemental analysis of the sample through Inductively Coupled Plasma techniques.

Introduction:

ICP-MS offers the possible analysis of all fourteen naturally occurring REE with very low detection limits. However, for material such as steatite pre-concentration is required to obtain results with accuracy and precision that can be used for characterisation. This method gives a procedure for the pre-concentration of the REE that is compatible with ICP-MS analysis.

Reagents:

Aristar or better grade reagents are used throughout this procedure. Double distilled analytical grade reagents are preferable. These should be distilled and stored in clean laboratory conditions. Reagents should be stored in PFA vessels.

1. Mixture of 90% Acetic acid (CH_3COOH) 5M - 10% Nitric acid (HNO_3) 5M

2. Mixture of 75% Acetic acid (CH_3COOH) 5M - 25% Nitric acid (HNO_3) 5M

3. Nitric acid (HNO_3) 0.015M

4. Ultrapure water

5, Anion exchange resin Bio-Rad 200-400 mesh.

Apparatus:

1. Savillex 50 ml PTFE screw-top beakers

2. 25 ml ion exchange column

3. 1-10 ml pipette

4. 50 ml measuring cylinder

5. 125 ml PFA bottles

6. Laboratory heat lamps

Method:

1. To ensure low procedural blank levels all stages should be conducted under clean laboratory conditions.

2. The anion exchange resin in the columns is pre-equilibrated in 5 ml of 90% Acetic acid (CH_3COOH) 5M - 10% Nitric acid (HNO_3) 5M mixture.

3. The sample is taken up in 2 ml 75% Acetic acid (CH_3COOH) 5M - 25% Nitric acid (HNO_3) 5M mixture, 30 minutes prior to loading onto the column.

4. The sample s loaded directly onto the resin bed for sorption, avoiding any contact with the sides of the column.

5. Immediately after the sample has been absorbed by the resin, 2 ml of 90% Acetic acid (CH_3COOH) 5M - 10% Nitric acid (HNO_3) 5M mixture is washed down the sides of the column, avoiding disturbing the resin.

6. REE separation is achieved by the elution of 50 ml of 90% Acetic acid (CH_3COOH) 5M - 10% Nitric acid (HNO_3) 5M mixture, which again is run down the sides of column to avoid resin disturbance. The elutant from the base of the column are discarded.

7. REE are stripped from the column with 15 ml Nitric acid (HNO_3) 0.015M. The elutant is collected immediate after the addition of the nitric acid. The sample is slowly dried down under heat lamps.

Quality Assurance

1. Standard Reference materials should be included in each sample dissolution run and subsequent analysis. These should be compared to reference values and accuracy quoted with reported values.

2, In order to minimise blank values all apparatus should be cleaned in 1.5 M HNO_3, 1.5 M HCl and ultrapure H_2O each for 24 hours. In addition columns and resin must be cleaned after every run. The following steps are recommended. 50 ml 1.5 M HNO_3, back-wash with ultrapure H_2O, 50 ml 1.5 M HNO_3, 25 ml 0.015M HNO_3.