RARE EARTH ELEMENT STUDIES OF A GRANULITE FACIES TERRAIN: THE LEWISIAN OF N. W. SCOTLAND.

* * *

CALVIN R. PRIDE

1978

DALHOUSIE UNIVERSITY

FACULTY OF GRADUATE STUDIES

The undersigned hereby certify that they have read and recommended to the Faculty of Graduate Studies for acceptance a thesis entitled " Rare-earth Element Studies of a Granulite Facies Terrain: The Lewisian of N.W. Scotland.

."

by Calvin R. Pride

in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Dated July 13, 1978

External examiner

Research Supervisor

Examining Committee

RARE EARTH ELEMENT STUDIES OF A
GRANULITE FACIES TERRAIN:
THE LEWISIAN OF N. W. SCOTLAND.

by

Calvin R. Pride

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

at

Dalhousie University
Halifax, Nova Scotia

July, 1978

TABLE OF CONTENTS

Page

CHAPTER 3 (continued):

APPENDICES

ABSTRACT

The Scourian granulite facies terrain comprises the most ancient portion of the Precambrian Lewisian complex of N. W. Scotland. It is composed of a cogenetic series of gneisses from ultramafic to felsic in composition--dominated by felsic gneisses of tonalitic chemistry, with lesser mafic and ultramafic varieties, and very minor granitic rocks. The terrain was affected by a granulite facies metamorphic event at approximately 2600 to 2900 m.y. at which time it became severely depleted in the incompatible elements U, Th and Rb, and possibly K. The physical conditions of granulite facies metamorphism have been estimated at 916 ± 33°C, 11 ± 1 kb, at very low partial pressures of water. Isotopic data restrict any previous upper crustal history to less than 150 m.y.

New REE data for whole rock and mineral separates of the Scourian complex show that:

a) overall, the Scourian complex has a small, but distinct, positive Eu anomaly.

b) individual rock type REE patterns are unlike most REE patterns of upper crustal rocks of equivalent major element chemistry.

c) whole rock REE abundances largely reflect the REE abundances of the major rock-forming minerals.

d) mineral REE patterns, abundances and distribution coefficients are very similar to those from dacitic rocks.

e) the REE content of the Scourian mineral phases is not a strong function of rock type.

f) the concordant granitic, and most of the discordant pegmatitic, rocks have anomalous REE abundances (low absolute concentrations and large positive Eu anomalies), unlike upper crustal granitic rocks.

The prefered hypothesis of this study is that the Scourian complex is the residuum, left after the generation and removal of melts of granitic composition. Trace element partial-melting modelling suggests that approximately 20% partial melting of a LRE enriched upper crustal Scourian precursor (moderately high in Ba) could account for virtually all of the trace element features of the Scourian rocks.

Evidence from geophysics, geochemistry and general geology indicate that granulite facies terrains are samples of lower crust. It is suggested, although tentatively at this stage, that the above mode of formation is not unique to the Scourian complex but is the mechanism whereby the heat-producing elements are concentrated in the upper crust. The REE data suggest that it may be possible to balance the observed continental upper crustal negative Eu anomaly with a postive Eu anomaly in the lower crust, yielding an overall continental crust with normal or chondritic Eu abundances.

The majority of the granitic rocks of the Scourian complex are interpreted as having formed, at a late stage of Scourian metamorphism, by disequilibrium partial melting of the Scourian gneisses, or by equilibrium partial melting with sub-solidus re-equilibration with the host gneisses.

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

I am most grateful to my supervisor, Dr. G. K. Muecke, for introducing me to the subject, helpful advice and fruitful discussion along the way, and never-waning enthusiasm throughout the project--particularly during the low-points that arose from time to time.

Dr. J. Dostal and Dr. Jagam are thanked for introducing me to activation analysis and for being so patient during the learning process.

The members of my committee, Dr. D. B. Clarke, Dr. M. Zentilli, Dr. M. J. Keen and Dr. J. Dostal, are thanked for their advice and positive criticism, particularly in the latter stages of the work.

And to all connected with my stay at Dalhousie, but especially to my fellow graduate students, thank you for a most stimulating three years.

CHAPTER 1

INTRODUCTION

General Introduction

Over the past decade, great progress has been made in the understanding of the rare earth element (REE) geochemistry of igneous and sedimentary rocks. By comparison, metamorphic rocks, especially those of high-grade terrains, have received little attention. In spite of this paucity of data, the hypothesis of REE immobility during progressive regional metamorphism, even into the granulite facies, has become generally accepted (e.g. Nance and Taylor, 1976).

The REE's form a very coherent group of trace elements and have been shown to be sensitive petrogenetic indicators. Thus, they have the potential of substantially extending our knowledge of metamorphic processes.

It is the aim of this study to investigate thoroughly the REE geochemistry of the Scourian granulite facies terrain of the Precambrian Lewisian complex, N.W. Scotland (Fig. 1-1). This terrain represents one of the most intensely studied sections of deep crust and is, therefore, particularly conducive to detailed geochemical investigations (Muecke, 1969; Holland and Lambert, 1975).

Medium-to high-pressure granulite facies terrains represent the most extensive surface exposure of deep crustal material and provide the geochemist with samples on which the fractionating effects of

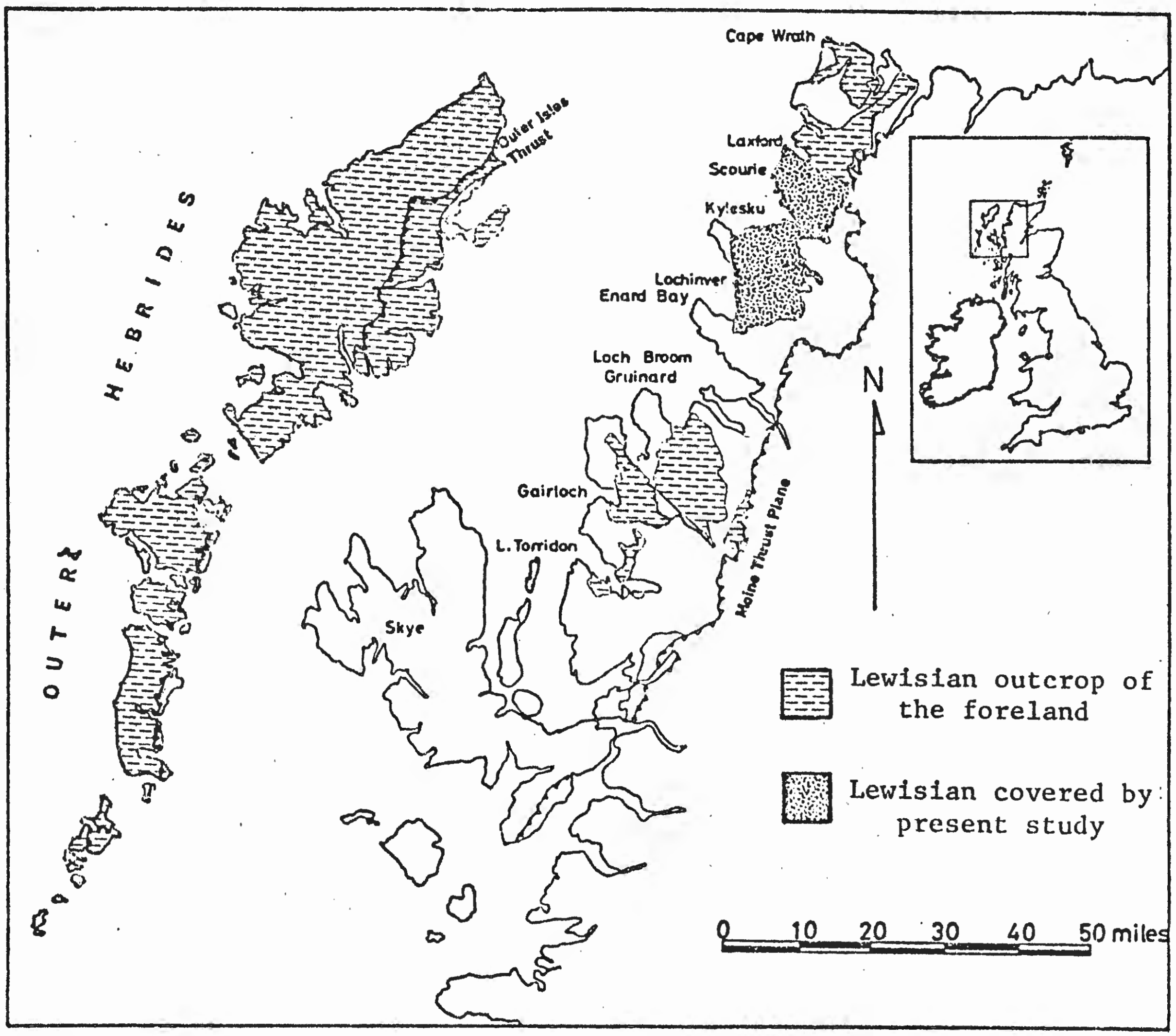


Fig. I-1 : Map of the Lewisian complex ,N.W. Scotland.

high-grade metamorphism and anatexis may be examined. Studies of this nature, when combined with other chemical and petrological information, geophysical data, and experimental results, place constraints on models of crustal evolution.

General Features of the REE

The lanthanides or REE include the elements from lanthanum to lutetium, atomic numbers 57 to 71. Pertinent data such as ionic radius, atomic weight and chemical symbol are given in Table 1-1.

The normal oxidation state in nature is +3--the only documented exceptions being Eu which may be reduced to the +2 state and Ce, which may be oxidized to the +4 state (Ahrens, 1964). They exhibit a virtually linear decrease in +3 ionic radius with increasing atomic number, known as the lanthanide contraction. The resultant coherent chemical behavior greatly hindered analysis by classical chemical methods as it was very difficult to separate completely individual elements; but with the advent of more sensitive analytical techniques (e.g. neutron activation), this same coherent behavior stimulated the interest of the geochemist.

The REE are not really as "rare" as their name might imply (Haskin and Frey, 1966; Haskin *et al.*, 1966). In the lithosphere, they have similar abundances to Sn, Pb and Co, and are more abundant than Ag or Au (Haskin *et al.*, 1966). They rarely form their own phases, and tend to be dispersed through the various rock-forming minerals (Haskin *et al.*,

Table I-1: REE Ionic Radii, Oxidation States, and Atomic Weight

(from Whittaker and Muntus, 1970).

Element	Chemical Abbreviation	Radius (A^{o}) of M3+ in Vl Coordination	Radius (A^{o}) of M^{3+} in Vlll Coordination	Oxidation State(s) in Nature	Atomic Weight
Lanthanum	La	1.13	1.26	3^+	138.91
Cerium	Ce	1.09 (0.88)**	1.22 (1.05)**	3^+, 4^+	140.12
Praseodymium	Pr	1.08	1.22	3^+	140.91
Neodymium	Nd	1.06	1.20	3^+	144.24
(Promethium)*	Pm	-	-	-	-
Samarium	Sm	1.04	1.17	3^+	150.35
Europium	Eu	1.03 (1.25)***	1.15 (1.33)***	3^+, 2^+	151.96
Gadolinium	Gd	1.02	1.14	3^+	157.25
Terbium	Tb	1.00	1.12	3^+	153.92
Dysprosium	Dy	0.99	1.11	3^+	162.50
Holmium	Ho	0.98	1.10	3^+	164.93
Erbium	Er	0.97	1.08	3^+	167.26
Thulium	Tm	0.96	1.07	3^+	168.93
Ytterbium	Yb	0.95	1.06	3^+	173.04
Lutetium	Lu	0.94	1.05	3^+	174.97

* Pm unstable - not found in nature.

** Radius of Ce^{4+}

*** Radius of Eu^{2+}

1966). They have been classified, along with the other large ion lithophile (LIL) elements such as U, Cs, Rb etc., as incompatible (e.g. Carmichael _et_ _al_., 1974). That is, they generally show a strong preference for the melt phase over coexisting mineral phases. The resulting trend during fractional crystallization is one of progressive enrichment of incompatible elements in the residual melt. Ferrara and Treuil (1975) called these elements "residual", and subdivided them into two broad groups based on the reason for their residual behavior:

1) The _incompatible_ elements such as Rb, Cs, Li and Be. Their large or small ionic radii prevent their preferential incorporation into crystal lattices.
2) The _hygromagmatophile_ elements such as Zr, Hf, La, Ce and U. Their high charge leads to the formation of stable complexes in the melt and hence their residual behavior. Within this group they distinguish between the strongly hygromagmatophile elements such as the light rare earths (LRE), U and Zr, and those which are weakly hygromagmatophile such as the heavy rare earths (HRE).

The highest levels of REE are therefore to be found in late stage rocks such as granite pegmatites, rhyolites, trachytes etc. The earth's crust also tends to be enriched in REE compared to the whole-earth system. This tendency increases with increasing LIL character (or increasing hygromagmatophile character), and thus the earth's crust and the previously mentioned late-stage rocks tend to be LRE enriched.

Data Presentation

REE analyses are generally presented as chondrite-normalized graphs. This procedure removes the effects of the odd-even relationship of elemental abundances (Oddo-Harkins rule) and produces a smooth curve (Haskin _et_ _al_., 1968). The resulting chondrite-normalized values are plotted on a logarithmic ordinate versus the REE atomic number (or ionic radius) as abscissa (Haskin _et_ _al_., 1968).

Although the normalizing procedure may be looked upon as just a means of standardizing REE data to produce a graph which is easier to interpret, it may also, and indeed probably does have, genetic implications. Many geochemists feel that chondritic meteorites represent the best available sample of non-volatile solar material (e.g. Urey, 1952; Taylor, 1964a) and it has been postulated that the earth, as a whole, has a chondritic REE chemistry (Haskin _et_ _al_., 1966; Frey, 1970). Thus, any deviation from this chondritic pattern takes on genetic significance.

The problem then arises as to which of the many sets of chondrite data to use in the normalizing procedure. It has been shown that considerable variability can exist between chondritic meteorites both in relative and absolute REE contents (Masuda _et_ _al_., 1973). This may be due to different initial contents or post-formational fractionation. The majority of chondrites, however, have very similar relative patterns and absolute values (Haskin _et_ _al_., 1966). The three most commonly used sets of normalizing values are given in Table 1-2. In Fig. 1-2, the North American Shale Composite (NASC) (Haskin _et_ _al_., 1968) is shown

Table I-2: REE in Chondrites. (ppm).

Element	A	B	C
La	0.330	0.30	0.378
Ce	0.88	0.84	0.976
Pr	0.112	0.12	-
Nd	0.60	0.58	0.716
Sm	0.181	0.21	0.230
Eu	0.069	0.074	0.0866
Gd	0.249	0.32	0.311
Tb	0.047	0.049	-
Dy	-	-	0.390
Ho	0.070	0.073	-
Er	0.200	0.21	0.255
Tm	0.030	0.033	-
Yb	0.200	0.17	0.249
Lu	0.034	0.031	0.0387

A. Average of 9 Chondrites : Haskin et al. (1968).

B. Average of 20 Chondrites : Schmitt et al. in Haskin et al. (1966).

C. Leedey Chondrite : Masuda et al. (1973).

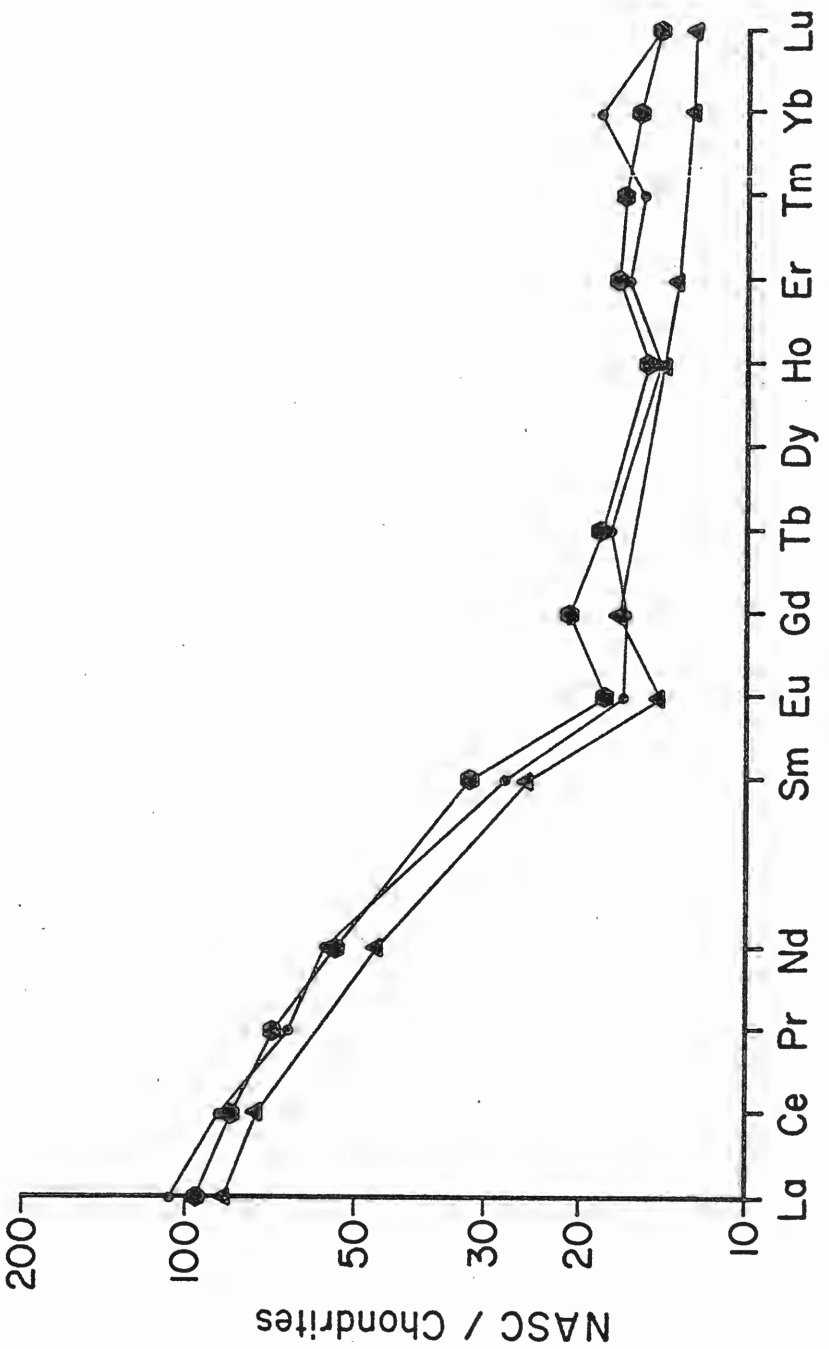


Fig. I-2 : NASC normalized to a) Average of 9 chondrites after Haskins et al., 1968 (hexagons), b) Average of 20 chondrites after Schmitt et al., 1963 (triangles), c) Leady chondrite after Masuda et al., 1973 (circles).

normalized to each of these three "chondrites". The resulting graphs are very similar in shape, and do not vary significantly in absolute value. The normalizing values used in this presentation are those of Haskin et al. (1968)--their "composite of 9 chondrites" (Table 1-2). This composite is probably the most widely used in normalizing procedures, facilitating comparison to the results of other workers.

Previous Work

1) Introduction

Excellent summaries of the state of REE geochemistry up to 1967 have been given by Haskin et al. (1966) and Haskin et al. (1968), and these studies form the basis of most subsequent work. In the past decade, a vast amount of data has been accumulated and, as is usually the case in scientific research, closer scrutiny has revealed an increased complexity.

2) Igneous Rocks

Volcanic rocks have received by far the most attention. The knowledge of the REE chemistry of a particular volcanic suite, when combined with estimated REE distribution coefficients between liquidus phases and melts of appropriate composition (usually determined from phenocryst-matrix studies), allows more rigorous testing of genetic models of basalt genesis. The REE data often place constraints on the nature of the magma source, degree of partial melting of this source, the nature and volume of fractionating phases, and the genetic relationships between members of the suite (e.g. Zielinski and Frey, 1970; Kay and Gast, 1973; Frey et al., 1974; Sun and Hanson, 1975).

The distinctive REE "fingerprint" of oceanic tholeiites (Frey et al., 1968; Schilling, 1971) is now well established. The virtually chondritic pattern, with slight LRE depletion, for ocean-floor tholeiites of all ages requires a unique and relatively simple process to be operative in their genesis (Schilling, 1971). More recent results (Frey et al., 1974), while confirming the general validity of the above statement, indicate that, in detail, the situation is more complex. Nonetheless, the consistent LRE depleted pattern is in striking contrast to continental tholeiites, which have LRE enriched patterns, as do most continental rocks (e.g. Schilling, 1971).

Granitic rocks have also been extensively investigated. The REE have proven to be useful trace elements in evaluating the possible sources and differentiation histories of granites (e.g. Buma et al., 1971; Emmermann et al., 1975; Albuquerque, 1977). Haskin et al. (1968) report the results of several "granite" composites of varying silica contents. In general, these rocks were found to be very similar to the NASC--presumably a good estimate of the continental upper crust (Haskin et al., 1966). They report two broad trends:

1) Increasing absolute content of REE (Σ REE) with increasing silica.

2) Decreasing Eu with increasing silica.

Reversals of trend 1) have been observed by some workers; that is, a decrease in Σ REE in the late-stage phases of granites (e.g. Emmermann et al., 1975).

One of the most striking features of upper crustal granites is the virtually ubiquitous negative Eu anomaly; that is, Eu is lower in abundance than that predicted by linear extrapolation between its two neighbours Sm and Gd. Thus, Eu is either retained in the residuum during granite genesis and/or is preferentially removed during fractional crystallization and emplacement (Buma et al., 1971). A third possibility is that the source region was initially relatively depleted in Eu. The anomalous behaviour is thought to reflect the stability of Eu^{2+} at normal crustal oxygen fugacities. The resulting similarity in size (and to a lesser extent charge) to Ca^{2+}, K^+ and Na^+ allows it to readily substitute for these elements in the feldspar structure (e.g. Haskin et al., 1966; Haskin et al., 1968; Philpotts, 1970; Buma et al., 1971). In the case of K^+ and Na^+, the substitution is a coupled one, and can be written:

$$Eu^{2+} + Al^{3+} = K^+(Na^+) + Si^{4+}$$

The implications of this general feature will be further discussed in the following section.

3) Sedimentary Rocks

In detrital sedimentary rocks, the REE can yield information on the provenance, age and composition of the source region, as well as indications of the weathering conditions (e.g. Ronov et al., 1967; Wildeman and Haskin, 1973; Ronov et al., 1974; Nance and Taylor, 1976).

REE patterns in chemical sediments, especially the presence or absence of Ce and Eu anomalies, are thought to reflect the REE chemistry of sea water, the nature of precipitating phases, and redox conditions in the atmosphere and at the site of deposition (e.g. Piper, 1974; Fryer, 1977).

Haskin *et al*. (1968), Wildeman and Haskin (1973), Wildeman and Condie (1973) and Nance and Taylor (1976, 1977) have documented via the study of clastic sediments of different ages, a decrease in the Eu content of the upper crust from the Precambrian to the Recent. This led Jakes and Taylor (1974) and Nance and Taylor (1976, 1977) to accomodate this trend into a model of continental crustal evolution. In their model, new material with normal or chondritic Eu is added to the crust via island arc andesitic volcanism. Crustal processes then dominate. Partial melting in the deep crust leads to the generation of a granodioritic upper crust with a negative Eu anomaly due to preferential retention of Eu by plagioclase in the residuum. Their model stressed the increasing importance of this process with time, in this manner explaining the relative decrease in Eu in the upper crust since the Precambrian.

As a corollary to their model, the relative Eu enrichment in the residual deep crust should provide another criterion in the search for lower crustal material now exposed at the earth's surface. They further proposed that this lower crust should be depleted in the other REE, when compared to upper crustal rocks, by a factor of two to three. There is other supporting evidence for this type of model of crustal evolution. There appears to have been a different thermal regime operative in Archean times, with a higher geothermal gradient (e.g.

Watson, 1973). Crustal evolution studies based on the changing chemistry and relative proportions of sedimentary rock types with time (e.g. Veiser, 1973) indicate that the early Archean crust was more mafic in character (dominated by material derived more directly from the mantle) than the crust of the Proterozoic and Phanerozoic. The crustal stratification resulting in a residual deep crust and granodioritic upper crust requires selective crustal reworking--a feature apparently only operative since late Archean or early Proterozoic times (Watson, 1973).

4) REE and Metamorphism

a) Low-grade metamorphism

As was the case with igneous rocks, studies of the effects of low-grade metamorphism on REE chemistry have centred on volcanic rocks. The general consensus is that the REE remain relatively immobile during low-grade alteration of submarine basalts (Frey *et al*., 1968; Graham and Nicholls, 1969; Philpotts *et al*., 1969; Schilling, 1971). Many workers have shown that the same is true for ophiolite complexes, which have undergone zeolite and greenschist facies metamorphism. (Montigny *et al*., 1973; Kay and Senechal, 1976; Smewing and Potts, 1976). Similarly, spilitization of both continental and oceanic basalts does not appear to substantially alter their REE patterns and abundances (Herrmann *et al*., 1974; Herrmann and Wedepohl, 1970).

However, there is now a growing amount of evidence that points to mobility of the REE during low-grade metamorphism, at least in certain cases. Detailed work by Frey *et al.* (1974) revealed changes in the REE chemistry of ocean floor basalts as a result of alteration and palagonitization, to the extent that some patterns of highly altered tholeiites changed from LRE depletion to LRE enrichment. Wood *et al.* (1976), in a study of Tertiary lavas from Eastern Iceland, deduced LRE mobility as a result of zeolitization. Even within a single flow, the LRE showed greater variability in zeolitized than in relatively fresh samples. Recent results by Hellman and Henderson (1977) on the Deccan Trap basalts, indicate that spilitization may, in certain circumstances, lead to an increase in the concentration of the REE.

b) Medium-and High-Grade Metamorphism

Haskin *et al.* (1968) found no significant difference in REE chemistry between a metamorphosed and an unmetamorphosed North American shale composite. Cullers *et al.* (1974) analysed 32 samples of metamorphosed pelitic rocks, from two Silurian formations in Maine ranging in grade from greenschist to amphibolite facies. They found no relationship between REE content and metamorphic grade, and therefore concluded that there had been no significant bulk movement of REE over any large distance.

Muecke *et al.* (1977) studied the effects of amphibolite facies metamorphism on the REE geochemistry of the White Rock metavolcanic suite, Nova Scotia. On the basis of strong correlations between the REE and other "immobile" LIL elements (e.g. Zr, Hf, Ti) and the constant REE chemistry across metasomatic zonations within the terrain, they concluded that the rocks have retained their pre-metamorphic REE chemistry.

Chou et al. (1976, 1977) report REE results for amphibolites from the English River gneiss belt, Ontario. The relatively flat patterns, similar in relative and absolute abundances to volcanic rocks from lower-grade greenstone belts, were taken to indicate a volcanic origin for these rocks. Kay et al. (1970) and Masuda et al. (1971) have shown that several ocean floor amphibolites and meta-gabbros of tholeiitic composition have the typical LRE depleted pattern of unaltered oceanic tholeiites.

Green et al. (1969, 1972) report REE results for amphibolite and granulite facies gneisses of similar major element chemistry from Norway. Although the granulites show strong depletions in U and Rb and high K/Rb ratios when compared to the amphibolites, there is no corresponding significant difference in REE chemistry. Furthermore, the relative and absolute abundances of REE (except Eu) are very similar to the NASC. They concluded that the granulite facies metamorphism, perhaps even involving partial melting, did not significantly affect the REE chemistry of the gneisses. Such a conclusion must be regarded with caution however, because of the small sample number (2 amphibolite and 5 granulite facies gneisses).

A composite of 16 charnockites from Mysore and Madras States, India was analysed for the REE by Spooner (1969). The resulting chondrite-normalized pattern is LRE enriched (a La/Yb ratio of approximately 4), with normal or chondritic Eu. He noted the similarity of this composite to gabbroic rocks of similar major element chemistry and suggested an igneous origin for these rocks.

c) REE in Metamorphic Minerals

Data on the REE chemistry of metamorphic minerals are very limited. Reitan and Roelandts (1973) analysed coexisting pyroxenes from pyroxene-granulites. The clinopyroxenes were found to have the higher absolute values of REE. The chondrite-normalized graphs for the clinopyroxenes showed a maximum in the middle REE range (Sm to Gd); whereas the orthopyroxenes showed a minimum in the middle REE range. Roaldset (1975) reported REE patterns for some metamorphic micas. Several workers have studied the REE abundances in accessory minerals of metamorphic terrains (Zayat and Kuts, 1964; Orsa *et al.*, 1967; Puchelt and Emmermann, 1976).

d) Summary

The evidence for REE immobility during metamorphism appears contradictory. On the one hand, large scale mobility especially during low-grade metamorphism seems to be untenable. On the other hand, REE mobility has been documented in certain cases of sea-water alteration, zeolitization and spilitization of basalts.

At higher grades, the data-base is smaller. Apart from this paucity of data, several other considerations militate against complete acceptance, at the present time, of the idea of REE immobility during high-grade metamorphism. These are:

a) The suggested marked effects of the formation of partial melts on REE chemistry (e.g. Balashov *et al.*, 1973; Dostal, 1975)

b) Theoretical considerations of intracrustal granite genesis, which should yield a residuum relatively depleted in REE.

c) The need of a "balanced Eu budget" for the crust as a whole.

Aims and Scope of Present Study

Field work and some sample collection was carried out in the fall of 1975, in the area from Inverkirkaig in the south to Richonich in the north (Fig. 1-1). Many whole rock samples and mineral separates were supplied by G. K. Muecke, resulting in virtually complete coverage of the major rock types and rock-forming minerals of the mainland Scourian assemblages.

Laboratory work mainly involved instrumental neutron activation analysis for the REE (La, Ce, Sm, Eu, Tb, Yb, Lu). Sc, Cr, Co, Hf and Th were also determined. Major element analyses were carried out where necessary.

The primary objective of the study was to investigate thoroughly the REE geochemistry of the Scourian complex. To this end, 39 whole rock and 31 mineral samples were analysed. Whole rock sample selection was weighted in favour of the more abundant rock types in order to obtain a REE estimate for the complex as a whole, and to determine the variability of REE abundances within individual rock types. The results for the pyroxene granulites proper are presented in Chapter 4. Special attention was directed to the granite sheets and pegmatites of the Scourian complex (Chapter 6), as a preliminary study revealed anomalous trace element abundances in these rocks compared to normal upper crustal equivalents.

A knowledge of the REE abundances in the rock-forming minerals is essential for an understanding of the REE geochemistry of the Scourian complex. Accordingly, samples of all of the major rock-forming minerals of the Scourian complex were analysed, covering the major rock types present. These results are presented in Chapter 5.

A description of the laboratory procedure and a discussion of precision and accuracy of the REE results are given in Appendix 1.

CHAPTER 2

THE GRANULITE FACIES AS DEEP CRUST

A simple application of the temperature and pressure estimates of Lachenbruch (1970) for the deep crust of orogenic belts to conventional metamorphic facies diagrams (e.g. Turner, 1968) leads to the conclusion that the rocks of the lower continental crust may be in the granulite facies. Any model of deep crustal composition and structure, however, must be compatible with evidence from seismology, heat flow and geochemistry, experimental petrology as well as general geological considerations. Although a detailed treatment of each of these aspects is beyond the scope of this study, a brief discussion of the constraints imposed by each is necessary in order to fully evaluate the results of this work.

Seismic Evidence

Continental crustal seismic data have conventionally been interpreted in terms of a two-tier crustal model--an upper granitic layer and a lower basaltic or gabbroic layer, often separated by the Conrad discontinuity. This model represents the simplest solution to the observed compressional wave velocities (Vp's) which average 6 km/s for the upper crust and 7 km/s for the lower crust (e.g. Birch, 1961; Nur and Simmons, 1969). Recent results, using higher resolution techniques, have stressed the heterogeneous nature of crustal structure (e.g. Smithson and Brown, 1977). As many as 10 major interfaces have been recognized within many vertical crustal segments (e.g. Sollogub *et al*., 1974).

Nonetheless, the seismic data do place limits on possible deep crustal composition. The Vp's observed for the lower crust generally vary between 6.4 and 7.4 km/s, with the majority falling between 6.5 and 7.0 km/s (Mueller, 1974). Laboratory measurements of Vp for various metamorphic rocks are presented in Table II-1. Amphibolite yields a Vp of approximately 7 km/s at atmospheric pressure. Extrapolation to the pressures of interest (6 to 15 kb) would yield higher Vp's--too high, in fact, for amphibolite to be a major component of the lower crust (Smithson and Brown, 1977). At a pressure of 10 kb, eclogites yield Vp's in the range 8.0 to 9.0 km/s, again too high for the lower crust, but typical of observed upper mantle velocities. The high density of eclogite (3.4 to 3.6 g/cm^3) compared to estimated average crust (2.84 to 2.92 g/cm; Woolard, 1970, Ringwood and Green, 1966) presents another argument against a deep crust in the eclogite facies.

Granulite facies rocks, however, yield Vp's and densities consistent with observed and estimated lower crustal values (Table II-1). At 6 kb pressure, quartzofeldspathic, intermediate and garnet granulites have Vp's of approximately 6.5, 6.6 to 7.0 and greater than 7.0, km/s respectively. In a recent review, Smithson and Brown (1977) concluded, mainly on the basis of seismic data, that the lower continental crust is probably composed of a heterogeneous mixture of felsic to mafic metamorphic rocks in the granulite facies. They further noted that the lower crust, while probably more intermediate in composition than the upper crust, must be distinctly less mafic than gabbro to account for the majority of observed Vp's.

Table II-1: Laboratory Measurement of Vp in Metamorphic Rocks.

Rock Type	Metamorphic Facies	Vp (Km/s) at 1 Kb	Vp at 6 Kb	Vp at 10 Kb	Density (g/cm^3)
Amphibolite*	Amphibolite	6.6-7.2	-	-	3.01
10 Eclogite**	Eclogite	-	-	8.0-9.0	3.4-3.6
Granodiorite***	Granulite	6.06-6.36	6.41-6.57	-	2.68-2.71
Plagioclase-pyroxene-hornblende gneiss***	Granulite	6.49-6.75	6.69-6.95	-	2.73-2.90
Syenite gneiss***	Granulite	6.40	6.70-6.71	-	2.83
Pyroxene-syenite gneiss***	Granulite	6.82	7.01	-	2.93
Hornblende granulite***	Granulite	6.51	6.99	-	2.98
Pyroxene-Hornblende granulite***	Granulite	7.11	7.37	-	3.03
Pyroxene granulite***	Granulite	6.68	7.40	-	3.08
17 granulites (including garnet granulite)**	Granulite	-	-	6.3-7.9	2.7-3.3

*Smithson and Shive, 1975.

**Manghnani _et al_, 1974.

***Christensen and Fountain, 1975.

Heat Flow and Geochemistry

The radioactive heat-procuding elements K, U, and Th are unique in that their crustal abundances can be estimated by two essentially independent means: (a) geophysically through the interpretation of surface heat flow data, and (b) geochemically, from surface abundance measurements and geologically realistic assumptions (Heier, 1973).

The average values obtained for surface heat flow from different geological environments are given below (Brume, 1969):

	Heat Flow ($mW/_{m}2$)
Exposed shields	29 - 38
Mid-continents (shield + Phanerozoic cover)	33 - 50
Young orogenic belts	71 - 105

The higher values for younger orogenic belts (e.g. Basin and Range, Western U.S.) indicate a steeper temperature gradient for these zones compared to shield terrains. This feature is confirmed by the lower intensity of magnetic anomalies over these zones due to a shallower depth to the critical Curie point temperature (Pakiser and Kietz, 1965).

Hyndman _et al_. (1968) showed that the above shield estimates are valid only for basic and ultrabasic rocks which make up less than 20% of the surface of shields. Their measurements in granitic rocks of the Australian shield give a heat flow of approximately 51.5 mW/m^2 units (HFU), higher than previous shield estimates of 29 to 38 mW/m^2

but still considerably lower than the heat flow of younger orogenic belts. They observed that the concentration of the heat producing elements K, U, and Th for the surface of shields is the same as that observed for the surface of younger orogenic belts, and therefore these radioactive elements are probably confined to a relatively thin surface layer in the shield terrains. Their models of the variation in concentration of crustal radioactive elements with depth showed a rapid decrease at approximately 20 km in shield terrains while the younger orogenic belts exhibited a greater thickness of crust with high levels of these elements.

Lachenbruch (1970) noted that the linear relationship between surface heat flow and heat production in plutons of orogenic belts is most easily explained in terms of an exponential decrease of heat production with depth in the crust - essentially the same model proposed by Hyndman et al. (1968). He envisaged a process in active orogenic belts involving crustal melting on a large scale (due to conduction in a thick sedimentary sequence, radioactive heating, tectonic thickening, or transient injection of heat and/or material from the mantle). The radioactive elements K, U, and Th would be strongly partitioned into the melt phase. Subsequent upward movement of these melts, and "sinking" of depleted residual material would be the mechanism whereby the radioactive heat-producing elements are concentrated upwards in the crust. Thus, shield terrains represent continental crust that has been stabilized via this mechanism, and younger orogenic belts represent unstable zones where this process is now operative.

Medium-to high-pressure granulite facies complexes exhibit lower abundances of the heat-producing elements U and Th (e.g. Sighinolfi and Sakai, 1977; Heier, 1973; Eade and Fahrig, 1971; Lambert and Heier, 1968a) and perhaps K (e.g. Heier, 1973; Holland and Lambert, 1972a, 1975; Eade and Fahrig, 1971; Sighinolfi, 1971) when compared to the average upper crust (see Chapter 3). Such terrains also show lower abundances of other incompatible elements such as Rb, Cs, Li and Be (e.g. Heier, 1973; Holland and Lambert, 1972b; Sighinolfi, 1972, 1971; Heier and Brunfelt, 1970). These low incompatible element abundances are consistent with the above heat flow models if the deep crust is in the granulite facies.

Geological and Experimental Evidence

Granulite facies complexes occur in virtually all Precambrian shield terrains (Oliver, 1969). They have also been reported from younger orogenic belts (e.g. Compton, 1960), and pyroxene-and garnet-bearing granulites are often found as xenoliths in diatremes (e.g. McGetchin and Silver, 1972). These latter two modes of occurrence may indicate that the conditions necessary for the formation of granulite facies assemblages are not unique to the Precambrian. Their more widespread occurrence in shield terrains may therefore be due to the great amount of time and special tectonic conditions required for their exposure.

Progressive regional metamorphism encompasses mainly a series of dehydration reactions (e.g. den Tex, 1965; Heier, 1973). Anhydrous medium-to high-pressure granulite facies assemblages may represent the end product of these processes. Partial melting, feasible under upper amphibolite conditions, may account for the paucity of granitic and pelitic rocks in medium-to high-pressure granulite facies complexes (Heier, 1973), which may represent the residuum, after granite genesis (Brown and Fyfe, 1970, 1972).

It has been suggested that in several places a vertical section of the crust has been exposed tectonically. Berckhemer (1969) considered the Ivrea zone of the southern Alps to be such an example. The section passes "downward" from granites, schists and gneisses, through a zone of migmatites and amphibolites, into pyroxene-bearing gneisses of the granulite facies. The lowermost crust is marked here by the appearance of lenticular diorites and gabbros intermixed with the pyroxene-granulite gneisses.

Evidence from experimental petrology is also consistent with a granulite facies lower crust. For example, anhydrous experimental work on rocks of intermediate and basaltic composition at assumed lower crustal temperatures and pressures yields mineral assemblages dominated by plagioclase, aluminous pyroxenes and pyrope-rich garnet (e.g. Ito and Kennedy, 1971, 1970; Green, 1970; Green and Ringwood, 1967). Such assemblages are observed in medium-to high-pressure granulite facies assemblages of similar bulk rock compositions to the experimental runs. The majority of ultramafic rocks in granulite facies complexes exhibit spinel lherzolite mineral assemblages which have been shown experimentally to form at pressures of 8 to 17 kb and temperatures of 700 to 1100°C, under anhydrous conditions (e.g. MacGregor, 1974, 1970; O'Hara, 1967). These pressures and temperatures are consistent with lower continental crustal estimates (Lachenbruch, 1970).

Summary

In this chapter, the phase and bulk composition of the lower continental crust as well as its structure was considered in the light of evidence from a broad spectrum of earth science investigation. It was shown that medium-to high-pressure granulite facies complexes conform, perhaps uniquely, to models envisioned for the lower continental crust as derived from geophysics, geochemistry, experimental petrology and surface geological observations.

CHAPTER 3

GEOLOGICAL SETTING OF STUDY

Introduction

The Lewisian complex of north-west Scotland forms a major part of the British Precambrian. It includes most of the Scottish mainland west of the Moine thrust, the Outer Hebrides, and some of the islands of the Inner Hebrides (Fig. 1-1). It is overlain unconformably by the late Precambrian Torridonian series, composed of unmetamorphosed arkosic sandstones and shales.

Probably no other section of Precambrian crust has received as much attention over so long a period of time. Unlike many other Precambrian shield terrains throughout the world, a detailed geological map of the Lewisian complex has been in existence since 1907, when Peach *et al*. published their memoir on the north-west highlands. This classic work formed the foundation of all subsequent geological research which, as predicted by these early authors, has led to an increasing awareness of the complex number of events and length of time represented by the Lewisian.

Geology and Geochronology of the Lewisian

Peach *et al*. (1907) subdivided the Lewisian rock types into five groups:

1) A fundamental complex composed of gneisses of plutonic affinity and lesser sediments.

2) Ultra-basic dykes
3) Dykes and sills of dolerite
4) A few dykes of exceptional composition
5) Granites and pegmatites.

They further subdivided the complex into three broad regions:

1) The Northern region, dominated by hornblende- and biotite-gneisses plus acid vein rocks.
2) The Central region, composed mainly of pyroxene-gneisses.
3) The Southern region, very similar to the Northern region but with more abundant metasediment.

They also recognized that the dolerite dykes were essentially unmodified in the central region, but foliated and deformed in the northern and southern regions.

Sutton and Watson (1951) used these dykes to establish a subdivision of the Lewisian into two major metamorphic events separated by a considerable time interval:

1) The older _Scourian_ or _pre-dyke_ event, involving a granulite facies metamorphism.
2) The younger _Laxfordian_ or _post-dyke_ event, involving an amphibolite facies metamorphism.

Subsequent geochronological work by Giletti _et al_. (1961) substantiated this subdivision, dating the Scourian at > 2,460 m.y. and the Laxfordian at 1500-1600 m.y.

Evans (1963, 1965) recognized another pre-dyke event, which he termed Inverian, dated at approximately 2300 m.y. This "event" was essentially an amphibolitization of the pre-existing Scourian granulites along WNW-trending shear zones.

Further work by many researchers (e.g. Moorbath et al., 1969; Moorbath and Park, 1972; Evans and Lambert, 1974) has contributed significantly to Lewisian geochronology. The resulting geochronological sequence of Lewisian events (Evans and Lambert, 1974) is given in Table III-1.

This general tectonic setting and geochronological sequence is by no means unique to the Lewisian. Watson (1973) noted that the age of Scourian metamorphism can be correlated with similar events from Precambrian shield terrains throughout the world (e.g. Kenoran in Canadian Shield). This age of between 2800 and 2500 m.y. seems to mark the close of universal crustal reworking - subsequent events did not markedly affect the stabilized cratonic cores (Watson, 1973). The resulting pattern is one of stable Archean cratons (e.g. Scourian, in Lewisian complex; Superior province, in the Canadian Shield; the Archean Block, of south-central Greenland) surrounded by later Proterozoic mobile belts, which generally include both reworked Archean material and younger supracrustals, (e.g. Laxfordian, in Lewisian; Ketilidean belt in Greenland; Churchill and Grenville provinces of the Canadian Shield). From a "Bullard" (1965) reconstruction of the pre-drift super continent, there is a suggestion that the shield terrains of Canada, Greenland and Great Britain were linked. The Scourian would then represent the deepest Archean crustal section and the Superior province of the Canadian Shield the shallowest section, on the

Figure III-1: Lewisian Geochronology
(after Evans & Lambert, 1974)

Ca 2900 m.y.:	primary age of pyroxene granulites.
2600 m.y.:	termination of pyroxene granulite facies metamorphism, formation of the pyroxene gneisses of the Scourie Assemblage.
2540 m.y.:	intrusion of potash pegmatites in both the mainland Lewisian and the Outer Hebrides.
2310 m.y.:	further potash pegmatites or recrystallization of first set.
2310-2200 m.y.:	amphibolite facies metamorphism actively affecting WNW - striking vertical belts up to 2 Km wide; development of isoclinal folds, new gneissose banding and destruction of all pre-existing structures. Formation of the Inver assemblage by hydration of the Scourie assemblage.
2200 m.y.:	Intrusion of ultramafic and mafic dykes into hot country rock, followed closely by their autometamorphism. The last members of the suite retain pyroxenic mineralogy.
1850 m.y.:	onset of decline of amphibolite facies metamorphism of the Laxford assemblage followed by slow cooling and foliated granite and intrusive pegmatite activity. Brittle deformation of pyroxene granulites and amphibolites.
1600 m.y.:	cessation of pegmatite activity, closure of biotite and hornblende to argon loss. Termination of brittle shear activity.
1400 m.y.:	closure of biotite to Rb and/or Sr migration.

basis of degree of metamorphism and abundance of recognizable supracrustals (Sutton, 1973).

Selected features of the Scourian Complex

The Scourie and Inver assemblages occupy the Central Region as defined by Peach et al. (1907), extending from Loch Broom in the south to near Scourie in the north (Fig. I-1). The northern boundary is transitional over a zone termed the Ben Stack Line by Holland and Lambert (1972). North from Scourie towards Laxford Bridge, the gneisses change in character from the pyroxene-granulites typical of the Scourie assemblage to biotite-hornblende gneisses typical of the Laxfordian assemblage (Peach et al., 1907; Sutton and Watson, 1951). The abundance of granitic material also greatly increases to the north within this zone.

1) Field Relations and Petrology

Detailed accounts of the field relationships and petrology of the Scourie (and Inver) assemblage have been given by Peach et al. (1907), Sutton and Watson (1951), O'Hara (1961), Khoury (1968), Evans (1963), Muecke (1969) and Evans and Lambert (1974). A brief summary of the more salient features will be given here.

The Scourian is structurally complex as is the case for most granulite facies assemblages. The dominant structural trend is one of low-angle dips and broad, low-amplitude primary structures (Evans and Lambert, 1974). Individual structures are rarely traceable for more than 1 km. The foliation exists on all scales from metres to millimetres. Contacts between rock types are generally sharp.

Unaltered Scourian pyroxene granulites are rare, occurring as remnants between Inverian amphibolitized shear zones. The degree of retrogression varies from complete obliteration of the granulite facies texture and mineralogy in the Inverian zones to rather mild effects such as the development of thin rims of secondary hornblende along contacts between augite and plagioclase. The degree of amphibolitization is also a function of rock composition--the acid gneisses being more susceptible than the mafic or ultramafic gneisses. The principal addition, resulting in the amphibolitization, appears to have been water (Evans and Lambert, 1974; Beach, 1974). The Scourie and Inver assemblages are otherwise essentially isochemical.

An estimated 80% of the Scourian terrain is composed of felsic or tonalitic gneisses. The other 20% is composed of intermediate, mafic and ultramafic gneisses (Muecke, 1969). The classification used here is that of Muecke (1969), based on the mafic index:

	Mafic Index
Felsic division	0-30
Intermediate division	30-50
Mafic division	50-80
Ultramafic division	80-100

The felsic gneisses are the most continuous. The ultramafics tend to occur as isolated rafts and schlieren in the more felsic units (Muecke, 1969), although in several localities they form more continuous, identifiable units (e.g. O'Hara, 1961). Conformable granite gneiss sheets and cross-cutting pegmatites are also present and are discussed at length in Chapter 6.

The principal mineral assemblages of the pyroxene-granulites are (Muecke, 1969):

1) Felsic Division
   Plagioclase(An31-38)+Quartz+Orthopyroxene±Clinopyroxene
2) Intermediate Division
   Plagioclase(An39-53)+Clinopyroxene±Orthopyroxene±Quartz±Garnet
3) Mafic Division
   Plagioclase(An47-68)+Clinopyroxene+Orthopyroxene±Hornblende±Garnet
4) Ultramafic Division
   a) Clinopyroxene+Orthopyroxene+Olivine±Hornblende
   b) Clinopyroxene+Orthopyroxene±Hornblende±Garnet±Plagioclase (An56-79)±Spinel

Potash feldspar, apatite, opaques and secondary hornblende and biotite are accessory phases of the felsic and intermediate division gneisses. Opaques and minor apatite and occasionally scapolite, are accessory phases of the mafic gneisses, and opaques are present in the ultramafic gneisses.

Muecke (1969) noted the apparent incompatibility of the following assemblages:

1) Olivine+plagioclase
2) Olivine+garnet
3) Hornblende+quartz

Muecke (1969) also noted several distinctive chemical features of the pyroxene-granulite minerals:

1) Pyroxenes are highly aluminous, from 3.3 to 6.0 weight per cent Al_2O_3 in cpx and from 2.6 to 4.8 weight per cent in opx.
2) Garnet is high in pyrope content (up to 33%)
3) Primary pargasitic hornblende is high in K, Ti and Al.

Based on a) the incompatibility of the assemblage olivine+plagioclase, b) the aluminum-rich nature of the pyroxenes and c) the high pyrope content of the garnets, the Scourie assemblage would be classified as medium- to high-pressure granulites in the scheme of Green and Ringwood (1967).

2) Physical Conditions of Scourian Metamorphism

a) Previous Estimates

In order to assess the importance of processes such as partial melting on the chemistry of the Scourian complex, it is essential to have a knowledge of the physical conditions of Scourian metamorphism. O'Hara (1960) estimated these conditions at 750-850°C and approximately 8 kb load pressure, based mainly on a comparison of the ultramafic mineral assemblages to experimental work. He subsequently revised these estimates upward to 950-1150°C (1975) and then to greater than 1250°C at a load pressure of 15 ± 2 kb (1976). This most recent temperature estimate is based largely on the application of the Stormer (1975) two-feldspar geothermometer to a textural interpretation of the "most primary" feldspars of the Scourian granite gneiss sheets. It is considered by other workers (Muecke, 1969; this study, Chapter 6) that these same rocks originally consisted of one homogeneous feldspar phase (now exsolved) and thus the Stormer two-feldspar geothermometer may not be applicable. Furthermore, Powell and Powell (1977) have recently shown that the high Ca content of the Scourian alkali feldspars (O'Hara, 1976), not taken into account by O'Hara, would lead to erroneously high temperature estimates.

O'Hara's pressure estimate is based mainly on the ultramafic assemblages. The general prevalence of spinel lherzolites in anhydrous ultramafic rocks of the granulite facies throughout the world, indicates a formational pressure of between 8 and 17 kb. He took the sparse occurrence of garnet lherzolite and the great rarity of plagioclase lherzolite to indicate pressures towards the higher part of this 8 to 17 kb range ie. 15 ± 2 kb. Such a generalization applied to a specific example not exhibiting garnet lherzolite assemblages (i.e. the Scourian) is of dubious merit.

Muecke (1969) estimated conditions of Scourian metamorphism at 700-800°C and 7-9 kb load pressure at very low partial pressures of water. He considered that a temperature maximum of 860°C was indicated by the presence of discrete magnetite and hercynite grains in the metaperidotites. The pressure estimate was based on his temperature estimate applied to the experimental work of Green and Ringwood (1967) on the gabbro-garnet granulite-eclogite transition under anhydrous conditions. The low modal abundance of garnet (1.1%) in a basic gneiss sample which closely approximates the quartz tholeiite composition used in the Green and Ringwood experiment, was taken to indicate that the conditions of Scourian metamorphism closely approximates the garnet-in curve of Green and Ringwood extrapolated down to the temperature range of interest (Fig. III-2).

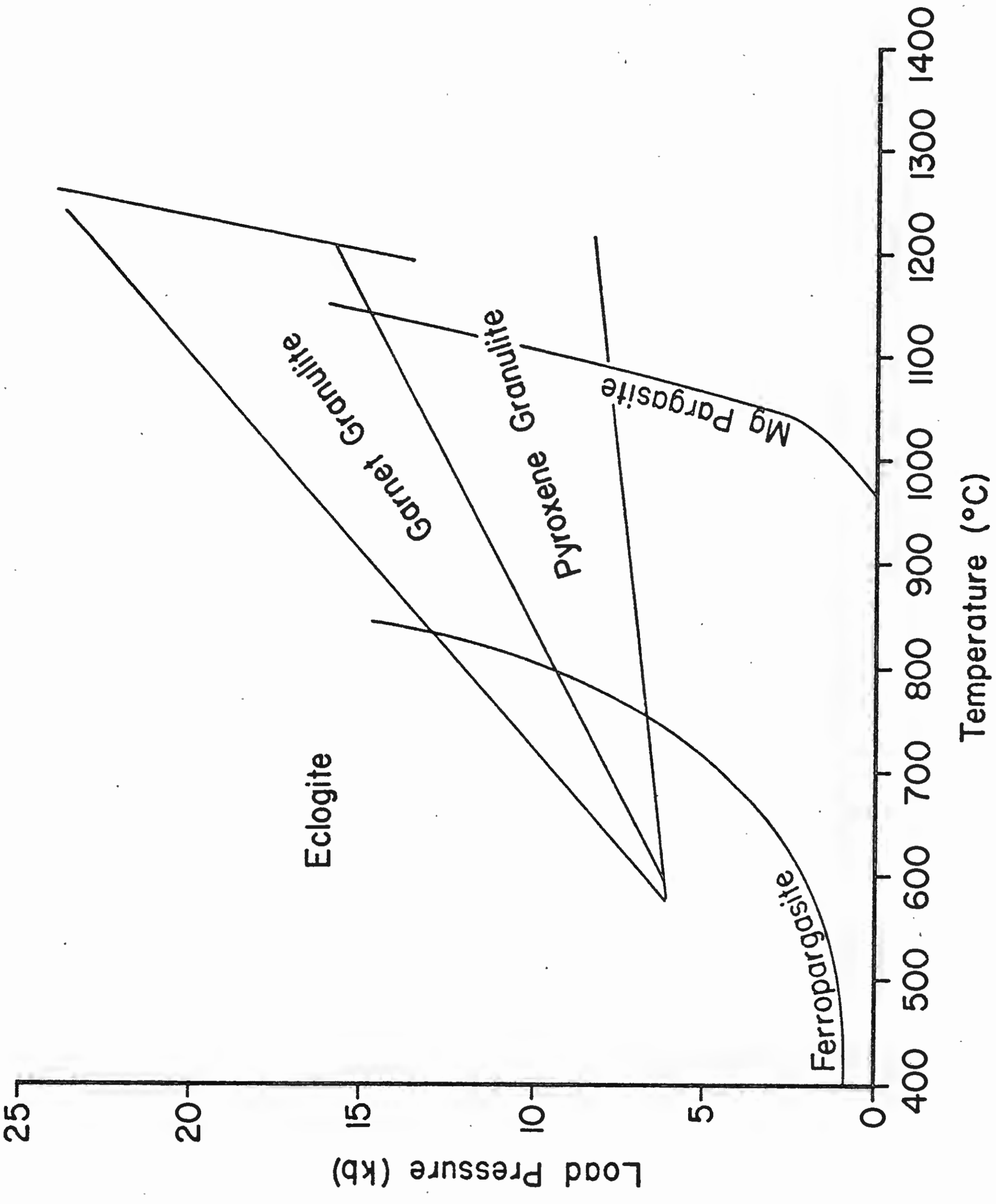


Fig. III-2 : Pressure - temperature diagram showing conditions for the appearance of garnet in quartz tholeiite compositions (after Green and Ringwood, 1967); stability of ferropargasite (after Gilbert, 1966) and Mg pargasite (after Holloway and Ford, 1975).

The data of Muecke (1969) and O'Hara (1960) have been reinterpreted in terms of new experimental work.

b) New Temperature Estimate

An upper temperature limit for the Scourian complex is implied by the presence of a primary pargasitic hornblende. The stability of pargasite as a function of pressure, temperature, P_{H_2O}, P_{O_2} , $Mg/_{Mg+Fe}$ ratio, and mole fraction of fluorine, has been extensively investigated (Holloway and Ford, 1975; Allen et al., 1975; Holloway, 1973; Gilbert, 1968; Gilbert, 1966). Under anhydrous conditions, the stability of pargasite is greatest for the pure Mg member (Gilbert, 1968). The stability is also raised as the mole fraction of fluorine (F) in the OH position is increased, (Holloway and Ford, 1975). The mole fraction of F in the Scourian hornblendes has not been determined but is probably less than 0.15(estimated from the analyses of Muecke, 1969) and thus should not have a significant effect on stability. The stability curves of pure Mg pargasite and ferropargasite (under anhydrous conditions) are given in Fig. III-2. The $Mg/_{Mg+Fe}$ ratio of between 0.6 and 0.7 for the Scourian hornblendes (Muecke, 1969) indicates a maximum formational temperature for the Scourian complex substantially below the stability curve for pure Mg pargasite, and thus substantially below 1100°C in the pressure range 11-15 kb (Fig. III-2). These considerations militate against the temperature estimate of greater than 1250°C given by O'Hara (1976) and provide an upper limit for temperature estimates using other methods.

Examination of equilibrium mineral assemblages and comparison to appropriate experimental work place broad constraints on the physical conditions of metamorphism. The compositions of coexising minerals, however, may allow a more precise estimate of such conditions. In this regard, the two-pyroxene geothermometer of Wood and Banno (1973) may be particularly useful. This approach is based on the solubility of enstatite in clinopyroxene coexisting with orthopyroxene. The appropriate reaction may be expressed as follows:

$$(Mg_2\ Si_2\ O_6)_{\substack{\text{orthopyroxene}\\ \text{solid solution}}} \rightleftarrows (Mg_2\ Si_2\ O_6)_{\substack{\text{clinopyroxene}\\ \text{solid solution}}}$$

This relationship has been shown to be essentially independent of pressure (Davis and Boyd, 1966). Wood and Banno (1973) use an ideal solution model coupled with an empirical approach, using experimental results on simple and complex systems in order to overcome the problems resulting from additional components and varying rock compositions. Their temperature relationship is expressed as follows:

$$T(°K) = \frac{-10{,}202}{\ln \dfrac{a^{\text{Clinopyroxene}}_{Mg_2Si_2O_6}}{a^{\text{Orthopyroxene}}_{Mg_2Si_2O_6}} - 7.65\ X^{M1}_{Mg} + 3.88\ \left(X^{Opx}_{Fe}\right)^2 - 4.6}$$

where $a^{Cpx}_{Mg_2Si_2O_6} = X^{M1}_{Mg} \cdot X^{M2}_{Mg}$ in clinopyroxene

$a^{opx}_{Mg_2Si_2O_6} = X^{M1}_{Mg} \cdot X^{M2}_{Mg}$ in orthopyroxene

X^{M1}_{Mg} = fraction Mg^{2+} in M1(2) site of pyroxene

$X^{Opx}_{Fe} = \frac{Fe^{2+}}{Fe^{2+}+Mg^{2+}}$ of orthopyroxene.

Using this equation, Wood and Banno reproduced experimental results to within 60°C over a wide range of rock compositions in the temperature interval 700°C - 1400°C.

Wells (1977) recalibrated this geothermometer using most of the available experimental data, resulting in the following temperature relationship :

$$T\ (^{\circ}K) = \frac{7{,}341}{3.355 + 2.44\ X_{Fe}^{Opx} - \ln K} \qquad K = \frac{a_{Mg_2\ Si_2O_6}^{Clinopyroxene}}{a_{Mg_2\ Si_2O_6}^{Orthopyroxene}}$$

His equation reproduces experimental results to within 70°C over the temperature range 800 - 1700°C, and yields more reliable results for Mg-rich two pyroxene assemblages.

The data of Muecke (1969) and O'Hara (1960) have been applied to these geothermometers and the results are presented in Table III-1. The mean temperature using the Wood-Banno equation is 902°C ± 34.

Using the Wells equation, the mean temperature is 916°C ± 33. These results for both geothermometers are consistent with Wood-Banno temperatures for many other granulite facies terrains, which yield temperatures of 780°C - 860°C for the hornblende granulite subfacies and temperatures greater than 860°C for the pyroxene granulite subfacies (Hewins, 1975; Wood and Banno, 1973). Hewins (1975) noted that the internal consistency, precision and apparent accuracy of the Wood-Banno geothermometer, despite varying rock compositions, makes it an important tool in granulite facies terrains. He noted also that higher temperatures

Table III-1: Wood-Banno and Wells Temperatures for the Scourian Gneisses

Sample Number	Rock Type	T °C (Wood-Banno)	T °C (Wells)
65-18*	Felsic gneiss	888	949
64-12*	Mafic gneiss	857	887
65-33*	Mafic gneiss	880	928
X291**	Basic gneiss	888	951
37,099***	Basic gneiss	875	912
67-109*	Ultramafic gneiss	910	921
X646**	Ultramafic gneiss	923	947
37,310***	Peridotite	971	887
X282**	Peridotite	924	856
	Mean T (°C)	902 ± 34°	916 ± 33°

* Muecke, 1969

** O'Hara, 1971

*** Muir and Tilley, 1958.

are most often obtained from mafic and ultramafic rocks suggesting that many such examples represent partial re-equilibration of the pyroxenes from originally higher igneous temperatures. Such a result is observed for the Scourian ultramafic gneisses and peridotites, using the Wood-Banno geothermometer. As noted by Wells (1977), however, these systematically higher temperatures for Mg-rich pyroxenes (the pyroxenes from the ultramafic gneisses and peridotites are more Mg rich than those of the other Scourian rock types) are due to large inaccuracies in the Wood-Banno geothermometer for Mg-rich compositions. The Wells temperatures show no such systematic relationship with rock (and hence pyroxene) composition. Accordingly, the temperature estimate accepted for this work is that obtained from the Wells geothermometer; that is, 916°C ± 33.

c) New Pressure Estimate

There are few reliable geobarometers applicable to granulite facies assemblages. Wood and Banno (1973) and Wood (1974) have developed a geobarometer based on a semi-empirical approach to the solubility of Al in orthopyroxene in equilibrium with garnet. A previous temperature estimate is required by the equation. Their derived pressures reproduce experimental results to within 3 Kb. The mineral data of Muecke (1969), for coexisting garnet and orthopyroxene, have been applied to this geobarometer using the temperature estimate derived in the previous section (i.e. 916 °C ± 33). The resulting pressures are approximately 6 Kb (for samples 65-33 and 67-109) and approximately 9 Kb (for sample 65-165). Given the uncertainty inherent in this method (approximately 3Kb), the uncertainty of the temperature estimate, and the broad range of calculated pressures, the results of this barometer are of little use in obtaining a reliable pressure estimate of Scourian metamorphism.

Another possibly useful approach is the Raheim-Green geobarometer (Raheim and Green, 1974; Raheim and Green, 1975), based on the pressure and temperature dependence of the Fe^{2+}/Mg^{2+} ratio of coexisting garnet and clinopyroxene. They attempted to calibrate this relationship experimentally in the pressure range 20 to 40 Kb. and in the temperature range 600-1400°C. The mineral data of Muecke (1969) and O'Hara (1961) have been applied to this geobarometer using the previously derived temperature estimate (916°C ± 33). The resulting pressures, in the range 27 to 45 Kb., are obviously too high, probably due to the rather simplistic model employed (i.e. it does not take into account the effects of substitutions for Fe^{2+} and Mg^{2+}) and the high pressures over which the calibration was made (20 to 40 Kb).

Perhaps the most applicable approach to a pressure estimate of Scourian metamorphism is that taken by Muecke (1969), discussed in the introduction to this section. The newly derived temperature estimate of 916°C ± 33 has been applied to the garnet-in curve of Fig. III-1 (Green and Ringwood, 1967), using the same assumptions as Muecke (1969). The resulting pressure estimate is 11 Kb ± 1, and probably represents a minimum pressure estimate, as it is difficult to assess how far above the garnet-in pressure, the Scourian pressure reached.

Thus, the temperature and pressure estimates adopted here for the Scourian granulite facies metamorphism are 916°C ± 33 and 11 Kb ± 1, at very low partial pressures of water, as evidenced by the anhydrous nature of the terrain as a whole, and the presence of an exsolved ternary feldspar phase in the Scourian granite sheets (see Chapter 6).

3) Geochemistry

a) Introduction

Determination of the average chemical composition of continental crustal units has proven a difficult task due mainly to problems of representative sampling. Limited exposure and mixing of metamorphic grades add to these problems in structurally complex granulite-facies terrains. In spite of these limitations, such studies are of obvious value in estimates of the mean chemistry of the continental crust, and in assessing aspects of crustal evolution. Several distinctive chemical features of granulite facies terrains have emerged from such studies and may have important implications for the composition of the lower crust.

b) Major Elements

The major element chemistry of the Scourian complex has been extensively investigated (Holland, 1966; Muecke, 1969; Bowes, 1972; Tarney *et al.*, 1972; Sheraton *et al.*, 1973; Holland and Lambert, 1972c, 1973, 1975). Holland and Lambert (1975) demonstrated that the Scourian complex is homogeneous on a megascopic scale. They also showed that the Scourian and Inverian zones were essentially isochemical (Table III-2).

The Scourie Group rocks yield smooth curves on Larsen-Nockolds type variation diagrams, and yield trends on triangular $MgO-FeO-Na_2O+K_2O$ plots similar to differentiation trends for the tholeiitic series (Muecke, 1969). Factor analysis of the various chemical parameters for the Scourie Group suite is also compatible with a plutonic-igneous

Table III-2: Average composition of shields (A), continental crust (B,C) and granulite facies terrains (D - H).

Wt. %	A	B	C	D	E	F	G	H
SiO_2	66.7	60.2	59.1	60.6	61.2	61.0	61.5	62.3
Al_2O_3	15.0	15.6	15.4	15.4	16.4	15.8	15.5	15.2
Fe_2O_3	4.5	7.9	7.8	7.2	6.2	7.9	6.2	6.4
MgO	2.3	3.9	4.2	3.9	3.0	3.0	3.5	3.3
CaO	4.2	5.8	6.5	5.7	4.4	5.3	5.9	6.0
Na_2O	3.6	3.2	3.1	2.8	4.0	3.6	4.0	4.0
K_2O	3.2	2.5	2.3	2.6	3.0	2.3	1.0	1.0
TiO_2	0.5	1.0	1.2	0.9	0.6	0.95	0.56	0.56
MnO	0.07	0.1	0.1	0.2	0.1	0.11	0.10	0.09
P_2O_5	-	0.2	0.2	0.2	0.16	-	-	-
(n)				(23)	(20)	(62)	(541)	(140)
Ppm								
Rb	110	90		70	56	45.8	3-9	10.7
U	2.45	2.7		0.4	0.5	-	<0.1***	<0.1***
Th	10.3	9.6		2.1	5.1	-	<0.45**	<0.45**
Sr	316	375		340	572	543	495	461
Pb	16.7	12.5		20	15.1	-	<15*	<15*
K/Rb	241	231		308	445	626	922	776

A Average of the Canadian Shield: Shaw et al. (1967, 1976).

B Average of the Continental Crust: Taylor (1964b).

C Average of the Continental Crust: Poldervaart (1955).

D Average of Musgrave Range, Australia: Lambert and Heier (1968b.)

E Average of Lofoten-Vesteralen Granulites, Norway: Heier and Thoresen (1971).

F Bahia Granulites, Brazil: Sighinolfi (1971).

G Scourie Assemblage, Scotland: Holland and Lambert (1975).

H Inver Assemblage, Scotland: Holland and Lambert (1975).

*Moorbath et al (1969). **This Study. ***Muecke (1969); Muecke (Pers. Comm.)

origin (Holland and Lambert, 1975). Muecke (1969) noted however, that such trends are not, in themselves, unequivocal evidence for an igneous origin. Similar trends can also be produced by high-grade metamorphism from diverse rock suites (including sediments), as has been documented by Heier (1960) for the high-grade Lofoten-Vesteralen area, Norway.

A "best estimate" for the Scourian complex as a whole (Holland and Lambert, 1975) is presented in Table III-2, and for comparison, various estimates of the major element composition of shields, the continental crust, and other medium-to high-pressure granulite facies terrains are also given. The Scourian is characterized by an overall intermediate major element chemistry approximating quartz diorite or tonalite in composition. With respect to other granulite facies terrains (e.g. Musgrave Range, Australia) and estimates for the continental crust (Table III-2), the Scourian shows a depletion in potash. Compared to the average of the Canadian Shield (Table III-2), the Scourian complex is more mafic, has lower silica, and is distinctly depleted in potash.

c) Trace Elements

It has been well documented that the Scourian complex exhibits strong depletions in the incompatible elements Rb and U (Holland, 1966; Muecke, 1969; Moorbath *et al.*, 1969; Holland and Lambert, 1975) compared to "normal crust". Results for Th from this study are consistent with this trend. Rb, U, and Th estimates for the complex as a whole (3-9, < 0.1, and < 0.45 ppm respectively) are an order of magnitude lower than estimates for the continental crust and the Canadian shield (Table III-2). When compared to other granulite facies terrains which also show incompatible element depletions (e.g. Lambert and Heier, 1968b Sighinolfi, 1969; Heier and Thoresen, 1971; Eade and Fahrig, 1971), the extreme nature of the Scourian complex depletions are emphasized (Table III-2).

Mean K/Rb ratios are also presented in Table III-2. This ratio has been extensively used as a petrogenetic indicator in igneous rock sequences. During differentiation, the larger Rb ion becomes more enriched in the residual melt than K, and hence the K/Rb ratio decreases with increasing differentiation. The Scourian complex has a mean K/Rb ratio of approximately 920 (Table III-2) with individual values as high as 4300 (Muecke, 1969). These values are much higher than normal upper crustal ratios, which generally fall within the limits of Shaw's (1968) main trend (150 to 300). The results are similar in this regard to K/Rb ratios reported from other medium to high pressure granulite facies terrains (e.g. Heier, 1973; Sighinolfi, 1969, 1971). The normal trend of decreasing K/Rb with increasing K content (that expected with differentiation) is reversed in the Scourian complex (Fig. III-3). Similar reversals have been reported from other granulite facies complexes (e.g. Heier, 1973), although this is not a universal feature of such terrains (e.g. Lewis and Spooner, 1973).

d) Isotope Geochemistry

The present day $^{87}Sr/^{86}Sr$ ratio of a rock is a function of its initial Rb/Sr ratio and age. Because of its lithophile character, Rb is strongly enriched in the earth's crust compared to the mantle. Rb/Sr ratios of crustal rocks are therefore much higher than estimates of primary mantle material.

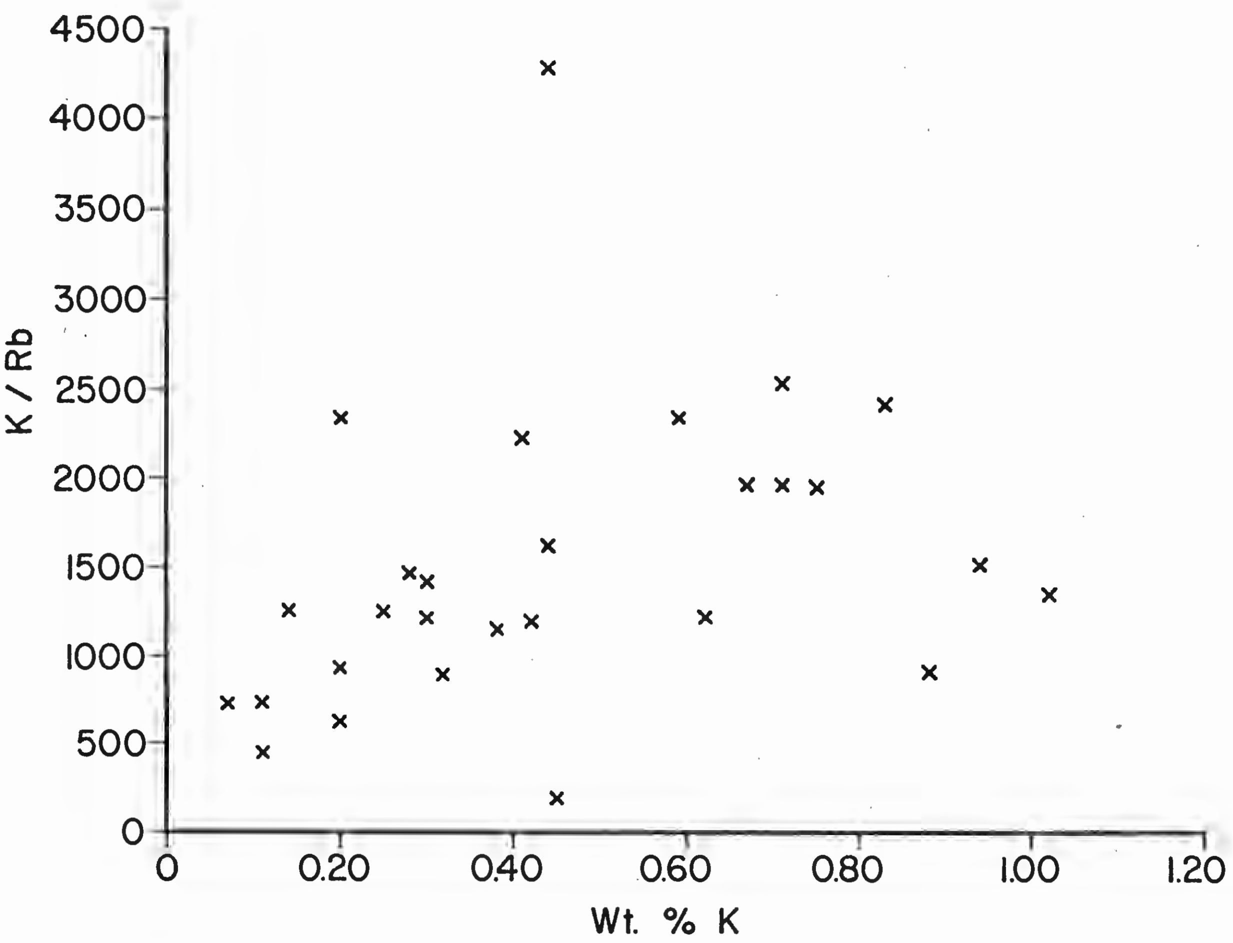


Fig. III-3 : K/Rb versus weight % K for Scourian gneisses (from Muecke, 1969).

Several studies have been made of $^{87}Sr/^{86}Sr$ ratios of the Scourie Group (summarized by Holland and Lambert, 1975). The present day ratio of 0.7021 ± 0.0004 is very low for crustal rocks greater than 2600 m.y. in age. Low present day (and initial) $^{87}Sr/^{86}Sr$ ratios are not unique to the Scourian complex, but are a consistent isotopic feature of Precambrian granulite facies terrains (Spooner, 1969; Lewis and Spooner, 1973). A rationalization of this feature may be sought in one of the following:

1) Formation of granulite facies assemblage by direct addition from the mantle, inheriting the low Rb/Sr ratio of this region (e.g. Holland and Lambert, 1975).
2) A preferential depletion of Rb in a crustal sequence due to granulite facies metamorphism <u>shortly</u> after initial formation (e.g. Moorbath et al, 1975).
3) Isotopic re-equilibration with the mantle during residency in the deep crust near the crust-mantle boundary (e.g. O'Hara, 1976).
4) A preferential depletion in Rb and daughter ^{87}Sr during metamorphism, due to the breakdown of Rb-enriched phases (such as the micas) and preferential removal of Rb and ^{87}Sr via a fluid or melt phase (e.g. Heier, 1964).

Clearly, the above mechanisms are not mutually exclusive. The aspect of possible depletion mechanisms will be discussed further in the next sub-section.

Moorbath et al (1969) investigated the Pb isotope geochemistry of the Lewisian complex. They concluded that these rocks underwent substantial but variable depletion in U at approximately 2900 m.y. ago. This "event" was considered to be the Scourian pyroxene-granulite facies metamorphism.

e) Possible Depletion Mechanisms

Given that many granulite facies terrains were at one time in the upper crust (as evidenced by the presence of metasediments in some complexes e.g. Heier, 1973) and presumably then had "normal" trace element abundances and ratios, what are the possible mechanisms of removal of these elements?

Rb and Cs tend to be concentrated in the micas in rocks of lower metamorphic grade. As a result, micas tend to have much lower K/Rb (and K/Cs) ratios than most other rock-forming minerals (Shaw, 1968). At the amphibolite-granulite facies boundary, the micas are broken down, resulting in the release of an aqueous phase. For example, one reaction proposed to account for the breakdown of muscovite is:

Muscovite + Quartz = Potash Feldspar + Sillimanite + H_2O

The Rb and Cs, concentrated in the muscovite would be strongly partitioned into the aqueous phase and in this fashion could be removed to higher crustal levels (Heier, 1964; Shaw, 1968). This breakdown of the micas could also account for the low present day $^{87}Sr/^{86}Sr$ ratios of granulites - at least for those complexes that have been through a crustal cycle. It might be expected that much of the ^{87}Sr produced by decay of ^{87}Rb would remain in the mica structure, if diffusion of ^{87}Sr to a more favourable site is not an efficient process (Heier, 1964). Hence, breakdown of this phase could lead to preferential removal of ^{87}Sr, along with Rb and Cs, via a fluid phase, leading to present day $^{87}Sr/^{86}Sr$ ratios approaching the initial values at the time of separation from the mantle reservoir.

Heier (1965, 1973) proposed similar breakdown reactions for epidote and zircon to account for the observed granulite facies depletions of U and Th. Much of the uranium is probably not located in the above mentioned minerals, but rather in interstitial material along grain boundaries making it much more susceptible to dissolution and mobility (Taylor, 1965).

The onset of partial melting under upper amphibolite facies conditions could explain the paucity of acid rocks in granulite facies terrains (Heier, 1973). As well, it may account for some of the observed incompatible element depletions, as these elements have a strong tendency to enter into the melt phase. The breakdown of the micas and hornblende may be closely connected with the formation of partial melts (Brown and Fyfe, 1970; Fyfe, 1973). Therefore, instead of an aqueous phase being produced via the breakdown on these hydrous phases, partial melting may result.

4. Summary

The Scourian complex underwent a period of granulite facies metamorphism at approximately 2900 m.y. Pressure-temperature estimates indicate that the conditions of this granulite facies metamorphism were approximately 916 ± 33°C, at a load pressure of 11 ± 1 Kb, and at very low partial pressures of water.

A subsequent localized amphibolite facies metamorphism at approximately 2200 m.y. (Inverian) did not markedly affect the Scourian geochemistry.

The primary Scourian mineral assemblages are those predicted from experimental petrology for recrystallization in the deep crust under essentially anhydrous conditions.

The Scourian complex has an overall intermediate chemistry, characterized by strong incompatible element depletions compared both to normal upper crustal sequences and other medium-to-high-pressure granulite facies terrains.

Although some of the major and trace element trends of the Scourian rocks are compatible with a plutonic-igneous origin; others, such as the trend of increasing K/Rb with increasing K, are opposite to those observed in normal differentiated sequences. Such data require, at least, that additional mechanisms were operative, such as depletion via an aqueous or partial melt phase. It is one of the aims of this study to assess the relative importance of these processes through a study of the REE geochemistry of the Scourian complex.

CHAPTER 4

GEOCHEMISTRY OF THE SCOURIAN COMPLEX

Introduction

It was shown in Chapter 1 that the REE are useful trace elements in determining the petrogenesis of differentiated igneous sequences. Furthermore, many igneous and sedimentary rocks have distinctive REE patterns which may serve as fingerprints of their previous history and associations. Evidence to date indicates that the REE are relatively immobile during low-grade metamorphism and perhaps even during high-grade metamorphism - at least up to the amphibolite facies. Data on the REE abundances of granulite facies terrains, however, are sparse.

In Chapter 2 and 3, it was shown that the Scourian complex is compatible with models of lower continental crustal composition based on evidence from seismology, heat flow, geochemistry and phase equilibrium studies. The Scourian complex exhibits strong depletions in many incompatible elements compared to normal upper crust and, to a lesser extent, other granulite facies terrains.

Thus, the whole-rock REE geochemistry of the Scourian complex has been investigated with the following goals in mind:

1) to obtain the mean REE chemistry of the complex as a whole.
2) to compare the REE geochemistry of the Scourian complex to upper crustal rocks.
3) to determine whether the REE data support any parentage for the complex as a whole; for example, plutonic igneous, extrusive igneous, metamorphic etc.

To these ends, sample selection was weighted in favour of the more abundant rock types of the Scourian complex, as the felsic and mafic gneisses make up an estimated 90 to 95% by volume of the terrain. This bimodal nature of the complex as a whole is consistent with observations of other workers in high-grade metamorphic terrains (e.g. den Tex, 1965). Samples were selected specifically to be free of the effects of subsequent metamorphic events (Muecke, 1969). Sample size was approximately 5 Kg, to assure representative compositions.

Major and trace element data for the analysed Scourian gneisses (Muecke, 1969) are given in Table IV-1 together with 7 new major element analyses, REE data, Sc, Cr, Co, Hf and Th results, and modal plagioclase content. The REE data include calculated REE parameters such as $\sum$ REE, La/Yb ratios and Eu/Eu* ratios where Eu equals observed Eu abundances and Eu* equals the Eu abundances obtained by linear interpolation between Gd and Sm, all values chondrite-normalized. Since Gd was not determined, the Gd value used in the Eu/Eu* calculation was estimated from a linear interpolation between Tb and Sm.

REE Geochemistry

1) Felsic Gneisses

Chondrite-normalized REE graphs of the 9 felsic gneisses are given in Fig. IV-1. They show consistent patterns which exhibit strong linear LRE enrichment, reflected by La/Yb ratios ranging from 13 to 63. Small but distinct positive Eu anomalies are the rule, with Eu/Eu* values up to 3.86. In absolute terms, all REE abundances are greater than chondrites. Many of the graphs exhibit an apparent positive Lu anomaly or negative Yb anomaly - it is difficult to distinguish between these two possibilities

Table IV-1: Major and Trace Element Analyses of Scourian Gneisses

	Felsic Gneisses									Intermediate and Mafic Gneisses								Ultramafic Gneisses		"Retrograde Gneiss"
Sample	65-18	67-66	67-52	66-25	67-34	67-119	65-181	65-191	67-41	65-39	65-38	65-41	66-11	65-33	64-12	65-165	67-30	67-109	65-179	37
SiO_2***	57.54	62.13	60.54	67.86	66.48	65.37	65.32	60.98	65.33	51.69	48.39	46.98	49.64	47.04	48.72	50.12	45.76	46.29	n.a.*	n.a.
TiO_2	0.96	0.78	0.43	0.37	0.54	0.52	0.49	0.93	0.51	0.73	1.12	0.97	0.70	0.92	1.04	0.90	2.06	0.55	n.a.	n.a.
Al_2O_3	19.51	16.60	15.52	16.40	16.51	16.89	17.44	17.11	16.22	17.21	16.13	17.21	16.82	15.55	15.38	14.78	12.26	12.07	n.a.	n.a.
Fe_2O_3	1.44	2.23	1.47	1.07	1.58	1.51	1.50	2.40	1.11	3.62	4.33	2.35	4.04	4.49	3.35	2.97	8.36	2.18	n.a.	n.a.
FeO	4.37	3.74	4.37	2.00	2.55	2.18	2.57	3.94	3.17	4.80	8.69	9.56	5.02	7.80	9.41	9.10	13.93	10.15	n.a.	n.a.
MnO	0.06	0.09	0.11	0.04	0.06	0.06	0.05	0.10	0.07	0.21	0.22	0.27	0.26	0.23	0.20	0.22	0.34	0.27	n.a.	n.a.
MgO	2.76	2.79	4.38	1.49	1.99	2.00	1.64	2.70	2.25	4.33	7.11	7.13	4.44	7.03	8.26	7.27	5.15	12.74	n.a.	n.a.
CaO	6.64	6.48	6.74	4.69	5.44	5.55	5.03	6.59	5.25	12.67	10.16	12.34	14.67	14.08	10.33	11.56	9.75	13.14	n.a.	n.a.
Na_2O	4.85	3.98	4.00	4.64	4.05	4.36	4.36	4.27	4.29	3.69	2.63	2.15	2.81	1.89	2.31	2.40	1.73	1.21	n.a.	n.a.
K_2O	0.89	0.50	1.20	0.72	0.84	1.08	1.24	0.56	0.87	0.47	0.49	0.11	0.32	0.24	0.32	0.14	0.06	0.22	0.13	n.a.
P_2O_5	0.29	0.17	0.12	0.08	0.11	0.10	0.17	0.25	0.10	0.06	0.11	0.04	0.05	0.05	0.09	0.06	0.13	0.02	n.a.	n.a.
H_2O^+	0.64	0.66	0.27	0.34	0.28	0.19	0.16	0.24	0.57	0.58	0.42	0.80	0.65	0.37	0.44	0.41	0.40	0.67	n.a.	n.a.
H_2O^-	0.22	0.20	0.21	0.22	0.23	0.21	0.32	0.20	0.16	0.27	0.25	0.16	0.15	0.18	0.21	0.14	0.13	0.12	n.a.	n.a.
Total	100.17	100.35	99.36	99.92	100.66	100.02	100.29	100.27	100.10	99.33	100.04	100.07	99.57	99.87	100.06	100.07	100.06	99.63		
Ppm																				
Rb	3.84	1.02	6.24	2.53	3.42	9.72	7.59	1.86	2.81	3.30	2.69	2.34	2.49	2.13	1.90	1.12	0.92	3.22	1.51	n.a.
U	n.a.*	0.050	n.a.	n.a.	0.036	0.138	0.092	n.a.	0.046	n.a.	n.a.	0.006	n.a.	n.a.	n.a.	0.007	n.a.	0.039	0.130	n.a.
K/Rb	1940	4284	1511	2336	1956	903	1343	2226	2530	1148	1617	449	1205	925	1463	1250	717	621	729	
Sc	10.9	15.5	19.1	13.4	10.7	14.1	8.29	16.7	11.4	44.9	48.2	47.6	43.9	47.8	49.1	51.3	59.9	55.6	32.2	2.1
Cr	76.4	52.2	285	92.1	10.7	114	56.0	54.9	88.0	506	226	348	480	389	366	273	n.a.	1,247	2,921	5.1
Co	18.1	17.5	21.0	19.4	13.7	12.9	12.3	10.1	13.5	44.2	48.3	53.1	49.0	51.6	48.0	64.3	72.0	79.9	81.9	48.8
Hf	n.a.	n.a.	2.7	2.2	2.7	3.1	3.8	4.9	3.8	1.4	n.a.	n.a.	n.a.	1.0	2.1	2.0	2.3	1.6	0.63	3.4
Th	0.33	n.a.	n.d**	0.10	0.19	0.92	0.12	n.d.	0.23	0.62	n.a.	n.a.	0.81	0.17	n.d.	n.d.	n.d.	n.d.	1.30	1.30
La	14.7	14.3	20.5	10.0	16.7	13.3	29.6	16.5	16.0	6.48	15.8	2.14	4.34	1.90	8.16	1.87	2.48	3.47	2.96	26.8
Ce	29.6	24.3	40.3	32.4	30.1	24.8	42.4	32.7	27.6	11.8	34.2	8.92	9.62	5.97	20.5	6.17	11.0	10.3	6.47	41.7
Sm	2.43	3.88	4.11	0.99	2.14	1.90	3.40	3.74	2.19	1.90	4.35	2.09	1.61	1.76	3.48	1.93	3.77	1.66	0.85	1.76
Eu	1.08	1.05	1.05	1.42	0.81	0.72	1.11	1.08	0.85	0.49	1.20	0.68	0.60	0.53	0.90	0.60	1.15	0.49	0.42	0.85
Tb	0.27	0.43	0.43	0.24	0.23	0.16	0.28	0.37	0.26	0.49	0.81	0.50	0.36	0.50	0.72	0.50	1.32	0.48	0.22	0.12
Yb	0.52	1.12	0.96	0.22	0.43	0.60	0.47	0.32	0.47	2.25	2.56	1.71	1.39	2.30	2.70	3.97	8.47	1.83	n.a.	0.21
Lu	0.09	0.20	0.21	0.05	0.11	0.16	0.12	0.18	0.12	0.28	0.41	0.32	0.25	0.39	0.45	0.35	0.71	0.24	0.20	0.06
ΣREE	48.7	45.3	67.6	45.3	50.5	41.6	87.4	54.9	47.5	23.7	59.3	16.4	18.2	13.4	36.9	15.4	28.9	18.5	-	71.5
$Eu/_{Eu*}$	1.45	0.88	0.83	3.86	1.23	1.28	1.11	0.95	1.24	0.68	0.80	0.88	1.03	0.76	0.72	0.82	0.72	0.75	1.31	1.68
$^{La}/_{Yb}$	28	13	21	46	39	22	63	51	34	2.9	6.2	1.3	3.1	0.8	3.0	0.5	0.3	1.9	-	128
Modal Plagioclase	71.1	62.0	n.a.	n.a.	66.1	65.2	68.2	62.8	67.6	n.a.	41.3	41.6	54.3	41.2	43.6	46.1	36.1	7.3	n.a.	n.a.

* n.a. = not analysed

** n.d. = not detected.

*** major element analyses are from Muecke , 1969.

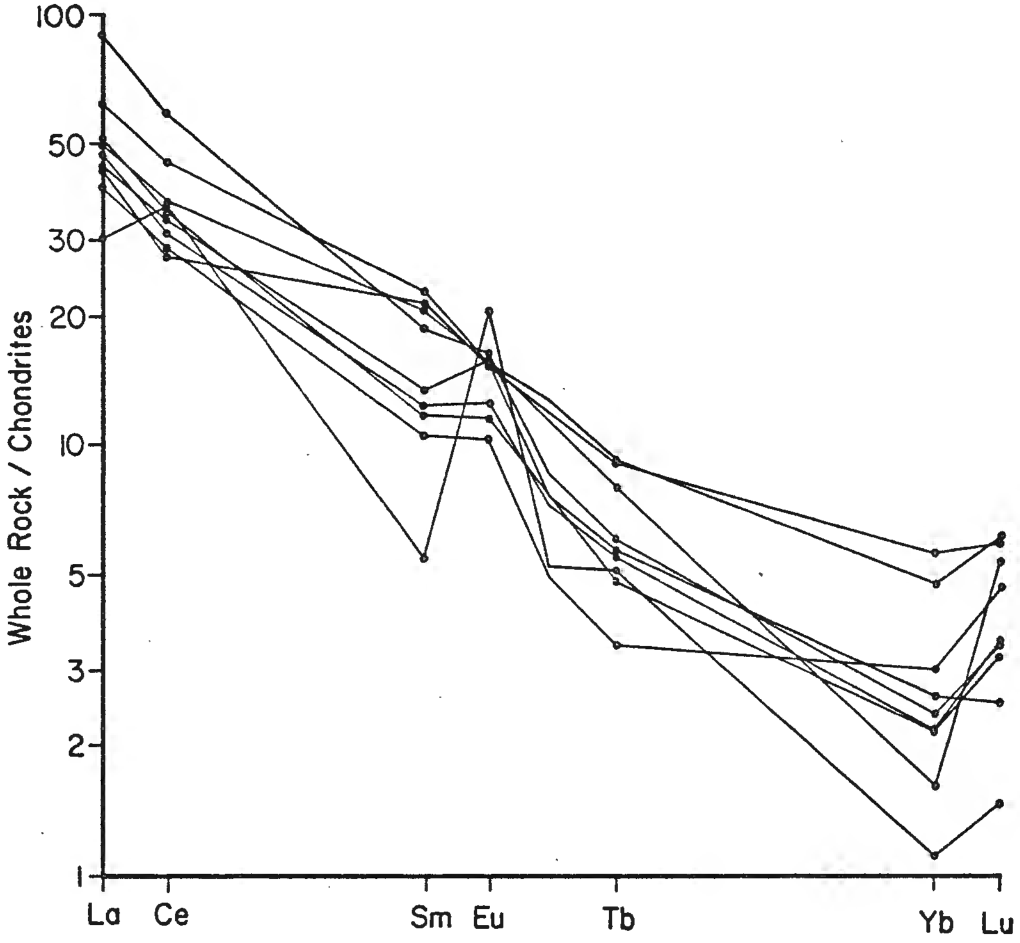


Fig. IV-1 : Chondrite-normalized REE graphs of the Scourian felsic gneisses.

due to a lack of other HRE data. The poor precision and accuracy of the Yb results, as discussed in Appendix 1, combined with relatively low abundances in the felsic gneisses make it virtually impossible to determine whether these observed anomalies are real or due to experimental error. The author favours the latter.

In an effort to observe if the Inverian "event" altered the REE chemistry of the Scourian gneisses; a completely amphibolitized felsic gneiss (all pyroxene converted to hornblende) from the Inverian zone to the north of Scourie was analysed for the REE. (Table IV-1). It shows a REE pattern very similar to the relatively fresh felsic gneisses (Fig. IV-2). Although based on only one sample, the tentative conclusion is that the amphibolitization of the felsic gneisses during the Inverian event did not markedly affect the REE abundances of the felsic gneisses. This result conforms to the postulate that, except for H_20 and $C0_2$, the Inverian event was essentially an isochemical reworking of pre-existing Scourian gneisses (e.g. Holland and Lambert, 1975).

The origin of the felsic gneisses is critical to an understanding of the Scourian complex as they make up an estimated 80% of the terrain by volume (Muecke, 1969). Since the felsic gneisses have tonalitic major element chemistry, it is of interest to compare them to results from other rocks of tonalitic composition. Although data in the literature are sparse, several tonalites have been reported with similar REE chemistry to the Scourian tonalites. Arth and Hanson (1975) report REE results for the Saganaga tonalite from an Archean granite-greenstone complex in N.E. Minnesota. Condie and Hunter (1976) report REE results for the 3.4 to 3.2 b.y. old "ancient tonalite" suite which intrudes the Archean Onverwacht Group of Barberton Mountain Land, Transvaal. The mean major and trace element

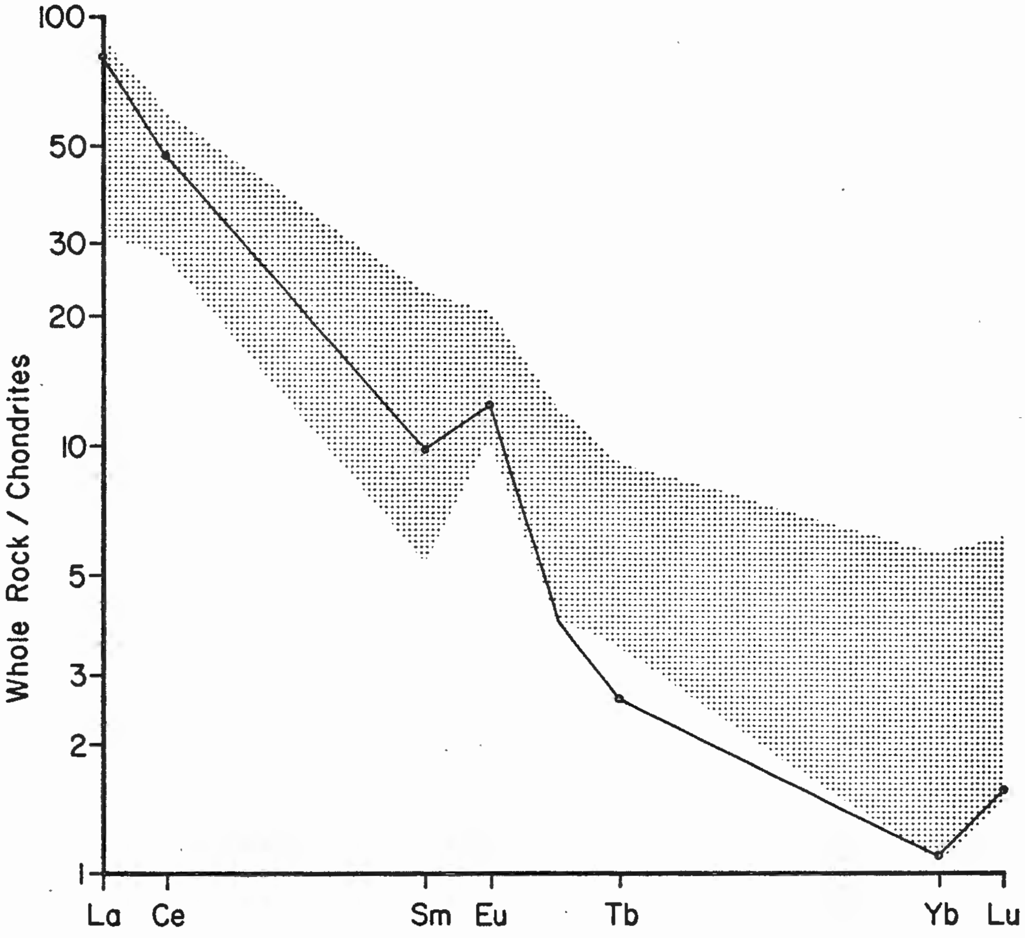


Fig. IV-2 : Chondrite-normalized graph of amphibolitized felsic gneiss compared to the REE range for unaltered felsic gneisses.

chemistry of these suites are presented in Table IV-2. Also presented in Table IV-2 is a REE analysis of a composite igneous rock of 60 to 70 weight per cent SiO_2 (Haskin *et al.*, 1968). The Scourian gneisses are more basic in character than either the Saganaga tonalite or ancient tonalites, as evidenced by lower K_2O, Na_2O and SiO_2 and higher CaO, MgO, FeO and Fe_2O_3. Chondrite-normalized REE graphs of the three tonalite means are presented in Fig. IV-3. The Scourian and ancient tonalite means have very similar absolute and relative REE patterns except for the presence of a distinct positive Eu anomaly in the Scourian tonalites (Eu/Eu* = 1.21) versus normal or chondritic Eu abundances for the ancient tonalites (Eu/Eu* = 1.06). It should be noted here, however, that Glikson (1976) reports 3 REE analyses of the ancient tonalites, which have a distinct positive Eu anomaly (Eu/Eu* = 1.38). The differences between the values reported by Glikson and those of Condie and Hunter probably reflect the larger sample number (12) of the latter authors. The Saganaga tonalite exhibits a small positive Eu anomaly and lower absolute concentrations of REE (most notably, lower HRE) than the other tonalites. Both the Saganaga tonalite and the ancient tonalite suite have been interpreted, mainly on the basis of REE modelling, as originating by less than 30% partial melting of eclogite at mantle depths (Arth and Hanson, 1975; Condie and Hunter, 1976; Glikson, 1976). Although there are some differences between the Scourian and Archean tonalites with respect to major and REE chemistry as mentioned above, some of these and other trace element differences (e.g. lower Rb and higher K/Rb ratios in the Scourian tonalites, Table IV-2) may be attributable to different metamorphic grade, i.e. granulite facies in the case of the Scourian tonalites and greenschist facies in

Table IV-2: Tonalite Means

	Saganaga Tonalite (Mean of 3)	Ancient Tonalites. (Mean of 12)	Scourian Felsic Gneisses (Mean of 9)	Composite "Granite", 60-70% SiO_2
Sources	1	2	3,4, this study	5
SiO_2	64.9	69.5	63.51	
Al_2O_3	17.6	14.8	16.91	
TiO_2	0.27	0.32	0.61	
Fe_2O_3	1.05	2.78*	1.59	
FeO	1.53	-	3.21	
MnO	0.04	-	0.07	
MgO	1.82	1.32	2.44	
CaO	4.32	2.97	5.82	
Na_2O	5.72	5.64	4.31	
K_2O	1.24	1.64	0.87	
P_2O_5	-	-	0.15	
Total	98.49		99.49	
Ppm	(Mean of 2)	(Mean of 12)	(Mean of 9)	
Rb	35	51	9 **	
Ba	667	249	643 **	
Sr	961	537	495 **	
La	-	17	16.8	43
Ce	13.5	24	32.7	83
Nd	7.82	-	-	44
Sm	1.68	2.3	2.75	8.5
Eu	0.599	0.68	1.02	2.0
Gd	1.53	-	-	7.4
Tb	-	0.26	0.297	-
Dy	0.673	-	-	-
Er	0.292	-	-	3.7
Yb	0.234	0.59	0.568	3.25
Lu	0.0424	-	0.137	0.54
Eu/Eu*	1.13	1.06	1.21	0.75
Ce/Yb	58	41	58	26
K/Rb	498	274	2,114	-

* Total Fe as Fe_2O_3

** Mean of Scourian complex, Holland and Lambert, 1975.

1. Arth and Hanson, 1975.
2. Condie and Hunter, 1976.
3. Muecke, 1969.
4. Holland and Lambert, 1975.
5. Haskin <u>et al</u>., 1968.

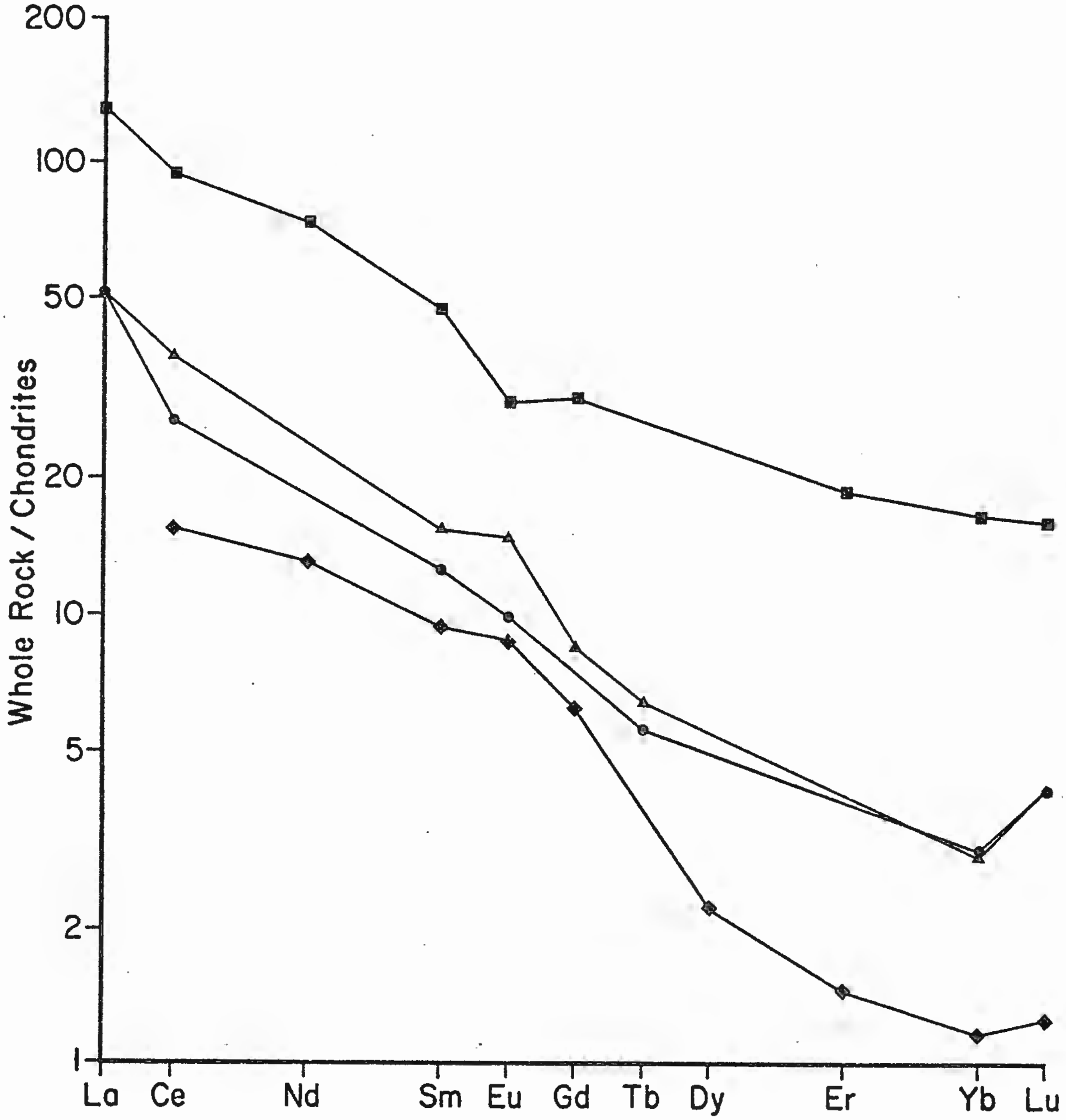


Fig. IV-3 : Chondrite-normalized REE graphs of the Scourian felsic gneisses (triangles) ,ancient tonalites (circles) ,Saganaga tonalite (diamonds) ,and a 60-70% SiO_2 composite (squares).

the case of the Saganaga and ancient tonalites.

Apart from the above mentioned tonalites, to the author's knowledge virtually no other crustal rocks have been reported with similar major element and REE chemistry to the felsic gneisses. Igneous rocks of similar silica contents generally have much greater REE abundances and, usually, negative Eu anomalies (Fig. IV-3). Archean clastic sediments, some of which approach the tonalites in major element chemistry, generally have higher REE concentrations and normal Eu abundances (Wildeman and Condie, 1973).

The felsic gneisses, therefore, exhibit REE patterns not commonly observed in upper crustal rocks of similar major element chemistry, with the exception of some Archean tonalites. This result tends to rule against an origin for these rocks of simple isochemical metamorphism of a normal upper crustal sequence, although they may be lower crustal equivalents of the Archean tonalites. The Archean tonalites, however, do not have the associated, cogenetic basic rocks, present in the Scourian complex but rather occur as isolated, intrusive diapirs. (Condie and Hunter, 1976).

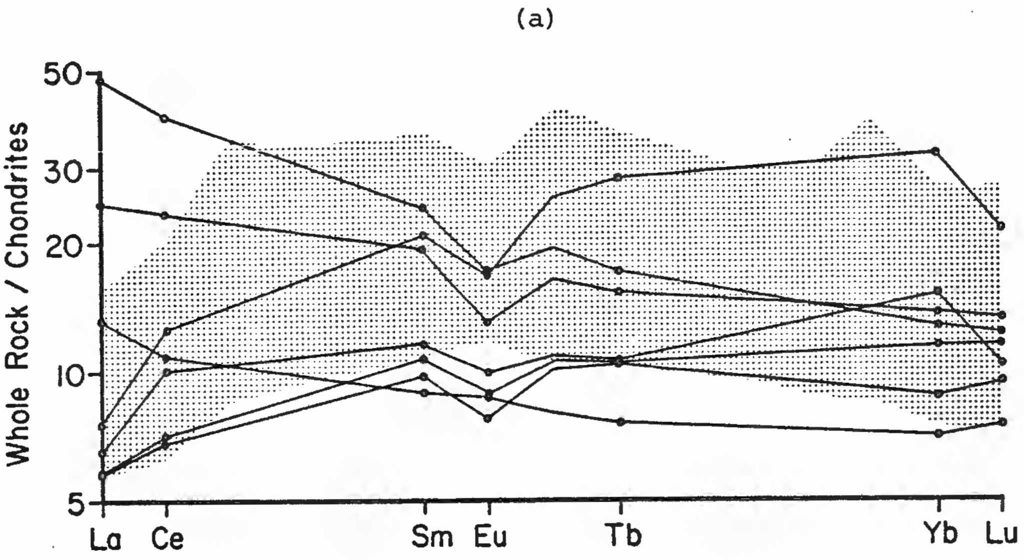
2) Mafic and Intermediate Gneisses

The mafic gneisses display chondrite-normalized graphs that vary from slight LRE depletion to slight LRE enrichment, reflected by La/Yb ratios of 0.3 to 6.2 (Fig. IV-4a). In contrast to the felsic gneisses, all but one of the mafic gneisses (#66-11) exhibit distinct negative Eu anomalies. The majority of absolute values fall between 8 and 25 times chondrites.

The only intermediate gneiss analysed (#65-39) exhibits a chondrite-normalized REE pattern indistinguishable from the mafic gneisses (Fig. IV-4b). Due to the similarity in major element (Table IV-1) and REE composition with the mafic gneisses, it is hereafter considered as a member of this subdivision.

The mafic gneisses have REE patterns unlike other continental mafic rocks of similar major element composition. Continental gabbroic rocks generally have lower concentrations of REE than the Scourian mafic gneisses and positive Eu anomalies (e.g. Frey _et_ _al_., 1968). Continental basalts generally have LRE enriched patterns considerably higher in absolute terms than the Scourian gneisses (e.g. Schilling, 1971).

The only crustal rock type with somewhat comparable REE patterns and abundances are oceanic tholeiites (Fig. IV-4a) and some tholeiites from Archean greenstone belts (Condie and Baragar, 1974). The Scourian gneisses, however, exhibit distinct negative Eu anomalies - a feature that is the exception rather than the rule for tholeiitic rocks (Schilling, 1971; Frey _et_ _al_, 1968; Frey _et_ _al_., 1974).



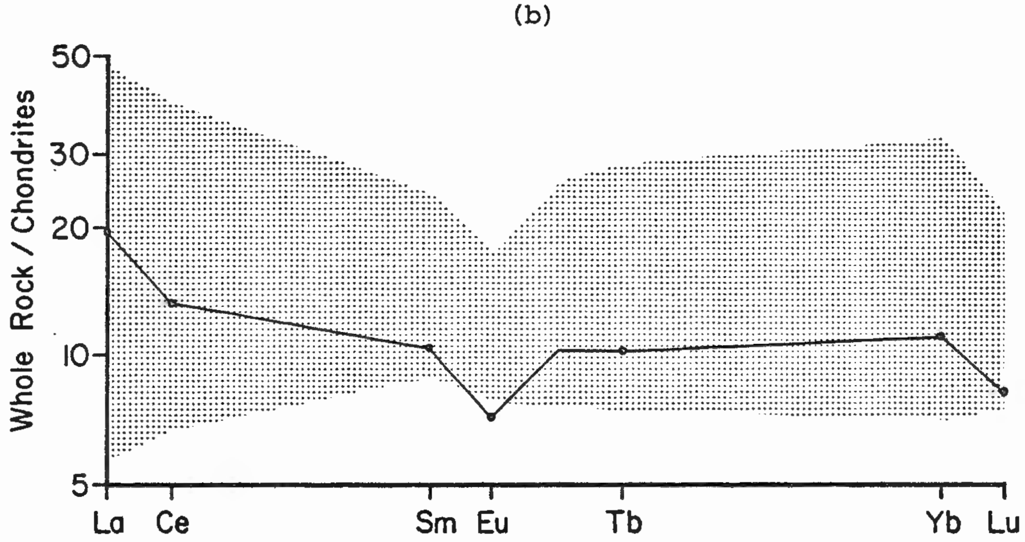


Fig. IV-4: a) Chondrite-normalized REE graphs of the Scourian mafic gneisses compared to the REE range of 12 oceanic tholeiites (Frey et al., 1968).

b) Chondrite-normalized REE graph of the intermediate gneiss (65-39) compared to the REE range for the mafic gneisses.

3) Ultramafic Gneisses

The 2 analysed ultramafic samples show relatively flat, chondritic REE patterns, approximately 5 to 10 times chondrites in absolute terms (Fig. IV-5). 65-179 has a positive Eu anomaly, whereas 67-109 has a negative Eu anomaly.

It is of interest to compare these results to those of alpine-type ultrabasic rocks (Fig. IV-5) since O'Hara (1965) has proposed that the Scourian and alpine-type ultrabasics may have a similar origin. 67-109, although ultramafic, is not ultrabasic and therefore, is probably more akin to the Scourian mafic rocks (supported by the REE results). 65-179, however, is a peridotite (Muecke, 1969). It has absolute concentrations of REE an order of magnitude greater than the alpine-type ultrabasics. The distinct positive Eu anomaly in this peridotite is also in contrast to the more normal or chondritic Eu of the alpine-type ultrabasic rocks. This result, although based on only one sample, suggests that a common origin for both ultrabasic rock types is unlikely. Further work in this area could prove rewarding.

4) REE Trends

Plots of La/Yb and ΣREE versus whole rock SiO_2 (Fig. IV-6 and Fig. IV-7) for the complete suite of analysed Scourian gneisses define broad trends of increasing La/Yb and ΣREE with increasing SiO_2 - a result consistent with differentiation trends for normal, cogenetic igneous rock sequences (e.g. Haskin *et al.*, 1968). A plot of Eu/Eu* versus SiO_2, however, shows that the normal igneous trend of an increasing negative Eu anomaly with increasing SiO_2 is reversed in the Scourian complex

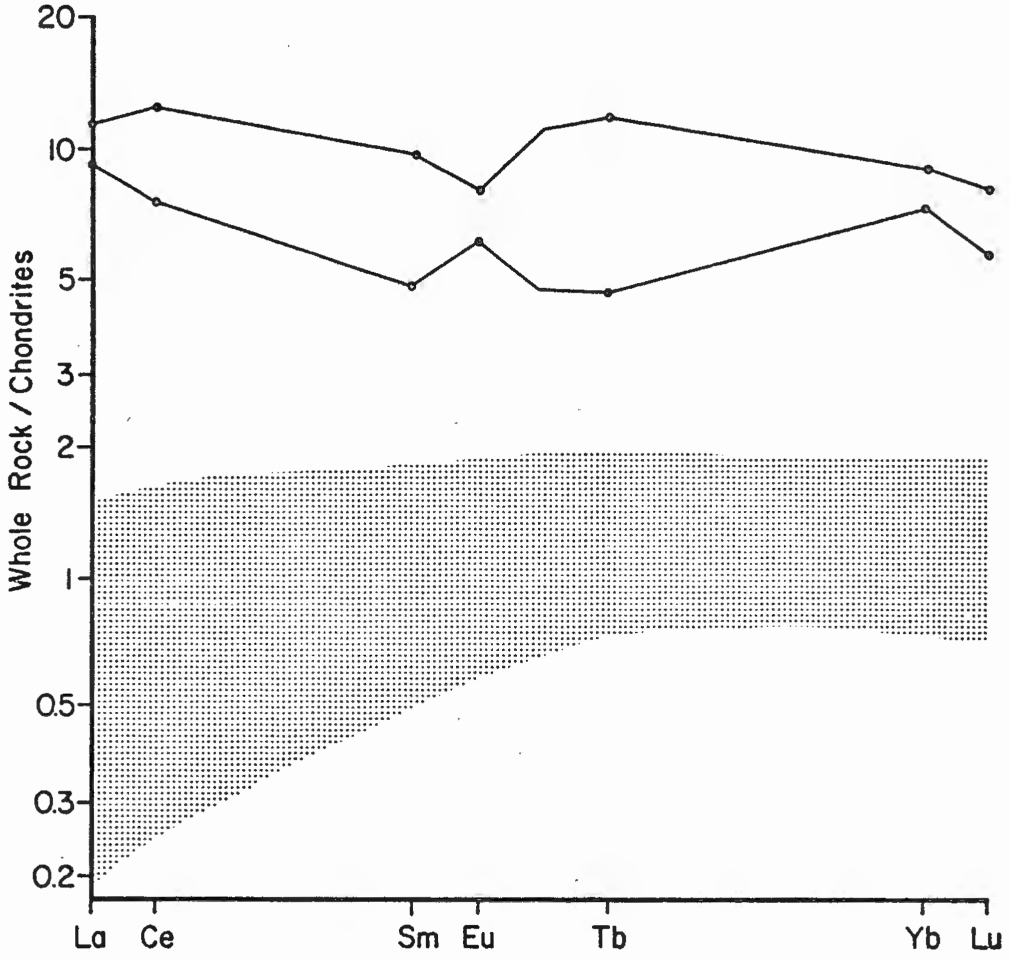


Fig. IV-5 : Chondrite-normalized REE graphs of Scourian ultramafic gneisses compared to REE range of alpine-type ultramafic rocks (after Frey, 1970; Loubet et al., 1975).

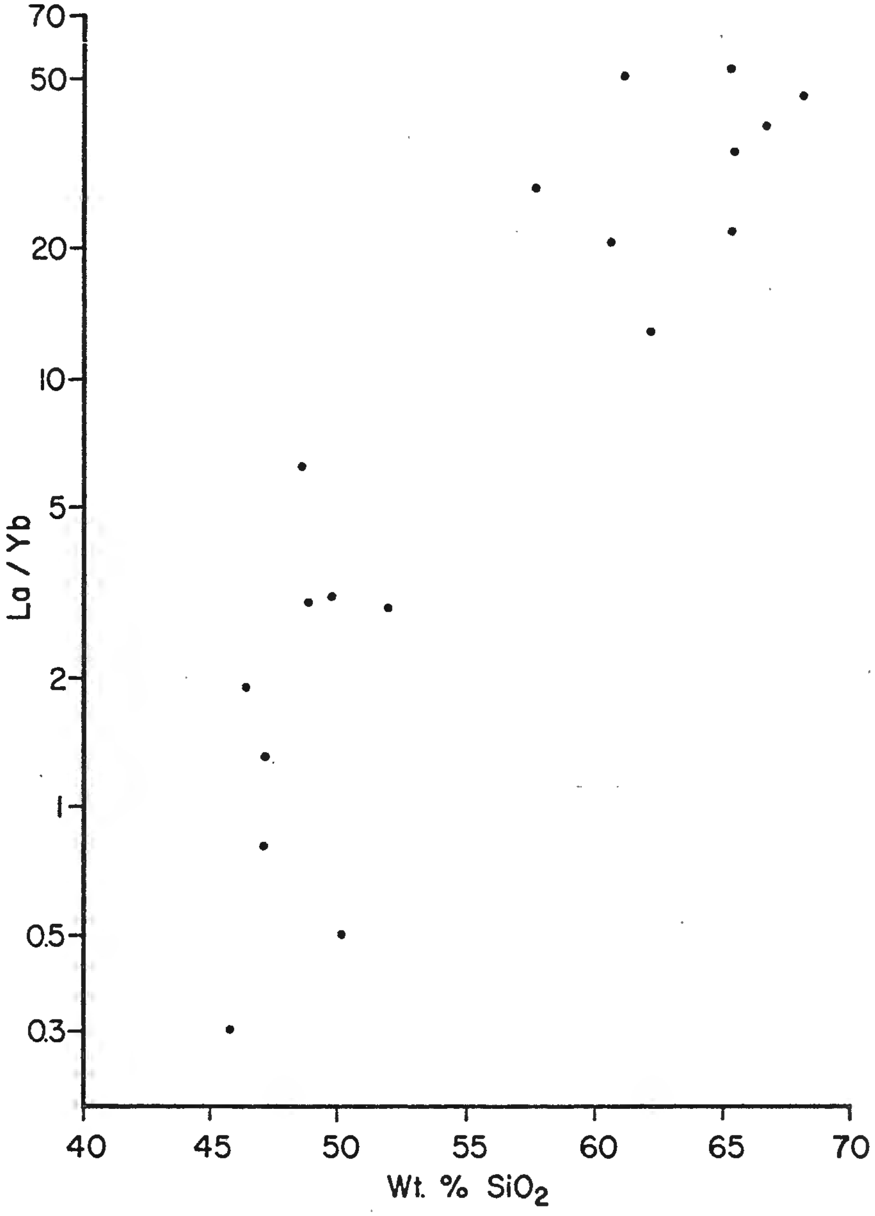


Fig. IV-6 : La/Yb versus whole rock SiO_2 for the complete suite of Scourian gneisses.

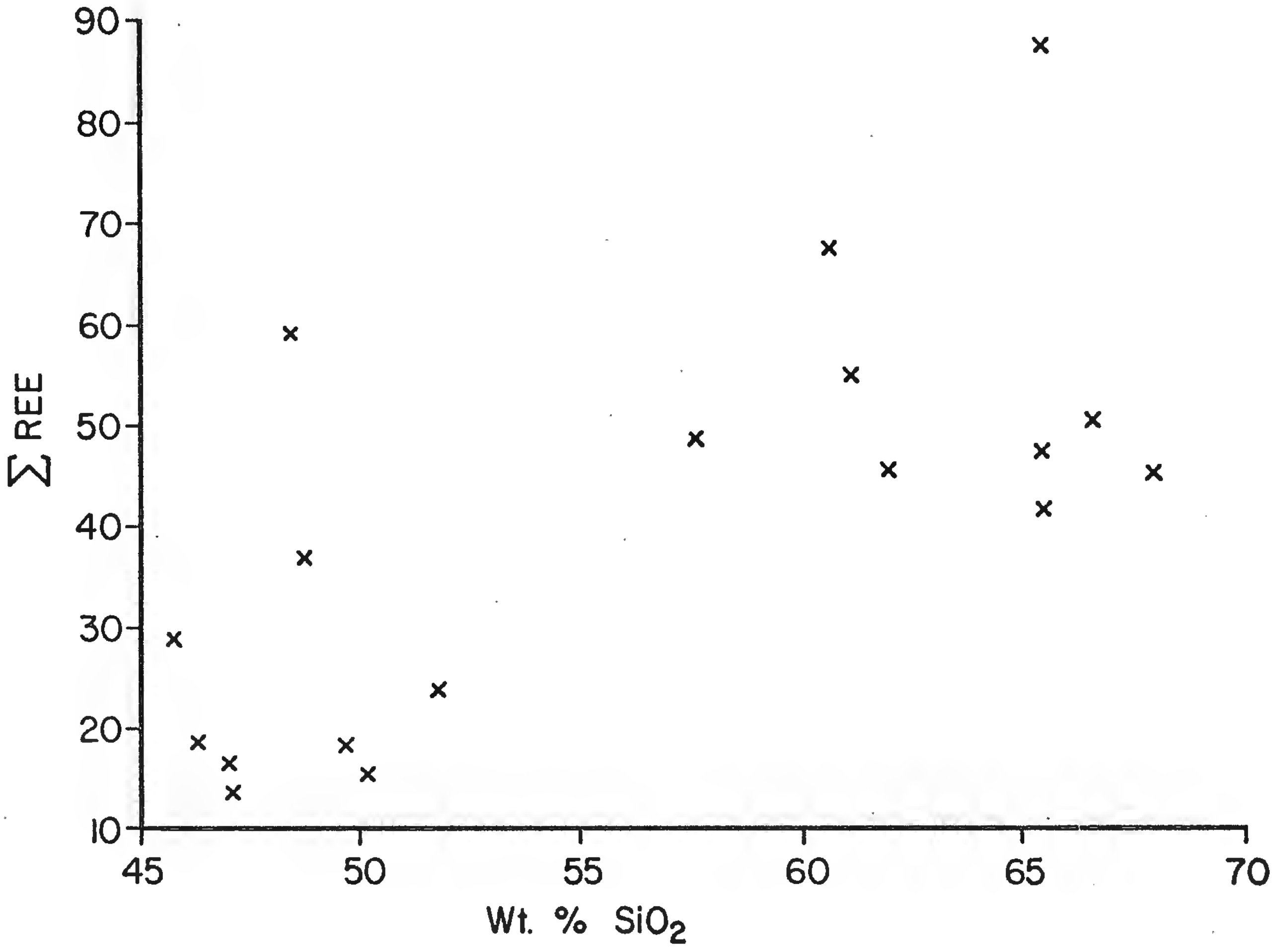


Fig. IV-7 : ΣREE versus weight % SiO_2 for the Scourian gneisses.

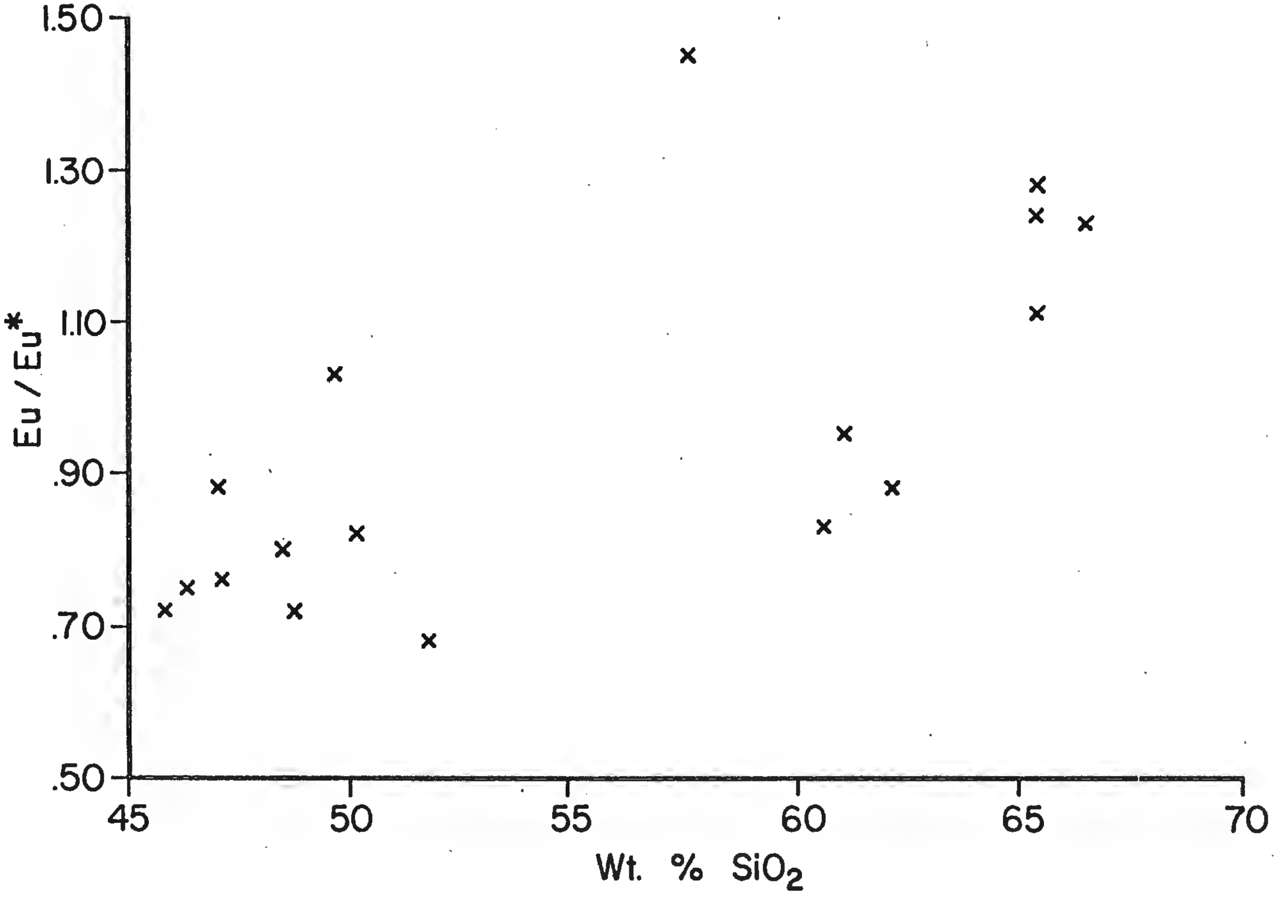


Fig. IV-8 : Eu/Eu* versus weight % SiO_2 for the Scourian gneisses.

(Fig. IV-8). This reversed trend continues into the SiO_2-rich granite sheets (discussed in Chapter 6), which show the largest observed positive Eu anomalies (Eu/Eu* as high as 11.3).

The correlation of increasing Eu/Eu* and, to a lesser extent La/Yb, with increasing modal plagioclase (Fig. IV-9 and IV-10) suggests that the primary control of both of these ratios is mineralogical. It is shown in the next chapter that plagioclase has the highest Eu/Eu* and La/Yb ratios of all the Scourian rock-forming minerals, confirming the above suggestion.

This correlation with modal plagioclase is in striking contrast to results from many cogenetic igneous sequences. For example, in certain granitic sequences, late-stage granites are observed to have the largest negative Eu anomalies in spite of a larger modal feldspar content (e.g. Emmermann _et_ _al_., 1975; Muecke, 1976, oral. comm.), which includes a large potash feldspar content. Potash feldspar has been shown to have an even greater Eu/Eu* ratio than plagioclase (e.g. Schnetzler and Philpotts, 1970). The only other recorded rock type showing this plagioclase control on the REE is anorthosite (e.g. Green _et_ _al_., 1972).

Interesting trends for the Scourian gneisses are also observed for plots of the REE versus CaO - an element that varies over a considerable range in the Scourian samples (4.00 to 15.00 weight %). The ΣREE are observed to decrease with increasing CaO (Fig. IV-11) - a relationship consistent with the normal igneous trends observed for La/Yb versus SiO_2. Sm and Lu, however, exhibit unusual correlations with CaO. For the felsic gneisses (CaO < 8.00%), Sm and La increase with increasing CaO (Fig. IV-12 and Fig. IV-13). For the mafic gneisses, on the other hand, both Sm and Lu decrease with increasing CaO (Fig. IV-12 and Fig. IV-13), although these relationships are less well-defined than for the felsic gneisses. As

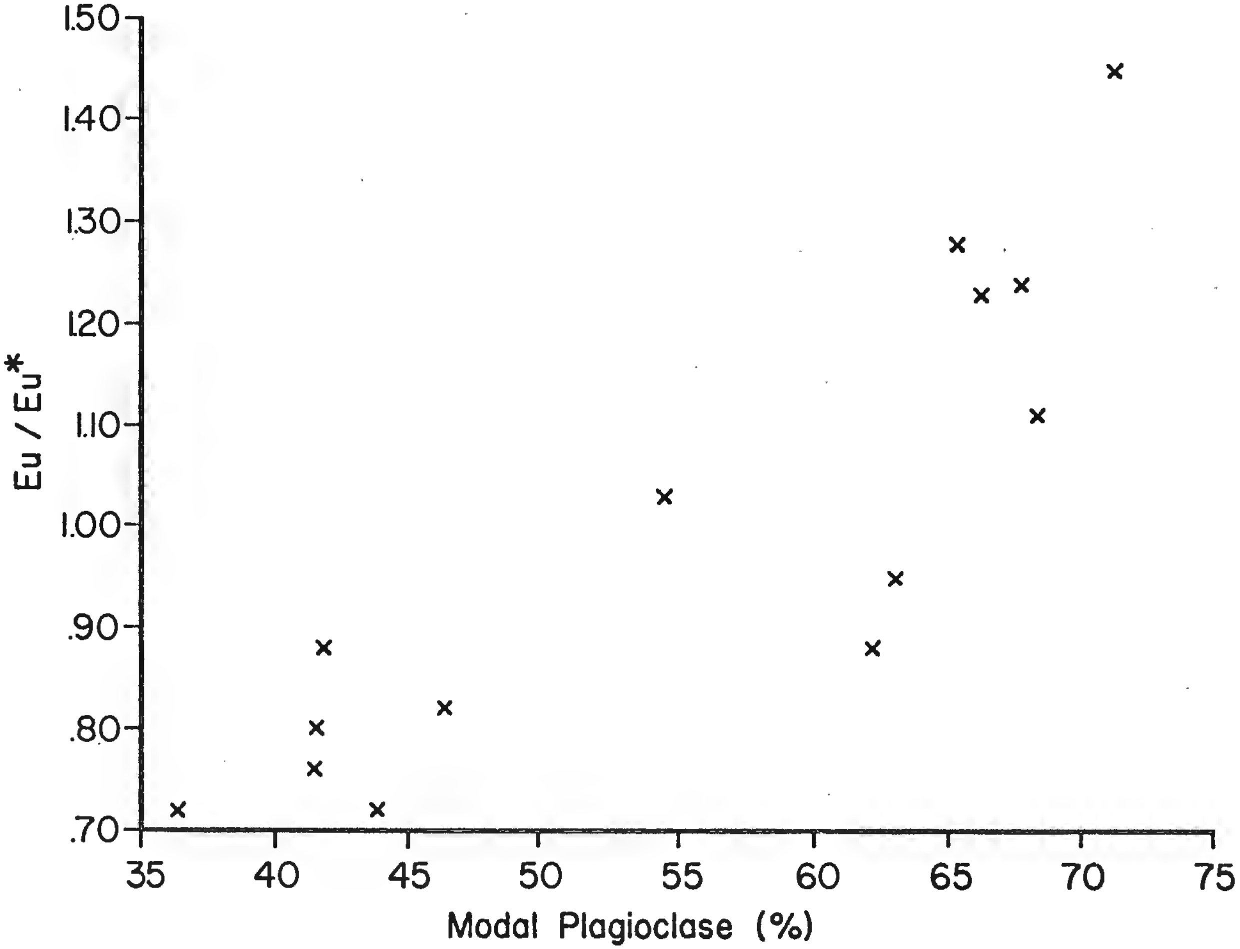


Fig. IV-9 : Eu/Eu* versus modal plagioclase content for the Scourian gneisses.

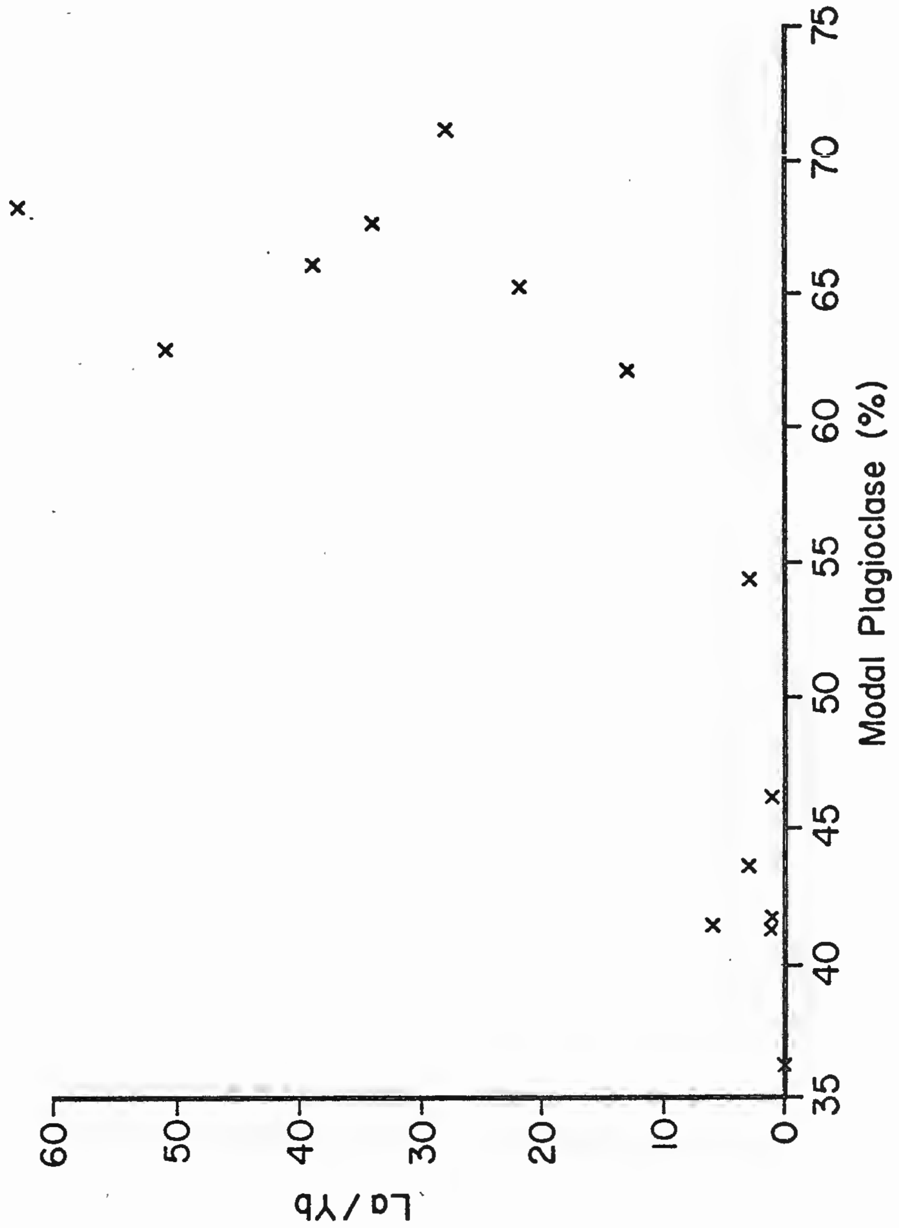


Fig. IV-10 : La/Yb versus modal plagioclase content for the Scourian gneisses.

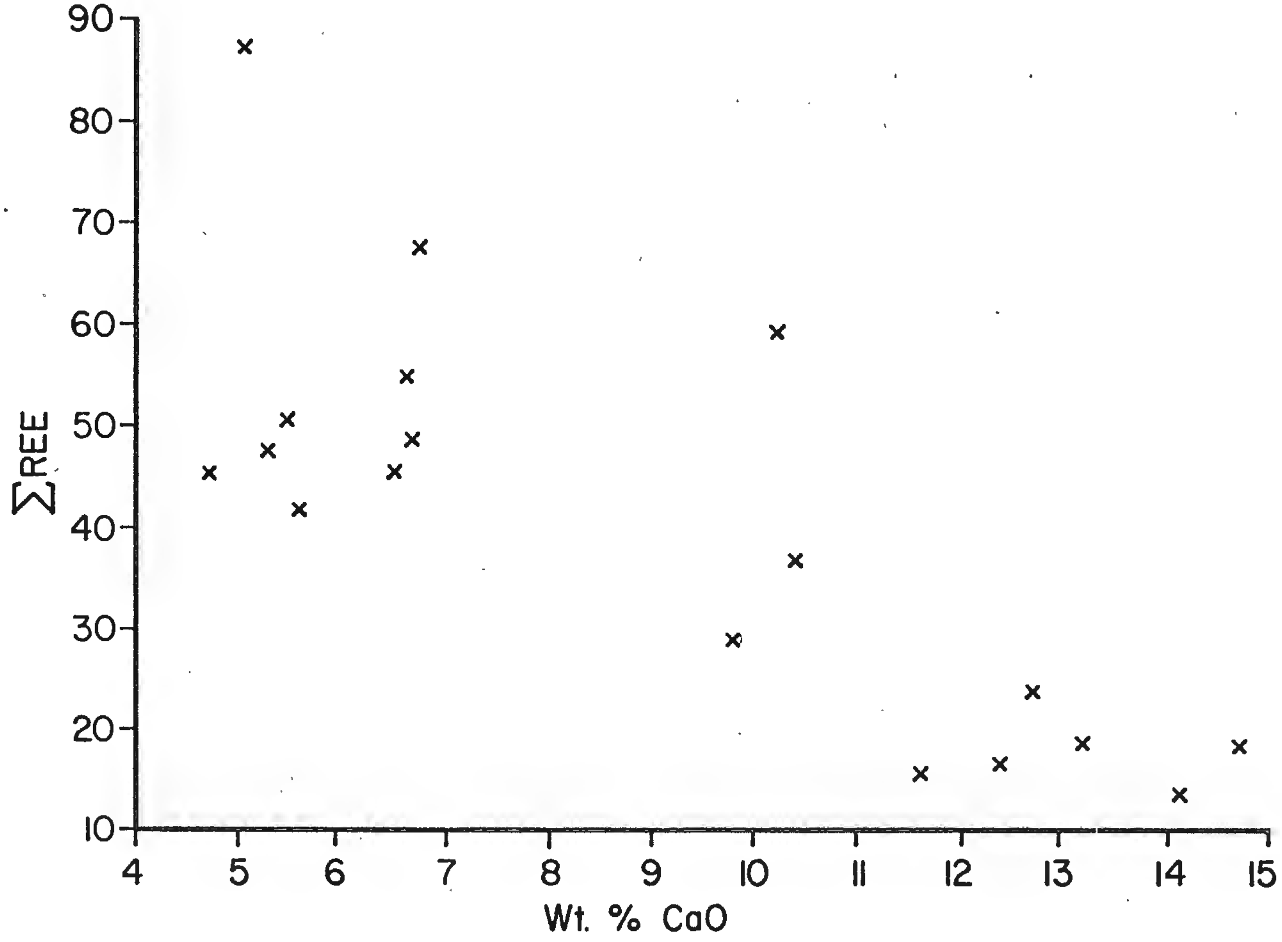


Fig. IV-11 : ΣREE versus weight % CaO for the Scourian gneisses.

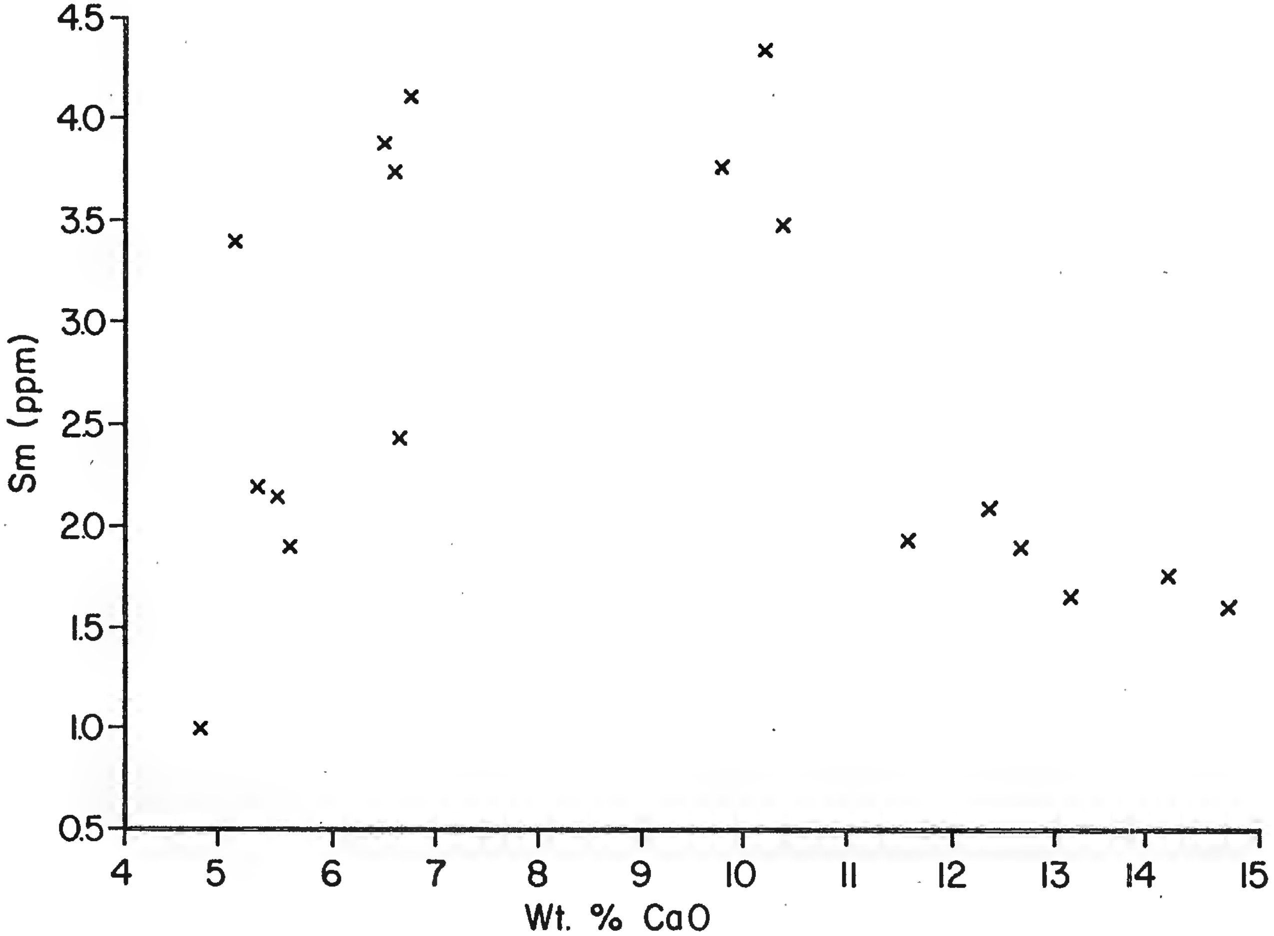


Fig. IV-12 : Sm versus weight % CaO for the Scourian gneisses.

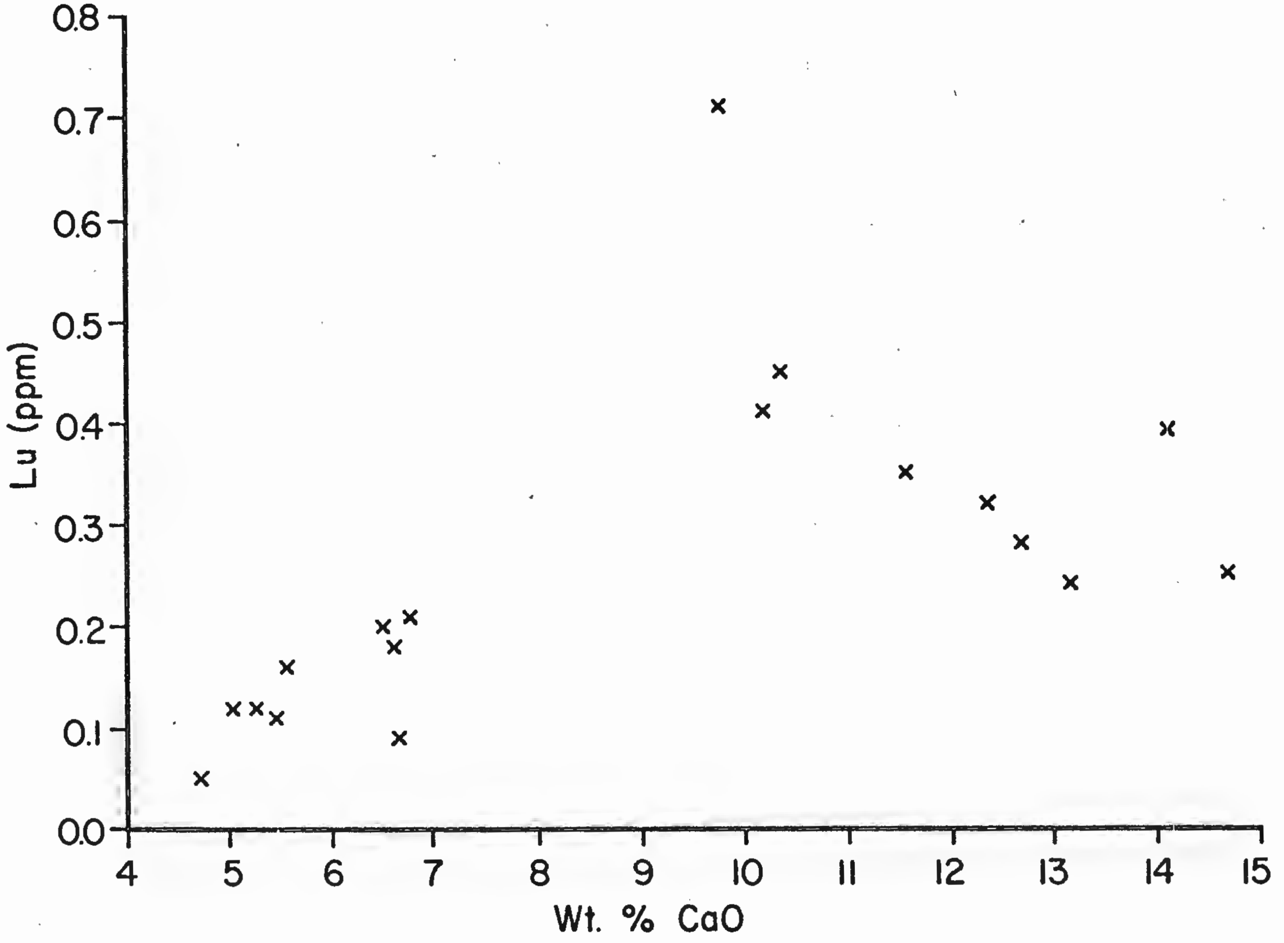


Fig. IV-13 : Lu versus weight % CaO for the Scourian gneisses.

was the case for the La/Yb and Eu/Eu* ratios versus SiO_2, these relationships with CaO may be best explained in terms of the mineralogy of the Scourian gneisses. An increase in modal Ca-rich clinopyroxene would account for the increase observed for both Sm and La with increasing CaO in the felsic gneisses. The decreasing Lu with increasing CaO observed in the mafic gneisses is not as simply related to modal mineralogy. If modal mineralogy is involved, the relationship is more complex. These and other mineralogical aspects will be discussed at greater length in the following chapter.

5) REE Chemistry of the Scourian Terrain

In previous discussions, it was shown that a lower crust of intermediate composition in the granulite facies is a reasonable model, and that the overall composition and mineralogy of the Scourian complex is compatible with such a model. It is, therefore, of interest to compare the mean REE geochemistry of the Scourian complex with REE estimates for the continental upper crust.

The mean REE content of the Scourian complex was determined by combining estimates of the relative proportions of the various Scourian rock types (Muecke, 1969) with the mean REE content of each rock type determined in this study. The relative weight proportions were assigned as follows

80% : felsic gneisses

20% : mafic and ultramafic gneisses, in equal proportions.

Changing the relative proportions of the mafic and ultramafic gneisses would not alter the results significantly, as their mean patterns and abundances are very similar. The resulting REE estimate for the Scourian complex as a whole is presented in Table IV-3. As a check on the validity of the REE

Table IV-3: Mean REE content of Scourian Complex (SM), NASC and Canadian Shield (CSM)

	SM (ppm) *	NASC (ppm) **	CSM (ppm)***
La	14.4	32	32.3
Ce	28.4	73	65.6
Sm	2.6	5.7	4.51
Eu	0.93	1.24	0.937
Tb	0.34	0.85	0.481
Yb	0.92	3.1	1.47
Lu	0.17	0.48	0.233

* this study

** Haskin _et al._, 1968.

*** Shaw _et al._, 1976.

estimate, a similar calculation was performed using the major element data to obtain a mean for the Scourian complex. The results compare favourably to Holland and Lambert's (1975) mean for the Scourian complex, which is based on 750 analyses (Table IV-4).

The chondrite - normalized pattern of the Scourian mean (Fig. IV-14) exhibits linear LRE enrichment, with a small but distinct positive Eu anomaly, which emphasizes the strong influence of the felsic gneisses. The value of 14.4 ppm obtained for La is considerably lower than Holland and Lambert's (1975) estimate of 26 ppm. Their result, however, is based on the XRF technique, which generally gives poor results for the lanthanides.

Two REE estimates of the continental crust are also given in Table IV-3. Haskin _et al_. (1966) considered that the NASC may be a good estimate of the REE composition of the upper continental crust, due to the homogenizing effect of the sedimentary cycle and the short residence time of the REE in transport. More recently, Shaw _et al_ (1974) has given an estimate of the REE content of the surface of the Canadian Shield.

Compared to the NASC, the Scourian has 2 to 3 times lower abundances of all the REE except Eu (Fig. IV-15a). Compared to the Canadian Shield mean, the Scourian has up to 2 times lower abundances (except Eu)--the difference being greatest for the LRE (Fig. IV-15b). Compared to both the NASC and the Canadian Shield mean, the Scourian mean shows a distinct positive Eu anomaly - approaching the Eu content of the two in absolute terms.

Thus, the Scourian complex exhibits lower abundances of REE (except Eu) compared to the continental upper crust. The relative Eu enrichment in the lower crust (i.e. Scourian complex) may balance the observed relative

Table IV-4: Comparison of Calculated Scourian Mean with that of Holland and Lambert (1975).

	Calculated Mean	Best Estimate (Holland and Lambert)
SiO_2	60.29	61.5
TiO_2	0.65	0.56
Al_2O_3	16.30	15.5
Fe_2O_3	1.91	6.2
FeO	4.43	
MnO	0.11	0.10
MgO	3.97	3.5
CaO	7.17	5.9
Na_2O	3.81	4.0
K_2O	0.75	1.0
P_2O_5	0.13	-
H_2O	0.62	1.3
Total	100.14	99.56

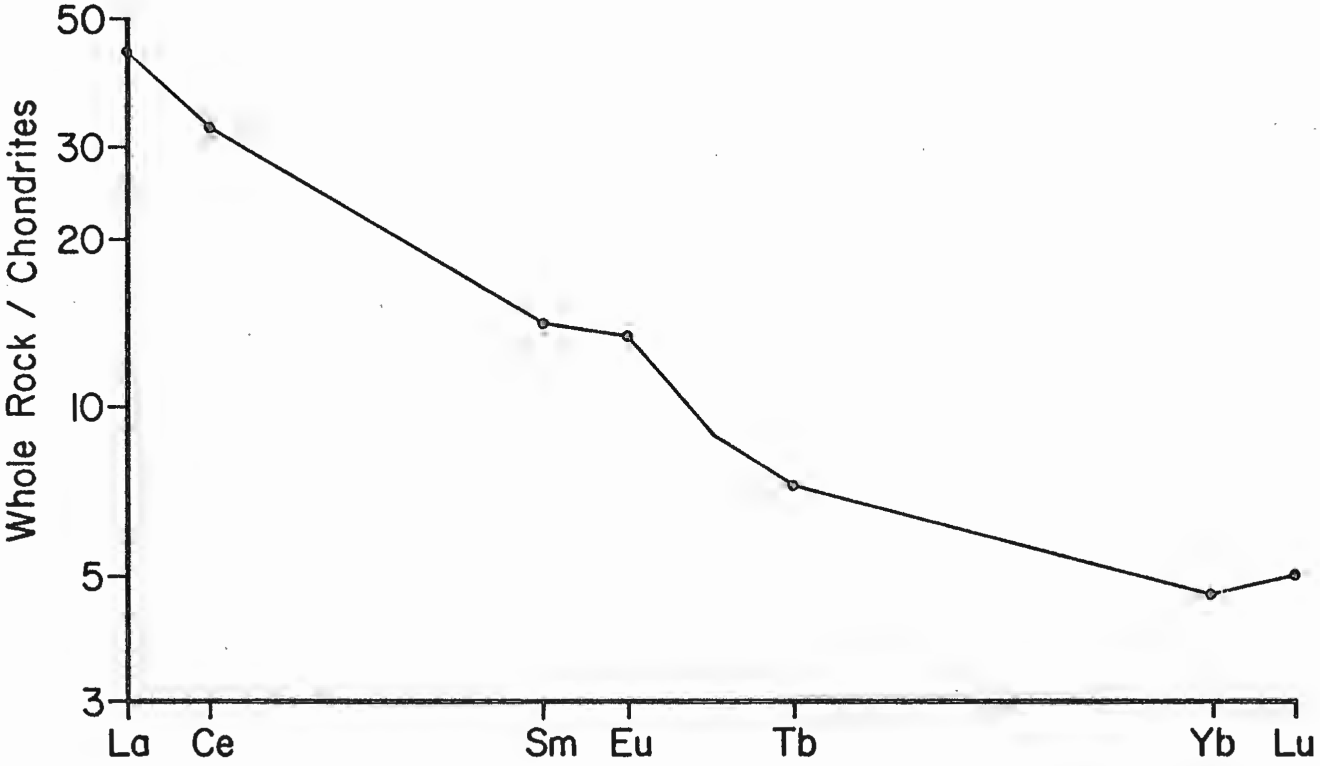


Fig. IV-14 : Chondrite-normalized REE estimate for the Scourian complex as a whole.

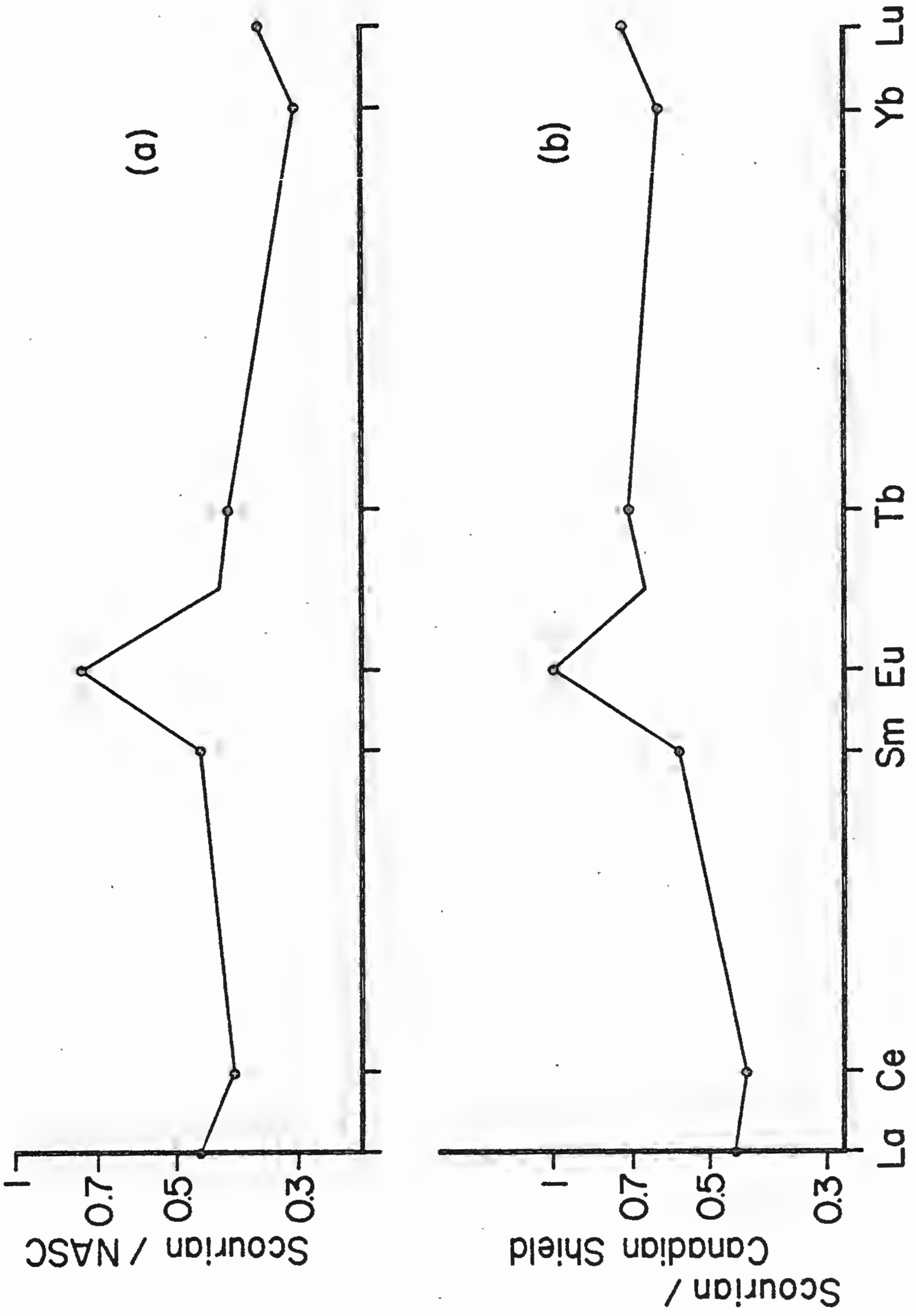


Fig. IV-15 : REE estimate for the Scourian complex normalized to a) the NASC (Haskin et al., 1968), and b) the Canadian Shield mean (Shaw et al., 1976).

Eu depletion in the upper crust, yielding an overall continental crust with normal or chondritic Eu abundances. A similar result, from theoretical considerations, was obtained by Jakes and Taylor (1974) and Nance and Taylor (1976).

Other Trace Elements (Sc, Cr, Co, Hf, Th)

The trace elements Sc, Cr and Co increase in abundance from the felsic to the ultramafic gneisses (Table IV-1). This trend is consistent with the known geochemical behaviour of these elements and is a result of the increasing importance of ferromagnesian minerals in the mafic and ultramafic gneisses, compared to the felsic gneisses. This is perhaps best exemplified by the limits of variability and mean values shown by these elements in each of the Scourian rock types:

	Sc (ppm)	Cr (ppm)	Co (ppm)
Felsic Division	8.3 - 19.1 ($\bar{x}$ = 13.3)	11 - 285 ($\bar{x}$ = 92)	10.1 - 21.0 ($\bar{x}$ = 15.4)
Mafic Division	43.9 - 59.9 ($\bar{x}$ = 49.1)	226 - 506 ($\bar{x}$ = 370)	44.2 - 72.0 ($\bar{x}$ = 53.8)
Ultramafic Division	32.2 - 55.6 ($\bar{x}$ = 43.9)	1,247 - 2,921 ($\bar{x}$ = 2,084)	79.9 - 81.9 ($\bar{x}$ = 80.9)

The means for the complex as a whole are considerably higher than crustal estimates. Sc has a mean value of approximately 20 ppm compared to approximately 7 ppm for the average of the Canadian Shield (Shaw _et al._, 1976). Cr has a mean value for the Scourian complex of greater than 150 ppm compared to 35 ppm for the Canadian Shield and 100 ppm for the continental crust (Taylor, 1964b). Co has a mean value of approximately 74 ppm compared to 11.6 ppm for the Canadian Shield and 25 ppm for

Taylor's mean of the continental crust. These results are consistent with the overall intermediate nature of the Scourian complex compared to estimates for the upper continental crust or whole continental crust.

Hf concentrations in the Scourian complex are generally low - in the order of several ppm (Table IV-1), with a maximum value of 4.9 ppm. It shows little variability from rock type to rock type. Hf is known to closely follow Zr in nature, due to a very similar ionic charge and size (Brooks, 1970). Brooks (1970) reported Zr/Hf ratios for two of the gneisses analysed in this study - 65-18 had a value of 47 and 64-12, a value of 25. These Zr/Hf ratios are not anomalous compared to the majority of values for crustal rocks. His value for Hf of 2.6 ppm for 64-12 compares favourably with the value of 2.1 ppm obtained in this study. The small fluctuations in Hf values observed in the Scourian gneisses probably reflects variable accessory zircon.

Th is very low in the Scourian samples (Table IV-1), often not detectable by the activation method. In the 10 samples with detectable Th, the mean value is 0.45 ppm. The maximum value observed is 1.30 ppm in one of the ultramafic gneisses (65-179). The mean value of 0.45 ppm may be taken to represent a maximum estimate of the Th concentration of the Scourian complex as a whole, and is considerably lower than crustal estimates of approximately 2.5 to 3.0 ppm, as discussed in Chapter 3.

Discussion and Conclusions

Perhaps the most encouraging aspect of the REE whole rock data is the consistency of REE patterns for each rock type investigated. This feature, when combined with the emergence of recognizable REE trends for the complex as a whole, implies that a common process(es) was operative in the formation of the Scourian gneisses, and that the REE data may be useful in deciphering the origin of these rocks.

The broad correlations of the REE with major elements (e.g. La/Yb and ΣREE vs. SiO_2) for the complete suite of Scourian gneisses support other major and trace element trends (discussed in Chapter 3) in suggesting a cogenetic origin for the Scourian gneisses. Bowes et al. (1971) proposed a meta-igneous origin for the Scourian gneisses, based on similar differentiation trends for some elements to those observed for Archean volcanic series. The REE patterns and trends, however, are unlike those observed in virtually all igneous rock sequences including Archean volcanics. Furthermore, Holland and Lambert (1975) noted that:

1) The Scourian gneisses show little increase of K compared to Si or $(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})$.
2) K, Na, Zr, Sr, Zn, Ti, total Fe, Mn, Ba, Ni and Cr versus the Larsen factor differ significantly from that of Archean volcanics.

These results tend to rule against a volcanic or "normal" plutonic-igneous origin for the Scourian complex.

Any theory or mechanism of formation of the Scourian complex must be compatible with the positive Eu anomaly for the terrain as a whole and the relative depletion in the other REE compared to upper crustal values. Intra-crustal partial melting leading to the generation of melts of the granite family and a residuum of "Scourian-like" material is compatible with these constraints. Granitic rocks have high concentrations of incompatible elements (which would be strongly partitioned into the melt phase during anatexis) and negative Eu anomalies. Since the vast majority of new material added to the crust directly from the mantle has normal or chondritic Eu abundances (e.g. Nance and Taylor, 1976), it is desirable to have a balanced Eu budget for the continental crust as a whole.

The origin of these rocks will be discussed at greater length after presentation of the mineral REE data.

CHAPTER 5

Mineral Geochemistry

Introduction

A knowledge of the mineral REE geochemistry is critical to an understanding of the REE geochemistry of the Scourian complex as a whole. It is important to know:

1) in which phases the bulk of the REE are located.
2) whether the REE reside in regular lattice sites.
3) whether the REE distribution coefficients (K_D's) between coexisting phases represent equilibrium distributions.
4) whether the REE mineral data favour any particular model of origin for the Scourian complex.

Very little data are available in the literature on the REE geochemistry of metamorphic rock-forming minerals. In igneous rocks, however, considerable REE mineral data have been accumulated, mainly from phenocryst-matrix studies of volcanic rocks (Nagasawa and Schnetzler, 1971; Schnetzler and Philpotts, 1968, 1970; Onuma et al, 1968). These results, combined with experimental work on mineral-liquid systems (Mysen, 1976; Wood, 1976; Irving and Frey, 1976; Drake and Weill, 1975; Cullers et al, 1973), and REE mineral results from ultrabasic and eclogitic rocks and inclusions (Frey and Green, 1974; Philpotts et al, 1972; Frey et al, 1971), indicate that the relative and absolute REE concentrations of an igneous mineral phase (and the mineral-liquid distribution coefficient) is probably a function of four major variables:

1) the composition of the melt
2) temperature
3) pressure
4) crystal-chemistry of the mineral phase

In addition, the fO_2 is an important variable controlling Eu behavior. The relative REE patterns appear to be less variable than the absolute concentrations of REE (e.g. Philpotts *et al*, 1972). The regularity of relative REE patterns for specific mineral phases from similar volcanic rock types indicates that the REE enter regular lattice sites in these phases and probably closely approximate equilibrium distributions (e.g. Philpotts, *et al*, 1972).

In this chapter, REE data for 31 mineral separates of Scourian rock-forming minerals are presented. Sample purity is estimated (by microscopic examination) at greater than 99.5% in all cases (Appendix 1). These samples represent most of the mineral phases for each of 7 of the whole rock samples presented in the preceeding chapter, and cover the spectrum of major Scourian rock-forming minerals.

REE Chemistry

1) Clinopyroxene

Major and trace element data for the seven analysed clinopyroxenes are given in Table V-1. Chondrite-normalized REE graphs (Fig. V-1) exhibit a maximum at Sm, and minima at La and Yb or Lu. The absolute

Table V-1: Major and trace element analyses of Scourian Clinopyroxenes

Sample No.	65-18	65-33	64-12	66-11	65-41	67-30	67-109
Host Rock Type*	f	m	m	m	m	m	u
SiO_2 **	52.07	49.93	50.02	49.28	49.49	50.98	50.56
TiO_2	0.34	0.59	0.53	0.66	0.74	0.42	0.34
Al_2O_3	3.32	4.96	4.53	5.17	5.96	3.39	6.02
Fe_2O_3	2.42	2.93	1.84	2.99	2.59	3.15	2.04
FeO	8.64	7.94	8.14	9.13	7.44	10.69	5.91
MnO	0.23	0.33	0.26	0.50	0.15	0.29	0.14
MgO	11.92	11.71	12.40	10.43	11.79	10.39	13.14
CaO	20.10	20.91	21.03	20.95	20.43	19.88	20.92
Na_2O	0.86	0.75	0.75	0.80	0.94	0.91	0.99
K_2O	0.06	0.02	0.05	0.05	0.03	0.00	0.02
Total	99.96	100.07	99.54	99.96	99.56	100.10	100.08
ppm							
La	8.58	1.60	7.30	3.80	2.60	4.40	4.40
Ce	44.5	11.5	19.8	12.0	12.9	27.8	12.6
Sm	10.8	3.30	8.10	3.30	4.80	11.3	2.10
Eu	1.37	0.70	1.15	0.69	0.88	2.00	0.51
Tb	1.53	0.85	1.18	0.74	0.54	2.92	0.41
Yb	2.63	3.88	4.38	3.74	0.88	5.80	1.91
Lu	0.42	1.00	1.02	0.95	0.31	1.18	0.37
ΣREE	69.8	22.8	42.9	25.2	22.9	55.4	22.3
Eu/Eu*	0.39	0.56	0.44	0.58	0.60	0.47	0.69
La/Yb	3.26	0.41	1.67	1.02	2.95	0.76	2.30
Sc	124	86.0	126	101	72.7	171	58.6
Cr	389	331	306	571	524	-	250
Co	46.5	43.5	34.9	91.8	60.7	53.7	51.5

* f, m, u = felsic, mafic, ultramafic gneisses.

** major element analyses are from Muecke, 1969.

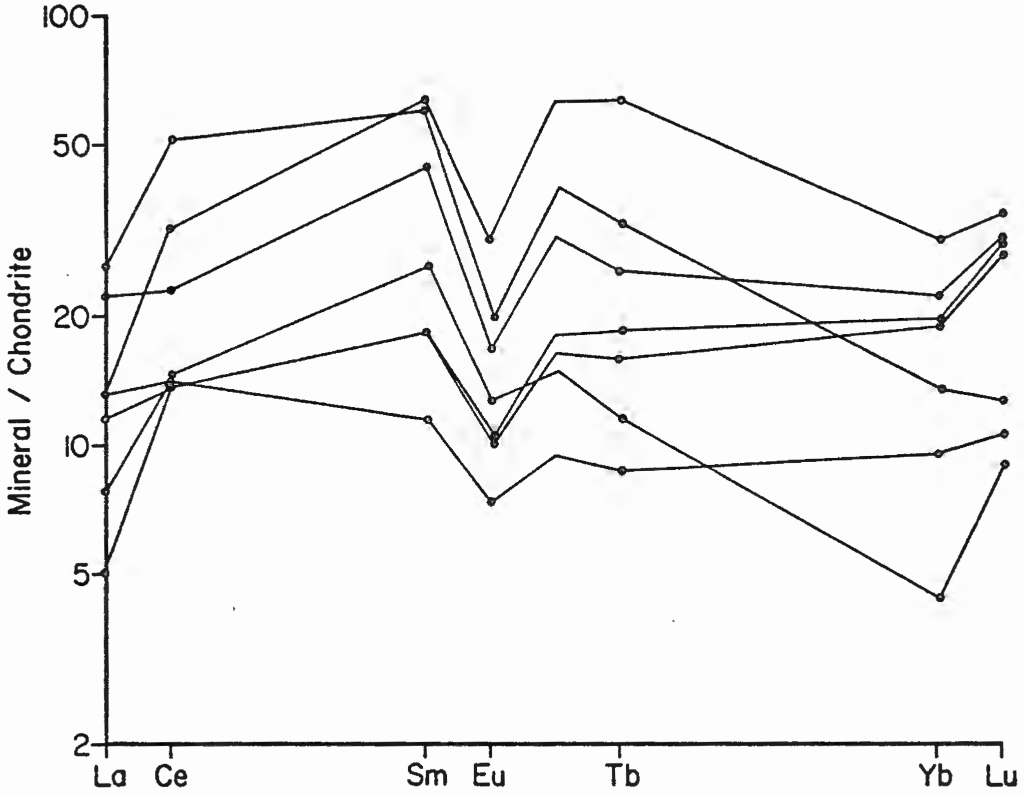


Fig. V-1 : Chondrite-normalized REE graphs of Scourian clinopyroxenes.

concentrations vary from 5 to 60 times chondrites; however, for any given element, the variation is less. All the clinopyroxenes show negative Eu anomalies, reflected by Eu/Eu* ratios of 0.39 to 0.69.

One of the most striking features of the clinopyroxene graphs (Fig. V-1) is their consistent relative patterns and, to a lesser degree their consistent absolute concentrations (for any given element, the maximum observed variation is approximately a factor of 5) in spite of a variation in rock type from ultramafic to felsic. This result is in sharp contrast to observations for clinopyroxene phenocrysts from volcanic rocks, which show higher levels of REE and higher La/Yb ratios with increasing acid character of the host rock (Nagasawa and Schnetzler, 1971). Even for a single basalt type, phenocryst clinopyroxenes show variations in absolute concentrations of REE of up to two orders of magnitude (Philpotts _et al_, 1972).

Schnetzler and Philpotts (1970) and Philpotts _et al._ (1972) have shown that the REE concentration of clinopyroxenes from some volcanic rocks, and ultrabasic and eclogitic inclusions, varies with the CaO and FeO content of the mineral. The CaO content of the Scourian clinopyroxenes varies over a narrow range (19.88 to 21.03% CaO) and hence shows no obvious correlation with the REE. FeO, on the other hand, exhibits greater variability (Table V-1) and does correlate, to a certain extent, with the REE data. Sm is observed to increase (Fig. V-2) and Eu/Eu* decrease (Fig. V-3) with increasing FeO. These trends are similar to results obtained by Philpotts _et al_, (1972) for clinopyroxenes from ultrabasic and eclogitic inclusions.

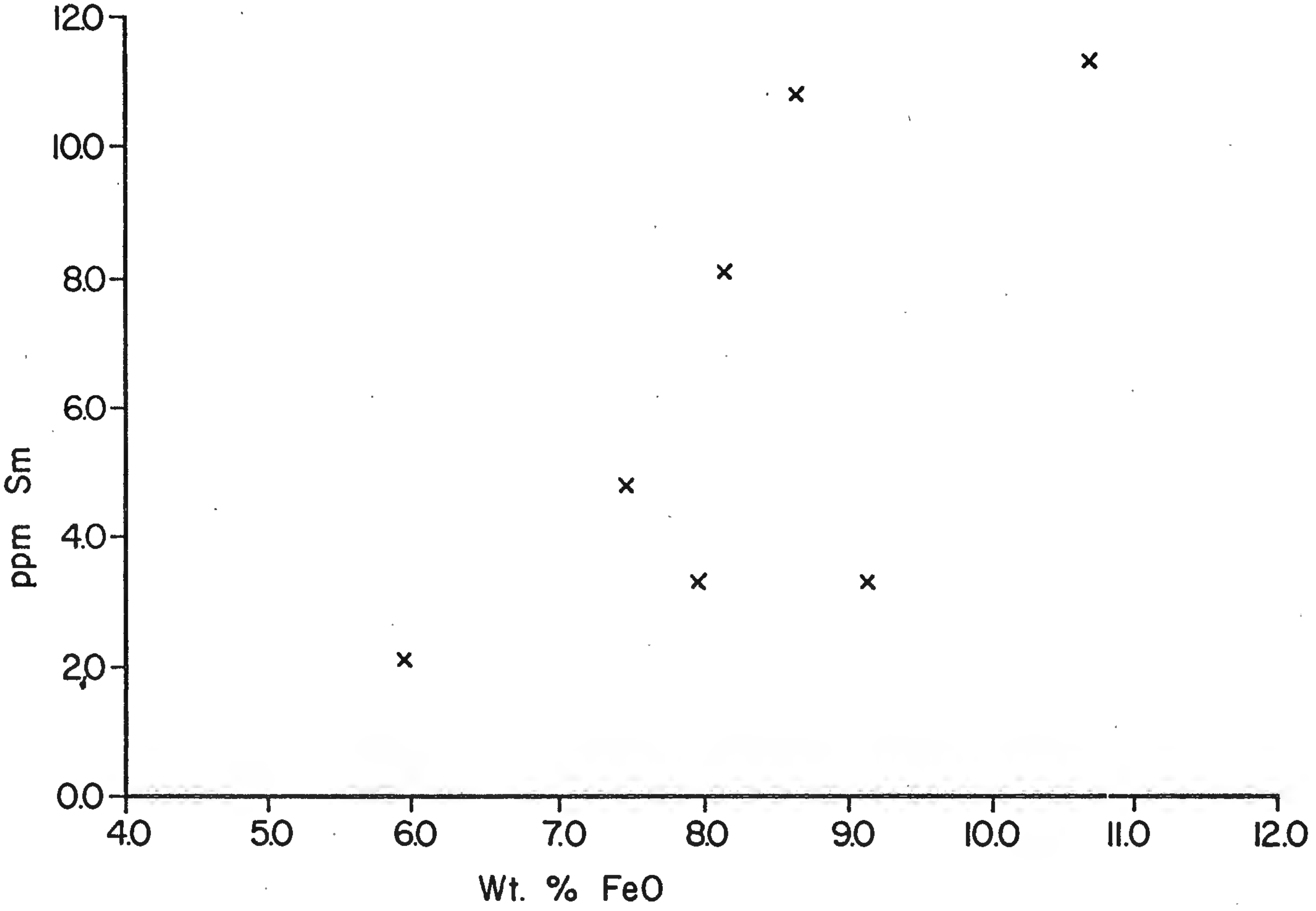


Fig. V-2 : Sm versus FeO for Scourian clinopyroxenes.

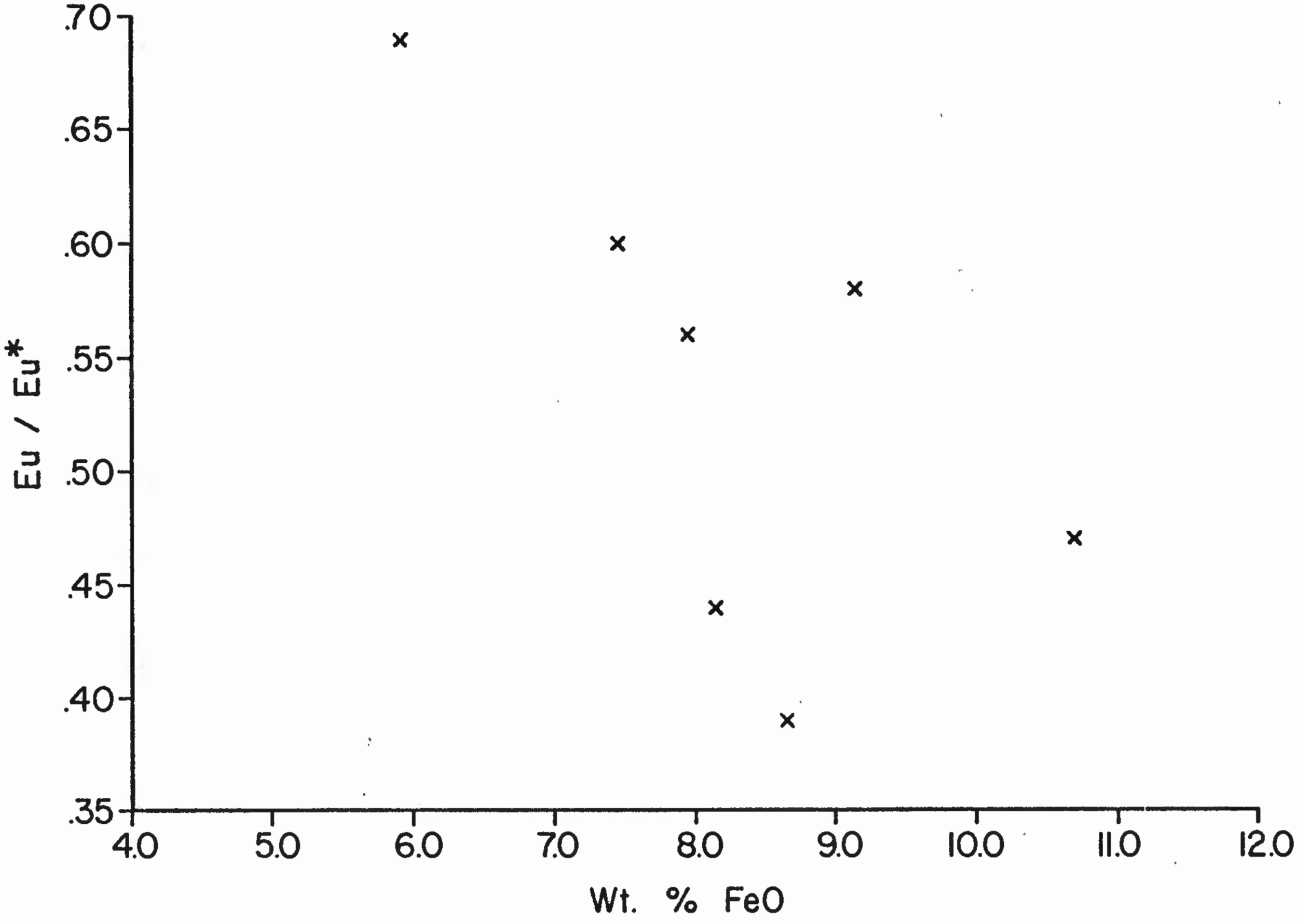


Fig. V-3 : Eu/Eu* versus FeO for Scourian clinopyroxenes.

The structure of the clinopyroxenes may be considered in terms of two major sites for cation substitution, M_1 and M_2. The larger eight-fold coordination M_2 site is dominated by Ca^{2+}; whereas the smaller six-coordination M_1 site is dominated by Mg^{2+} and Fe^{2+}. The general formula for clinopyroxene may be written:

$$M_2M_1Z_2O_6$$

where M_2 represents Ca^{2+}, Na^+ and K^+ in eight-fold coordination, M_1 represents Mg^{2+}, Fe^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+} and Al^{3+} in six-fold coordination, and Z represents Si^{4+} and Al^{3+} in four-fold coordination.

The observed REE distributions may be interpreted in terms of a Ca effect. The ionic radius of Ca^{2+} (1.20Å) corresponds closely to the ionic radii of Nd^{3+} (1.20Å) and Sm^{3+} (1.17Å) (all radii used in this chapter are from Whittaker and Muntus, 1970 and are those appropriate to the coordination number). Thus, from this similarity in size (and a charge difference of only one), it is not surprising that the maximum relative REE value observed for the clinopyroxenes occurs in the Sm position. The smaller M_1 site, occupied mainly by Mg^{2+} and Fe^{2+}, would not be expected to readily allow REE substitution as all of the REE have ionic radii greater than Mg^{2+} (0.80Å) or Fe^{2+} (0.86Å). The previously mentioned correlations of increasing Sm and decreasing Eu/Eu* with increasing FeO are more difficult to explain on the basis of crystal-chemistry. It may be purely a size effect; that is, the Fe^{2+} radius is greater than the Mg^{2+} radius and therefore the greater the Fe content, the more readily the larger REE ions may enter the M_1 position. Two other considerations, however, rule against this possibility:

1) The M_2 site should swamp any effect from the M_1 site, as the REE will be strongly concentrated into the larger M_2 location.

This is confirmed by the work of Morris (1975) which shows that the REE are largely concentrated in the M_2 sites in the pyroxenes.

2) The relatively small Lu ion should show an even greater correlation with FeO due to a closer similarity in size to Fe^{2+} compared to Sm. This trend is not observed.

2) Orthopyroxene

Major and trace element data for the six analysed Scourian orthopyroxenes are given in Table V-2. The chondrite-normalized REE graphs (Fig. V-4) exhibit minima in the middle REE range, higher LRE values, and maxima generally at Lu. All the orthopyroxenes have distinct negative Eu anomalies, with Eu/Eu* ratios from 0.43 to 0.89. They have the lowest absolute concentrations of REE of all the major Scourian rock-forming minerals analysed, except quartz. In absolute terms, the REE concentrations vary from 0.5 to 15 times chondrites (less for any given element), clustering between 1 and 5 times chondritic abundances. As was observed for the clinopyroxenes, the relative REE patterns are all very similar and the absolute values of REE vary over a narrow range (approximately a factor of 5) compared to variations observed in volcanic orthopyroxene phenocrysts (e.g. Philpotts et al, 1972; Nagasawa and Schnetzler, 1971; Schnetzler and Philpotts, 1970).

Many of the orthopyroxenes show anomalously high Ce values (Fig. V-4) - probably a result of the difficulty in separating the Ce and Fe photopeaks (145 and 142 KeV, respectively) during spectral analysis. Low Ce combined with high Fe concentrations leads to a swamping of the Ce by the Fe peak.

The observed REE patterns and abundances for the orthopyroxenes are predictable, at least in part, on the basis of crystallographic consider-

Table V-2: Major and trace element analyses of Scourian Orthopyroxenes.

Sample No.	65-18	65-33	64-12	65-165	67-30	67-109
Host Rock Type*	f	m	m	m	m	u
SiO_2 **	51.26	51.14	51.03	49.74		51.92
TiO_2	0.12	0.14	0.13	0.15		0.08
Al_2O_3	3.29	3.01	3.61	2.88		4.81
Fe_2O_3	1.64	1.97	1.78	1.56		1.16
FeO	24.43	23.28	22.42	25.17		17.66
MnO	0.49	0.70	0.59	0.57		0.25
MgO	17.62	18.68	19.03	17.90		22.54
CaO	0.97	0.98	1.06	1.91		1.42
Na_2O	0.15	0.06	0.16	0.07		0.15
K_2O	0.12	0.04	0.05	0.03		0.03
Total	100.09	100.00	99.86	99.98		100.02
Ppm						
La	3.03	0.83	1.23	0.89	0.75	1.68
Ce	11.4	(1.94)	3.82	2.07	3.13	4.65
Sm	0.59	0.27	0.41	0.15	0.36	0.38
Eu	0.12	0.05	0.13	0.03	0.09	0.07
Tb	0.10	0.11	0.09	0.06	0.16	0.07
Yb	0.56	1.04	0.51	(1.60)	1.03	0.26
Lu	0.14	0.57	0.14	0.38	0.20	0.04
ΣREE	15.9	4.8	6.33	5.19	5.17	7.16
Eu/Eu*	0.58	0.43	0.89	0.45	0.51	0.53
La/Yb	5.43	0.80	2.41	0.56	0.72	6.36
Sc	30.6	34.5	32.9	46.8	34.5	17.7
Cr	123	141	135	222	11.2	993
Co	71.6	132	86.8	116	98.2	101

* f, m, u = felsic, mafic, ultramafic gneisses.

( ) = value obtained by extrapolation.

** major element analyses are from Muecke, 1969.

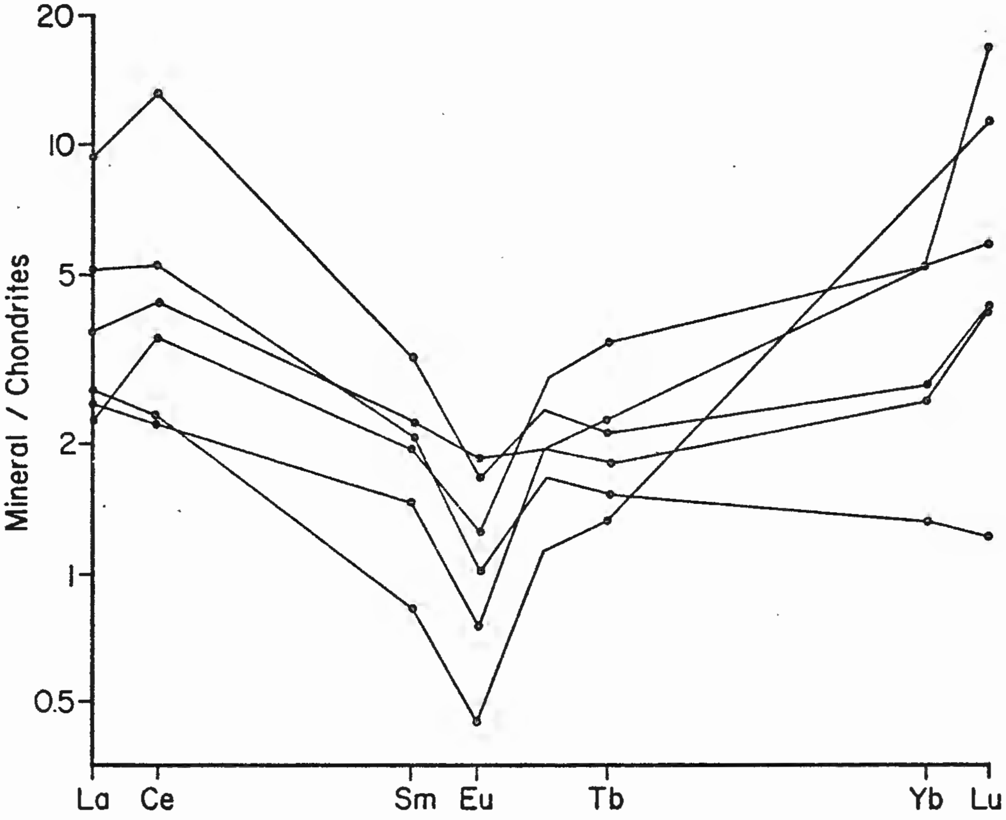


Fig. V-4 : Chondrite-normalized REE graphs of Scourian orthopyroxenes.

ations. In the orthopyroxenes, the M_1 and M_2 sites are occupied almost exclusively by Mg^{2+} and Fe^{2+} in six-fold coordination. Since both Mg^{2+} and Fe^{2+} have ionic radii smaller than all the REE, the observed maximum at Lu, the smallest of the REE (0.94 Å), is consistent with these size considerations. With increasing size, there should be a steady decrease in concentrations of the REE. This represents the observed trend up to approximately Sm; but the relative abundances from Sm to La increase - that is, against the trend predicted from crystal-chemistry. Similar trends have been observed for orthopyroxene phenocrysts from acid volcanic rocks (Nagasawa and Schnetzler, 1971). which were interpreted as resulting from equilibration with a LRE enriched melt. This feature does not appear to be a function of orthopyroxene composition, such as amount of Ca present in the orthopyroxenes. There are LRE depleted orthopyroxenes with greater than 1.5 per cent CaO (Philpotts et al., 1972) such as observed in the Scourian examples, and orthopyroxenes from acid volcanic rocks showing high LRE concentrations with CaO contents less than 0.5 per cent (Nagasawa and Schnetzler, 1971).

There are no obvious correlations of REE with major element chemistry for the orthopyroxenes, probably due to the narrow range of major element chemistry of the analysed samples (Table V-2).

3) Plagioclase

Partial major and trace element data for the 9 analysed Scourian plagioclases are given in Table V-3. Chondrite-normalized graphs (Fig. V-5) exhibit LRE enrichment with La/Yb ratios as high as 324 - the highest of any of the Scourian minerals. Values for the HRE, Yb and Lu, are all very low,

Table V-3: Partial Major and trace element analyses of Scourian Plagioclases

Sample No.	65-18	65-33	64-12	66-11	65-41	65-165	67-30	67-109
Host Rock Type*	f	m	m	m	m	m	m	u
CaO ****	6.98	12.30	10.60	10.71		11.27	11.07	12.08
Na_2O	6.91	4.21	5.23	5.30		5.19	4.92	4.29
K_2O	0.68	0.17	0.14	0.42		0.23	0.15	0.17
Fe_2O_3	0.36	0.34	0.25	0.04		0.18	0.07	0.10
Mole % An	34.4	61.1	52.4	51.5		53.9	54.9	60.3
Optical An	33	58-75	54	52	58	53-64	36-62	46-68
Ppm								
La	12.0	1.99	8.78	4.41	3.34	3.13	3.65	6.93
Ce	14.6	3.67	11.8	5.08	5.03	4.76	7.79	6.06
Sm	0.54	0.35	0.54	0.61	0.30	0.36	0.51	0.20
Eu	0.81	0.43	0.56	0.40	0.46	0.62	1.21	0.23
Tb	0.04	0.08	0.10	0.15	0.07	0.11	0.10	0.05
Yb	0.04	0.12	0.12	0.15	0.05	0.10	0.04	0.08
Lu	0.01	0.02	0.02	0.02	0.007	0.01	0.007	0.008
ΣREE	28.0	6.7	21.9	10.8	9.3	9.1	13.3	13.6
Eu/Eu*	5.2	3.4	3.0	1.8	4.1	4.3	6.8	3.0
La/Yb	324	16.6	73.2	29.4	65.5	31.3	86.9	88.8
Sc	0.1	0.5	1.0	0.1	0.2	0.2	0.2	0.3
Cr	n.d.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Co	0.5	3.6	4.5	1.0	1.0	0.5	0.1	0.6
Hf	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Th	n.a.***	0.14	0.08	0.30	0.11	0.12	0.23	0.10

* f,m,u = felsic, mafic, ultramafic, gneisses
** n.d. = not detected
*** n.a. = not analysed
**** major element analyses and plagioclase compositions are from Muecke, 1969.

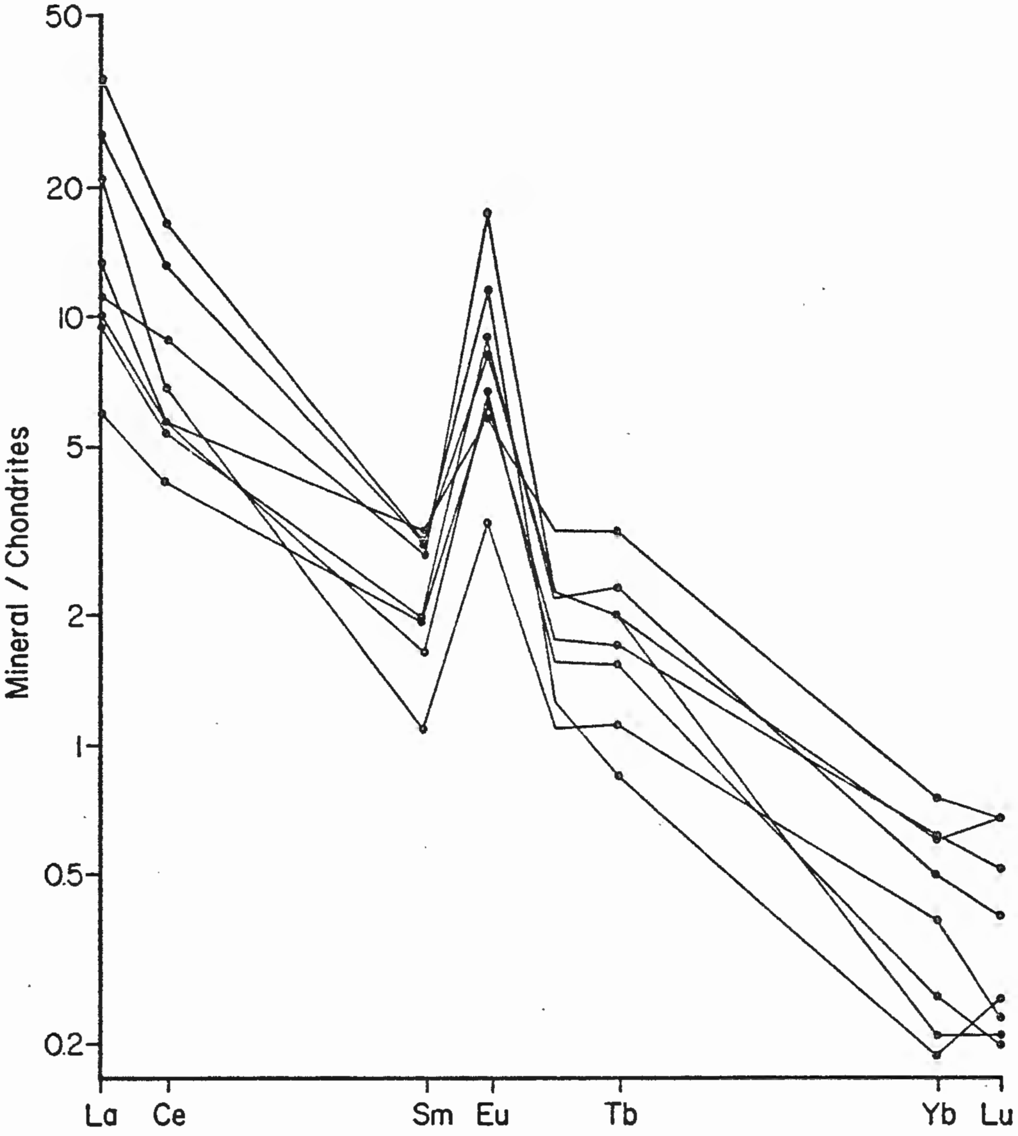


Fig. V-5 : Chondrite-normalized graphs of Scourian plagioclases.

usually much less than chondrites. The accuracy here is probably poor as the abundances are near the detection limit of the method.

The most distinguishing feature of the plagioclase REE patterns is the ubiquitous large positive Eu anomaly, reflected by Eu/Eu* ratios from 3.0 to 6.8. Plagioclase is the only major Scourian mineral to exhibit a positive Eu anomaly. The presence of positive Eu anomalies in the feldspar structure seems to be due to the ease of entry of Eu^{2+} into the major cation position, replacing Ca, K, and Na (see Chapter 1). The positive Eu anomalies observed in the Scourian plagioclase may be taken to indicate that these rocks formed under a relatively low f_{O_2} (e.g. Drake, 1975). It has been shown that the size of the Eu anomaly is also a function of the composition of the feldspar - Eu/Eu* increasing with increasing alkali content (e.g. Schnetzler and Philpotts, 1970). The lack of a strong correlation between Eu/Eu* and anorthite content for the Scourian feldspars (Fig. V-6) suggests that the observed differences in Eu/Eu* are not a result only of feldspar composition. Variable f_{O_2} may be another important factor.

4) Garnet

Major and trace element data for the five analysed Scourian garnets are given in Table V-4. The chondrite-normalized REE graphs (Fig. V-7) show linear HRE enrichment, with La/Yb ratios from 0.01 to 0.04. Most of the garnets have small negative Eu anomalies. In absolute terms, all values are greater than chondrites, with maximum values for Yb and Lu of 40 to 200 times chondritic abundances.

Two analytical problems are of importance in assessing the garnet REE results. The high Yb and Lu values, although valid in a general sense, are

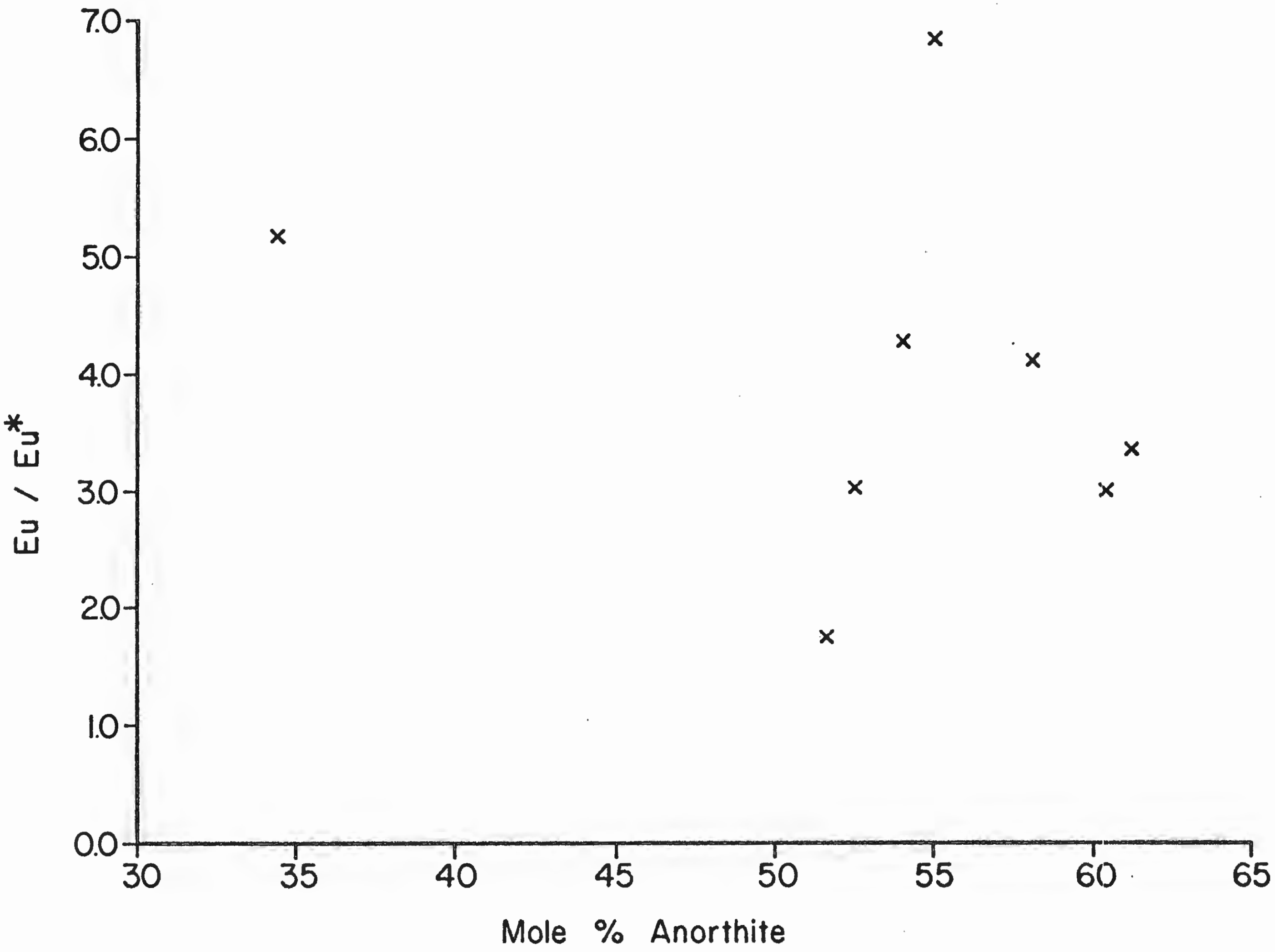


Fig. V-6 : Eu/Eu* versus anorthite content for Scourian plagioclases.

Table V-4: Major and Trace Element analyses of Scourian garnets.

Sample No.	65-33	65-41	65-165	67-30	67-109
Host Rock Type*	m	m	m	m	u
SiO_2 ***	38.76	39.04	38.66	37.48	39.46
TiO_2	0.09	0.14	0.16	0.10	0.06
Al_2O_3	21.15	21.36	21.62	21.62	22.22
Fe_2O_3	2.24	1.83	2.26	2.12	1.97
FeO	22.53	22.76	23.33	26.19	19.53
MnO	1.69	0.94	1.21	1.30	0.80
MgO	6.60	7.37	6.80	4.03	9.91
CaO	6.79	6.69	6.42	7.37	6.15
Na_2O	0.07	0.11	0.06	0.08	0.06
K_2O	0.02	0.06	0.02	0.01	0.02
Total	99.94	100.30	100.54	100.30	100.18
Ppm					
La	0.34	0.52	0.69	1.22	0.41
Ce	1.93	3.59	6.81	4.59	3.22
Sm	1.10	1.75	1.70	4.10	0.81
Eu	0.39	0.68	0.63	2.00	0.44
Tb	1.78	1.55	1.87	2.82	0.83
Yb	38.5	13.6	25.2	15.3	9.60
Lu	4.89	1.37	5.66	3.10	1.20
ΣREE	48.9	23.1	42.6	33.1	16.5
Eu/Eu*	0.34	0.57	0.47	0.83	0.72
La/Yb	0.01	0.04	0.03	0.08	0.04
Sc	119	118	196	768	111
Cr	422	583	369	N.A.**	1,103
Co	59.6	70.1	47.1	47.6	73.2

* f, m, u = felsic, mafic, ultramafic gneisses.

** not analysed.

*** major element analyses are from Muecke, 1969.

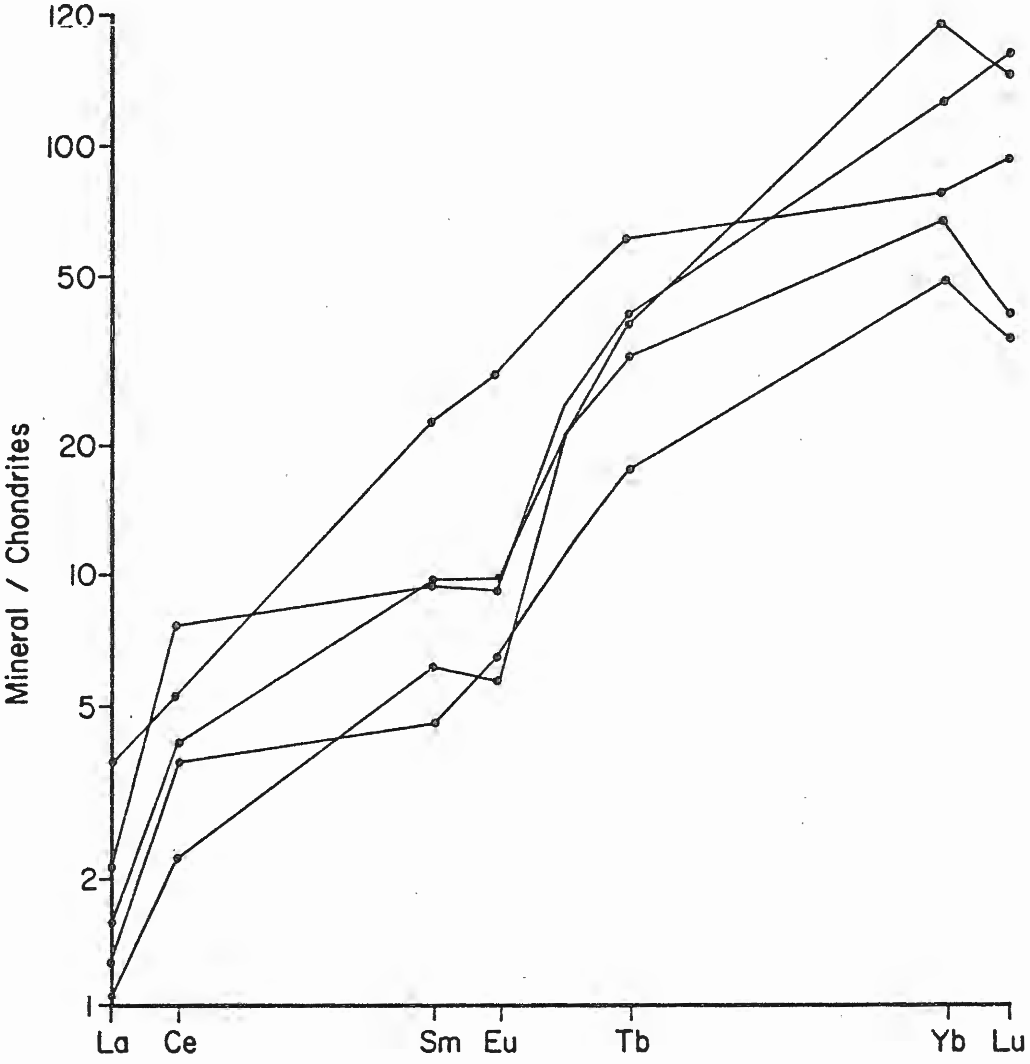


Fig. V-7 : Chondrite-normalized REE graphs of Scourian garnets.

probably not as accurate as many of the other REE, as they are many times higher than the standard used (AGV -1). The apparent Ce anomalies (Fig. V-7) are probably due to the swamping effect of 25 to 30 per cent total iron on the Ce 145 KeV photopeak, as discussed for the orthopyroxenes.

The general formula for garnet may be written:

$$X_3\, Y_2\, Si_3\, O_{12}$$

where X represents Fe^{2+}, Mg^{2+}, Ca^{2+} and Mn^{2+} in eight-fold coordination, and Y represents Fe^{3+}, Al^{3+} and Cr^{3+} in six-fold coordination. The observed maximum for the HRE is probably a result of the dominance of Fe, Mg and Ca in the garnet structure, in a small eight-fold coordination site (Deer et al, 1971).

5) Hornblende

Major and trace element data for the two analysed hornblendes are given in Table V-5. They have the highest REE concentrations of all the Scourian minerals analysed, up to 70 times chondrites. The chondrite-normalized REE patterns (Fig. V-8) show slight LRE enrichment, which is more pronounced for the hornblende from the ultramafic gneiss (67-109). The hornblende REE patterns are very similar in relative form to those of the clinopyroxenes, including the ubiquitous negative Eu anomaly.

The general open structure of hornblende allows it to act as a "sink" for many elements not readily incorporated in other mineral structures. This feature is reflected by the highly variable major and trace element composition of the hornblende group (e.g. Deer et al., 1971). The high Ca and Na content (11 and 2%, respectively) of the Scourian hornblendes is consistent with the observed large concentrations of REE in these eight-fold coordination sites.

Table V-5: Major and trace element analyses of Scourian Hornblendes

Sample No.	64-12	67-109
Host Rock Type*	m	u
SiO_2 **	42.79	41.61
TiO_2	2.06	1.69
Al_2O_3	13.42	15.52
Fe_2O_3	3.26	2.53
FeO	10.61	8.95
MnO	0.16	0.09
MgO	11.80	13.00
CaO	11.31	11.58
Na_2O	1.66	2.37
K_2O	1.32	0.98
H_2O+	1.50	1.56
Total	99.89	99.88
Ppm		
La	15.6	12.5
Ce	64.1	33.7
Sm	12.2	3.87
Eu	2.56	0.99
Tb	2.53	0.56
Yb	9.60	1.10
Lu	1.10	0.13
ΣREE	108	52.9
Eu/Eu*	0.59	0.78
La/Yb	1.63	11.4
Sc	112	48.5
Cr	389	1,781
Co	70.0	79.5

* f, m, u = felsic, mafic, ultramafic gneisses

** major element analyses are from Muecke, 1969.

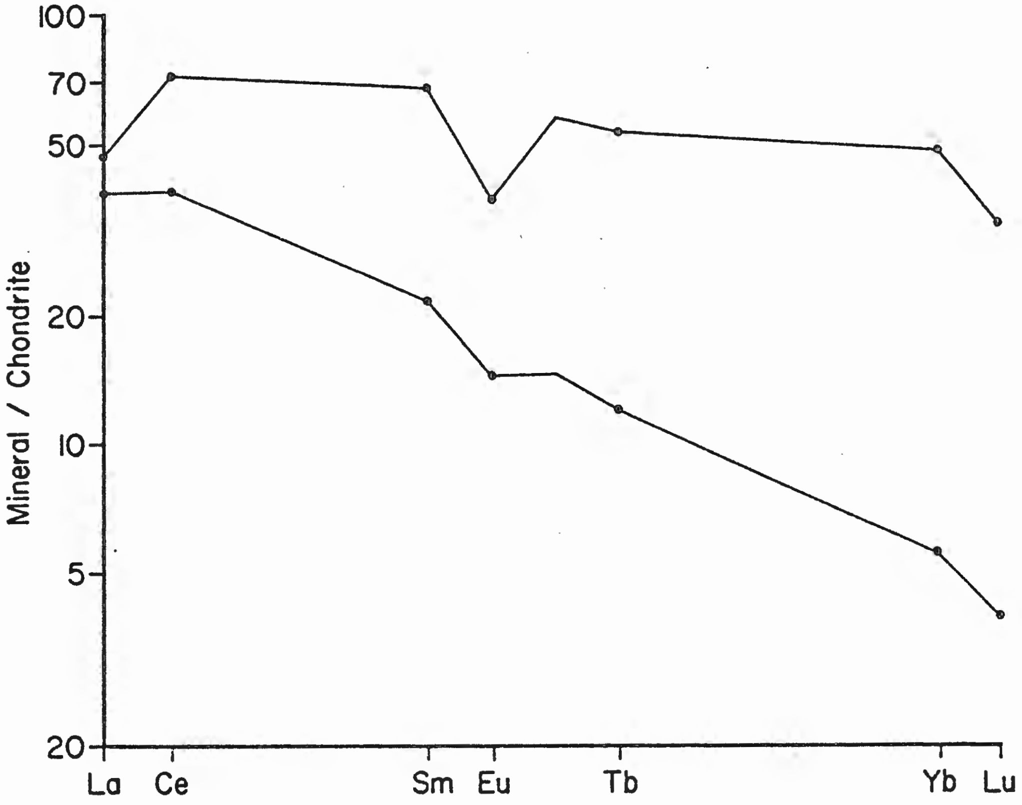


Fig. V-8 : Chondrite-normalized REE graphs of Scourian hornblendes.

6) Scapolite and Quartz

Trace element data for two scapolite samples and one quartz sample are given in Table V-6. Predictably, quartz is very low in REE - all elements except Yb are less abundant than in chondrites (Fig. V-9). The quartz separate may be judged to have been very pure, as the major contaminant would be plagioclase, and the quartz exhibits a negative rather than a positive Eu anomaly. The REE are probably located in inclusions in the quartz, which is strongly rutilated (Muecke, 1969).

Two scapolite samples were analysed for the REE - one was from the Scourian complex (#66-11) and the other from Evans _et_ _al_., (1969) (#CA63A). Both scapolite chondrite-normalized REE graphs are similar (Fig. V-9) except for the Tb value of 66-11, which appears to be anomalously high.

The absolute and relative REE concentrations are similar to results for plagioclase, except for a smaller positive Eu anomaly in the scapolites.

Mass Balancing of REE

In order to ascertain where most of the REE are located in the Scourian gneisses, mass balances were performed using the REE mineral data, modal analyses (Table V-7) and the known densities of the minerals (Deer _et_ _al_., 1971). The calculated REE concentrations were then compared to the whole rock REE data (Chapter 4). The results of this operation are presented in Table V-8. The major rock-forming minerals, which were analysed for the REE, account for approximately 83 to 99 weight per cent of each whole rock sample. Bearing in mind the approximations involved in mass balancing calculations of this nature, and the uncertainties in the REE mineral and whole rock data (Appendix 1), the results indicate

Table V-6: Trace Element analyses of two Scapolites and a quartz sample.

Sample No.	66-11 (Scapolite)	Ca 63A (Scapolite)	67-30 (Quartz)
Ppm			
La	14.8	12.1	0.26
Ce	28.5	22.9	0.57
Sm	1.43	1.11	0.15
Eu	0.57	0.55	0.02
Tb	0.38	0.14	0.04
Yb	0.40	0.42	0.32
Lu	0.07	0.05	0.01
ΣREE	46.1	37.3	1.37
Eu/Eu*	1.03	1.56	0.42
La/Yb	36.9	29.0	0.81
Sc	1.5	-	0.4
Cr	11.2	2.3	0.8
Co	70.0	-	0.6
Hf	-	10.3	-
Th	0.65	0.56	0.12
Host Rock Type*	m		m

m = mafic gneiss.

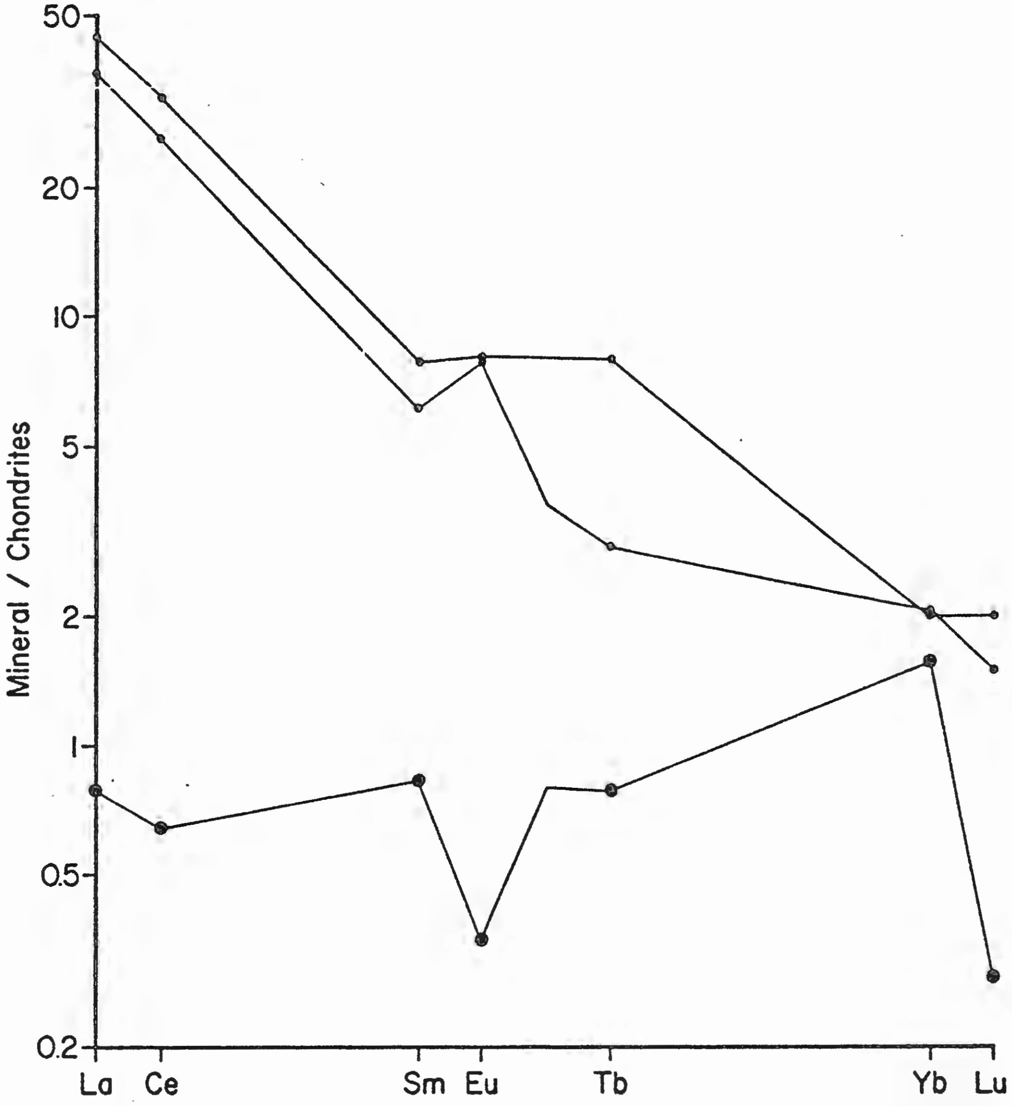


Fig. V-9 : Chondrite-normalized graphs of two scapolites (small circles-upper graph is Scourian 66-11 and other is from Evans *et al.*, 1969) and quartz (large circles).

Table V-7: Modal Analyses of Scourian Gneisses

	65-18	64-12	65-41	65-33	67-30	66-11	67-109
Rock Type*	f	m	m	m	m	m	u
Clinopyroxene	7.5	13.1	32.8	28.7	21.9	35.5	42.4
Orthopyroxene	6.7	17.7	4.4	14.0	11.8	-	13.5
Hornblende	-	13.9	-	10.1	-		17.7
Garnet	-		16.0	1.1	11.3	-	17.9
Plagioclase	71.1	43.6	41.6	41.2	36.1	54.3	7.3
Quartz	7.5	-	-	-	7.6	-	-
K-feldspar	0.9	-	-	-	-	-	-
Apatite	0.3	0.3	0.1	0.1	0.2	0.1	-
Opaques	1.8	4.8	2.0	4.0	11.1	5.3	0.2
Biotite (Secondary)	3.0	1.2	0.5	0.2	-	0.5	-
Hornblende (secondary)	0.6	5.5	1.0	0.7	-	1.1	0.4
Calcite	0.6	-	-	0.1	-	1.0	-
Zircon	-	-	-	-	-	-	-
Spinel	-	-	-	-	-	-	0.6
Scapolite	-	-	-	-	-	2.2	-

* f, m, u = felsic, mafic, ultramafic gneisses
(from Muecke, 1969).

Table V-8: Per cent of whole rock REE accounted for by major rock-forming minerals.

Sample #	65-18	64-12	65-41	65-33	67-30	66-11	67-109
Weight % of Minerals	88	91	92	83	83	89	99
% La	65	88	104	72	93	89	124
% Ce	51	89	81	87	91	79	120
% Sm	55	104	106	68	86	99	106
% Eu	65	92	91	74	93	78	98
% Tb	63	90	110	66	81	100	96
% Yb	56	88	179*	84	41	109	168*
% Lu	71	89	119*	123	99	152	175*
Rock Type**	f	m	m	m	m	m	u

* significant modal garnet content (>15%).

** f, m, u = felsic, mafic, ultramafic gneisses.

that the majority of the REE (generally greater than 80%) can be accounted for by the major rock-forming minerals (Table V-8). The felsic gneiss (#65-18) shows the lowest percentage (51 to 71%). In several cases, the Yb and Lu values obtained are too high (up to 179%) - beyond the likely errors in the mass balance calculation. In each case, however, there is significant modal garnet present (Table V-8). Thus, the high values are probably due to the poor accuracy of the Yb and Lu values of the garnet analysis.

These results contrast sharply with those of many granitic rock sequences. Buma *et al*, (1971) and Condie and Lo (1971) have shown that in such rocks, a significant amount of the REE (>50%) are often located in minor, accessory phases such as apatite and zircon (< 1% modal abundance). The low modal abundances of apatite and zircon in the Scourian samples (Muecke, 1969) is probably the main reason for the observed mass balance results.

REE Distribution Coefficients

For equilibrium mineral assemblages, the values of the distribution coefficient (K_D) between coexisting phases, for trace elements following Henry's Law of dilute solutions, are constant, or nearly so (e.g. Broecker and Oversby, 1971). The relationship may be written:

$$K_D = \frac{X^A_{Tr}}{X^B_{Tr}} = \text{constant}$$

where X^A_{Tr} and X^B_{Tr} are equal to the concentration of the trace element in phase A and B respectively.

REE K_D's for coexisting mineral pairs of the Scourian granulites have been calculated (Appendix 2). All mineral pairs (including clinopyroxene-plagioclase, clinopyroxene-orthopyroxene, hornblende-clinopyroxene, clinopyroxene-garnet, and orthopyroxene-plagioclase) exhibit consistent patterns (Figures V-10 to V-13). The observed variability of K_D for each element within a mineral pair is almost always much smaller than the observed elemental variability for a particular mineral type. This observation is most noticeable for the light and middle REE (La to Eu), which are generally present in the highest concentrations and are, therefore, the most easily and accurately analysed. For example, the observed K_D's of clinopyroxene-plagioclase pairs (Fig. V-10) show tight groupings for the elements La, Ce and Eu; whereas, the HRE Tb, Yb and Lu show greater variability. This greater variability for the HRE is probably largely a result of the poorer precision and accuracy of the HRE in the plagioclase due to very low concentrations.

The consistent K_D patterns and narrow range of absolute K_D values for the mineral pairs suggest that they represent equilibrium distributions. The observed K_D patterns of clinopyroxene-plagioclase (Fig. V-10) and orthopyroxene plagioclase (Fig. V-13) confirm the anomalous enrichment of Eu in the plagioclase structure.

Discussion of Mineral REE Results

Each of the analysed Scourian mineral phases exhibits consistent relative and, to a lesser extent, absolute REE distributions, predictable for the most part from crystal-chemical considerations. This result indicates that the REE occupy regular lattice sites in the Scourian

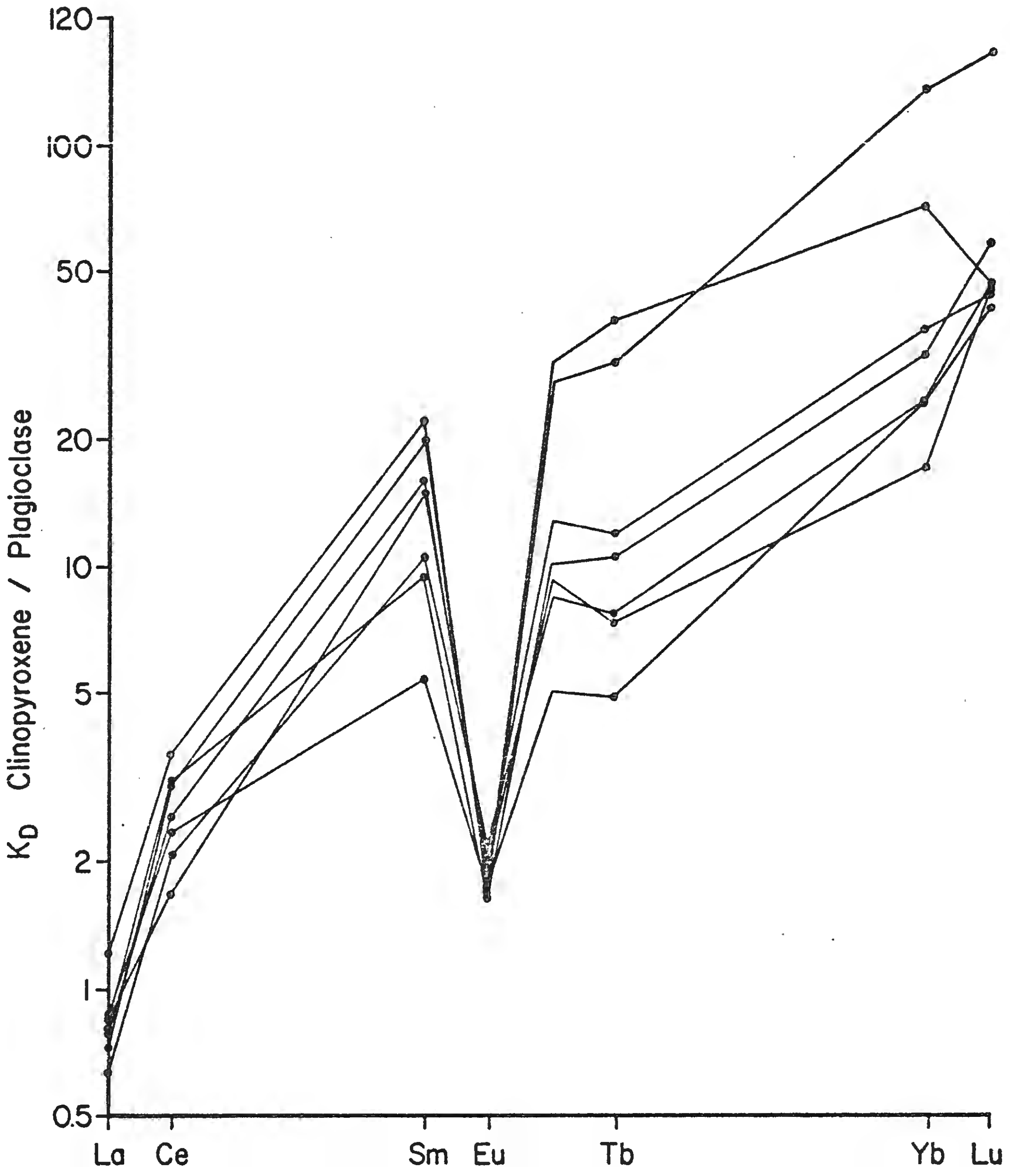


Fig. V-10 : REE distribution coefficients for coexisting Scourian clinopyroxene/plagioclase pairs.

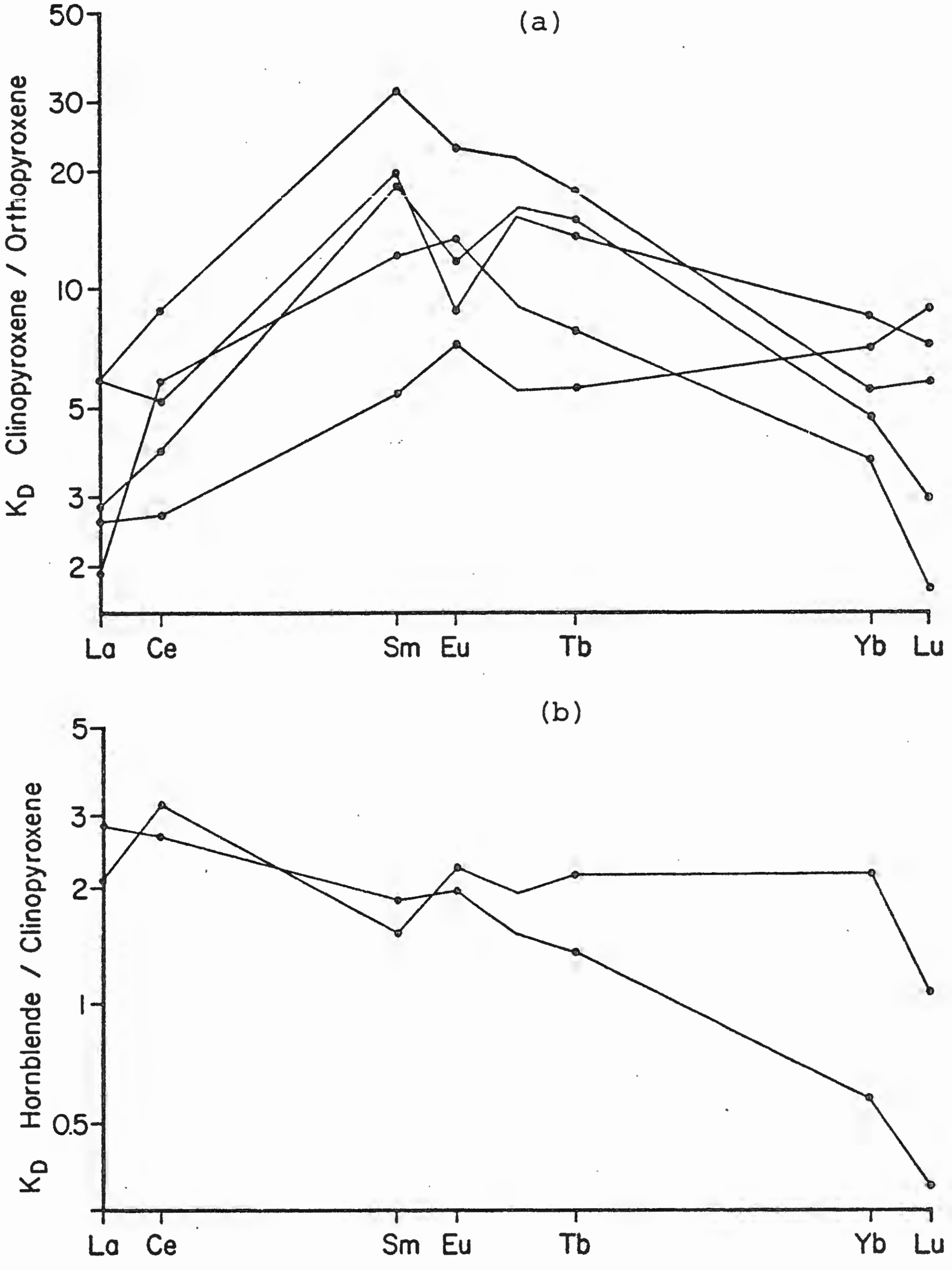


Fig. V-11 : REE distribution coefficients for coexisting Scourian a) clinopyroxene/orthopyroxene pairs and b) hornblende/ clinopyroxene pairs.

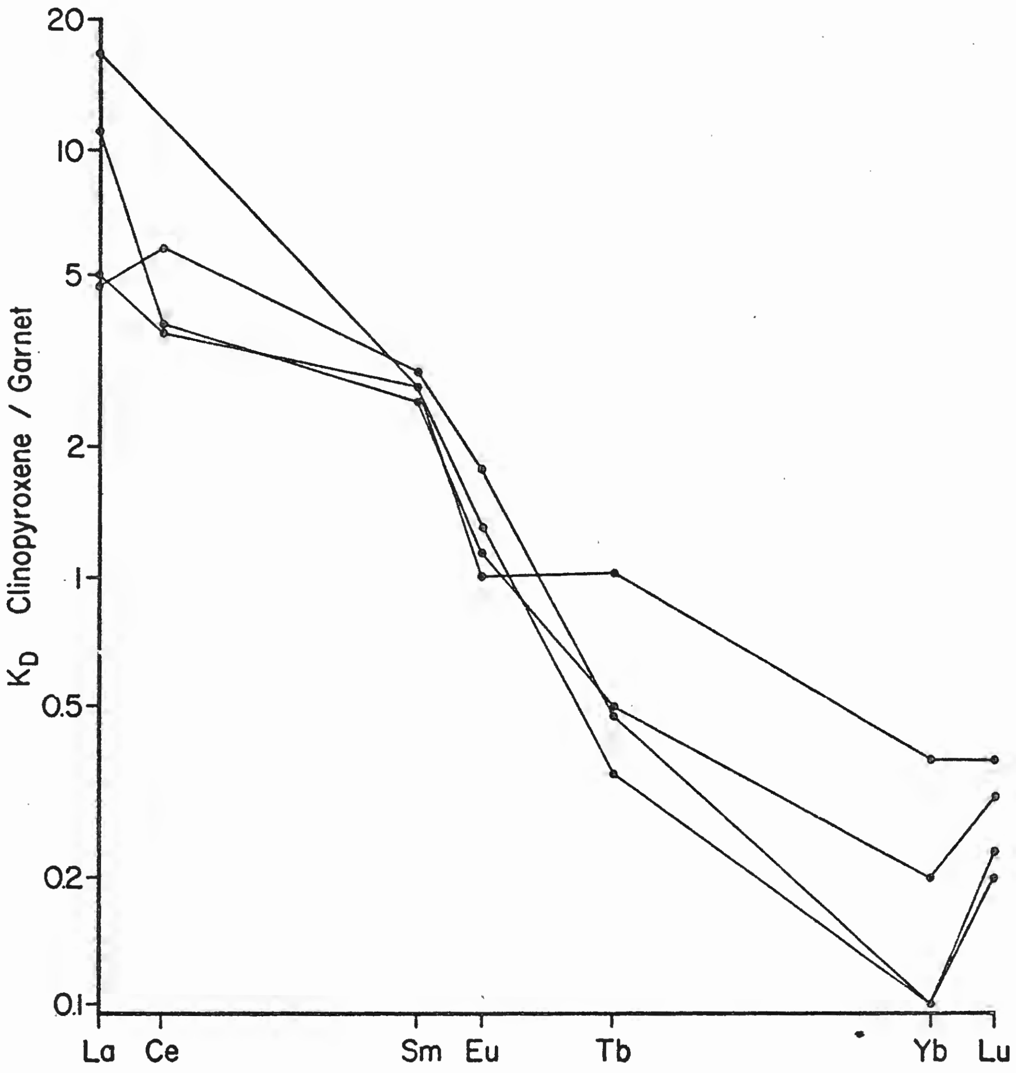


Fig. V-12 : REE distribution coefficients for coexisting Scourian clinopyroxene/garnet pairs.

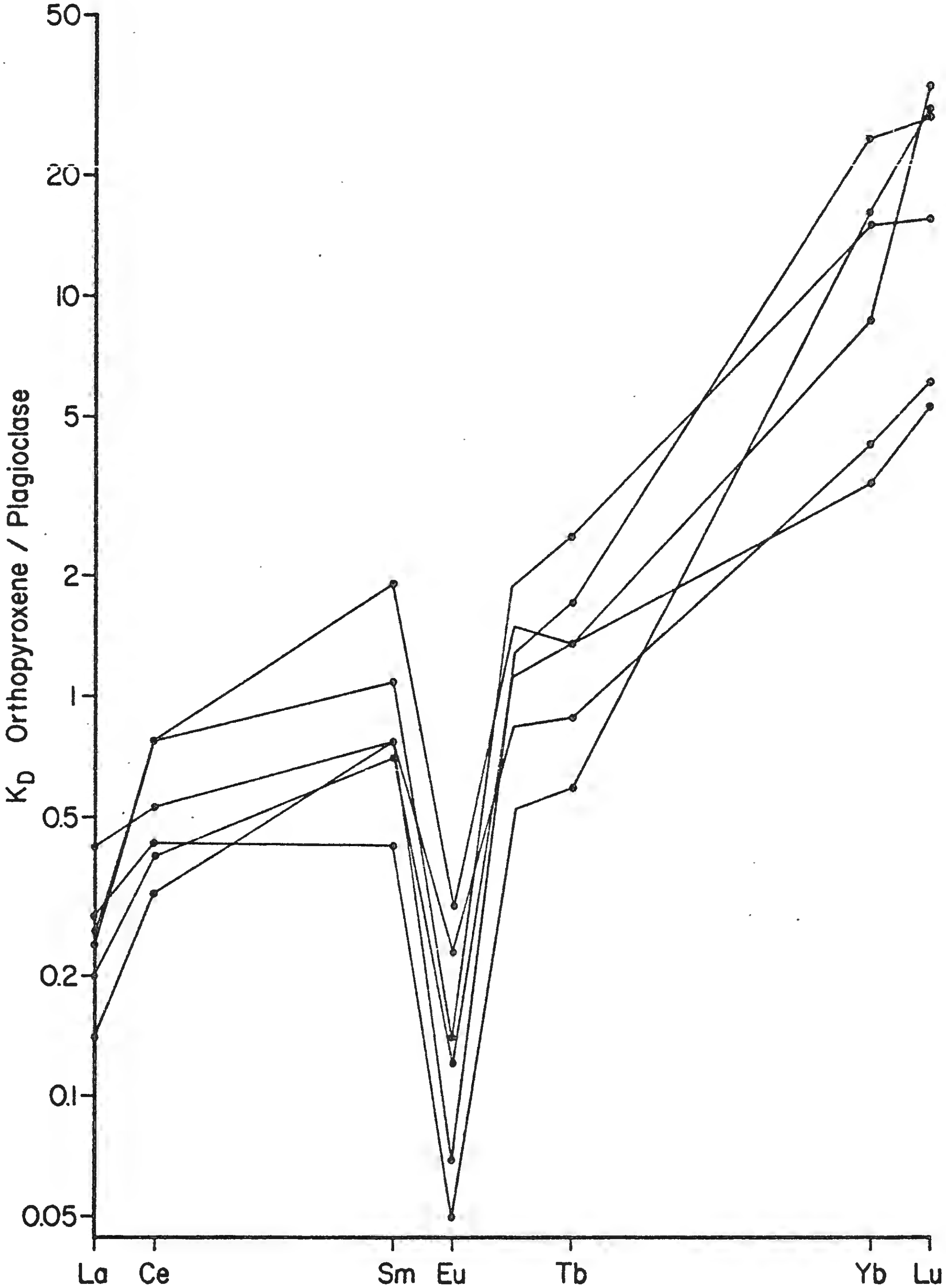


Fig. V-13 : REE distribution coefficients for coexisting Scourian orthopyroxene/plagioclase pairs.

minerals. Although the minerals come from a variety of rock types ranging in composition from felsic to ultramafic, the absolute concentration for any given REE from a given mineral phase varies over only a maximum range of a factor of 5. This result contrasts sharply with results from basaltic rocks, where the absolute concentration of a particular REE for a particular phase often varies over 2 orders of magnitude and shows even greater variation as the composition of the rock type changes.

As mentioned previously, there is a paucity of data on the REE content of metamorphic minerals. It may be of interest, however, to compare the REE mineral results to those of porphyritic igneous rocks and ultrabasic and eclogitic inclusions especially since partial melting may have been an important process in the evolution of the Scourian complex (Chapters 3, 4). Mean REE mineral data for various rock types have been calculated from published data and are presented, in tabular form, in Appendix 3, along with the sources of the data. Means are used here for simplicity and clarity of presentation. Although it has been shown that the absolute REE concentrations of a particular mineral type may vary over a considerable range for any given rock type, the general trends shown by the mineral means are thought to be real

Chondrite-normalized REE means for clinopyroxenes from rhyolites, dacites, the Scourian granulites, basalt-andesites and the Lizard peridotite are presented in Fig. V-14. The absolute values of REE and La/Yb ratios generally increase with increasing acidic character of the rock, as noted by Nagasawa and Schnetzler (1971). The Scourian clinopyroxene mean shows a REE pattern very similar in relative form to the

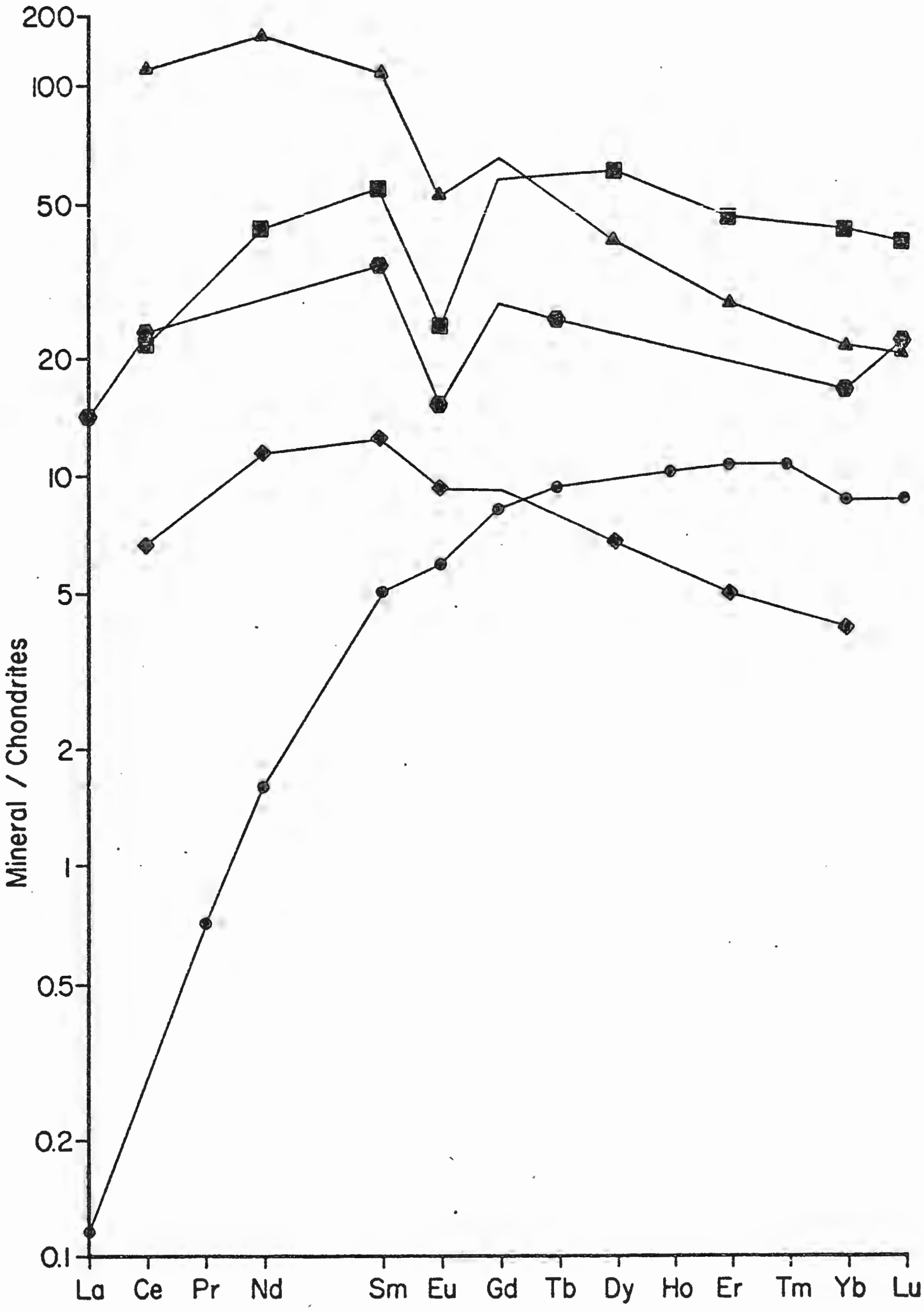


Fig. V-14 : Chondrite-normalized REE means for clinopyroxenes from rhyolites (triangles), dacites (squares), Scourian granulites (hexagons), basalt-andesites (diamonds) and the Lizard peridotite (circles).

dacitic mean, but is slightly lower in absolute abundances.

A similar result is observed for the orthopyroxene means (Fig. V-15). The Scourian and dacite means have the same relative patterns, which show a minimum in the middle REE range and have distinct negative Eu anomalies. The granulite mean has slightly lower absolute concentrations. The basalt-andesite and Lizard peridotite means, on the other hand, have much lower absolute concentrations and the patterns are linear with HRE enrichment. As mentioned earlier, the relatively high LRE values observed for the granulite and dacite orthopyroxenes is against the pattern expected from crystal-chemical considerations alone - which predict a maximum at Lu, decreasing continuously to La. In the case of dacitic orthopyroxenes, this LRE enrichment is probably a result of equilibration with a melt which was LRE enriched (Nagasawa and Schnetzler, 1971). This important observation will be referred to in a later discussion.

Mean chondrite normalized plagioclase patterns are presented in Fig. V-16. The granite plagioclase has the highest concentration of REE and the highest La/Yb ratio. The dacitic and Scourian granulite patterns are, again, very similar - except for a larger positive Eu anomaly for the dacite plagioclase mean (probably related to a higher f_{O_2} in the Scourian rocks). The basalt-andesite mean has the lowest La/Yb ratio and ΣREE.

Various hornblende chondrite-normalized means are given in Fig. V-17. The relative and absolute REE abundances of the Lizard and basalt-andesite hornblende means are very similar. They show the lowest absolute concentrations of all the hornblendes, with very small negative and positive

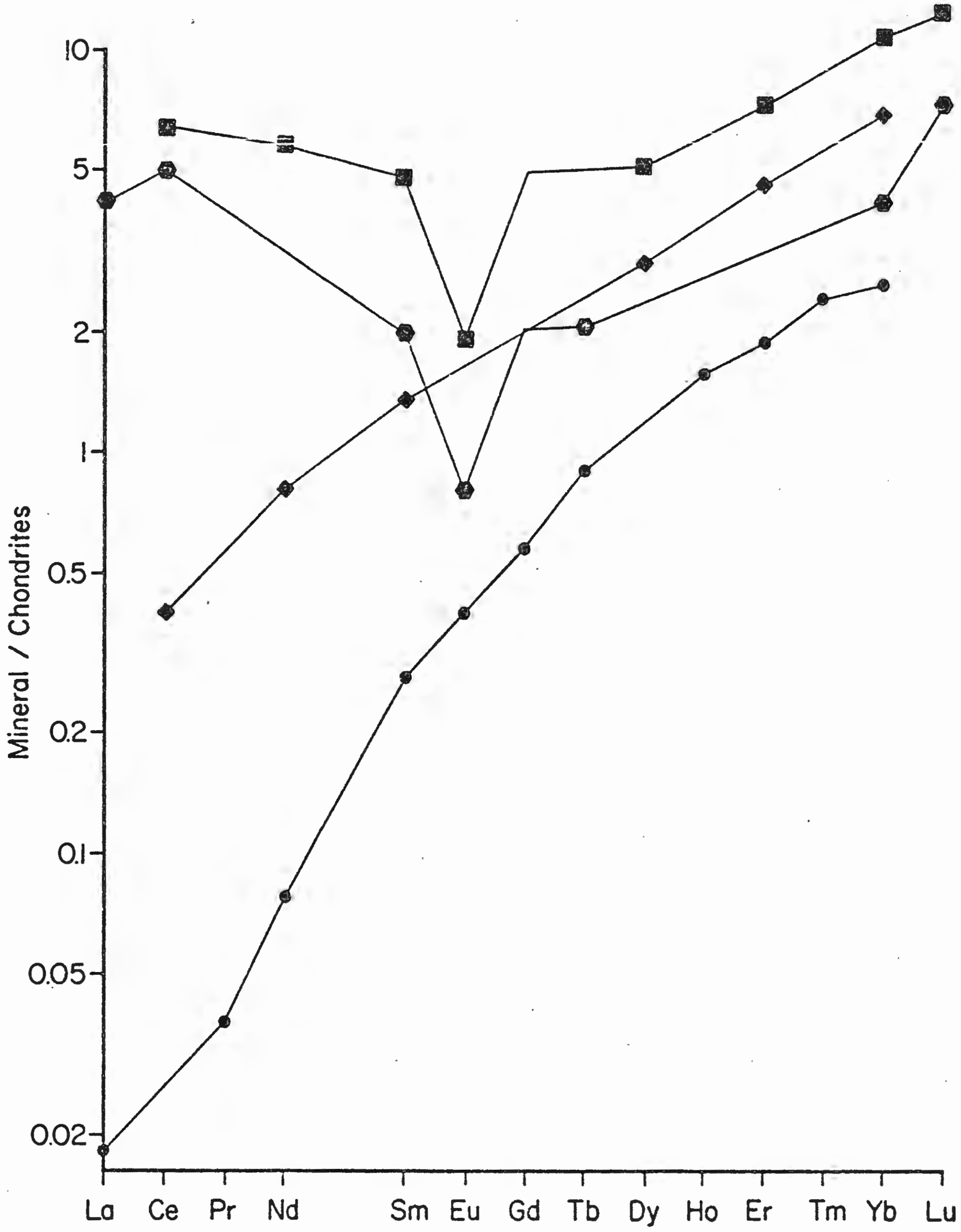


Fig. V-15 : Chondrite-normalized REE means for orthopyroxenes from dacites (squares), Scourian granulites (hexagons), basalt-andesites (diamonds) and the Lizard peridotite (circles).

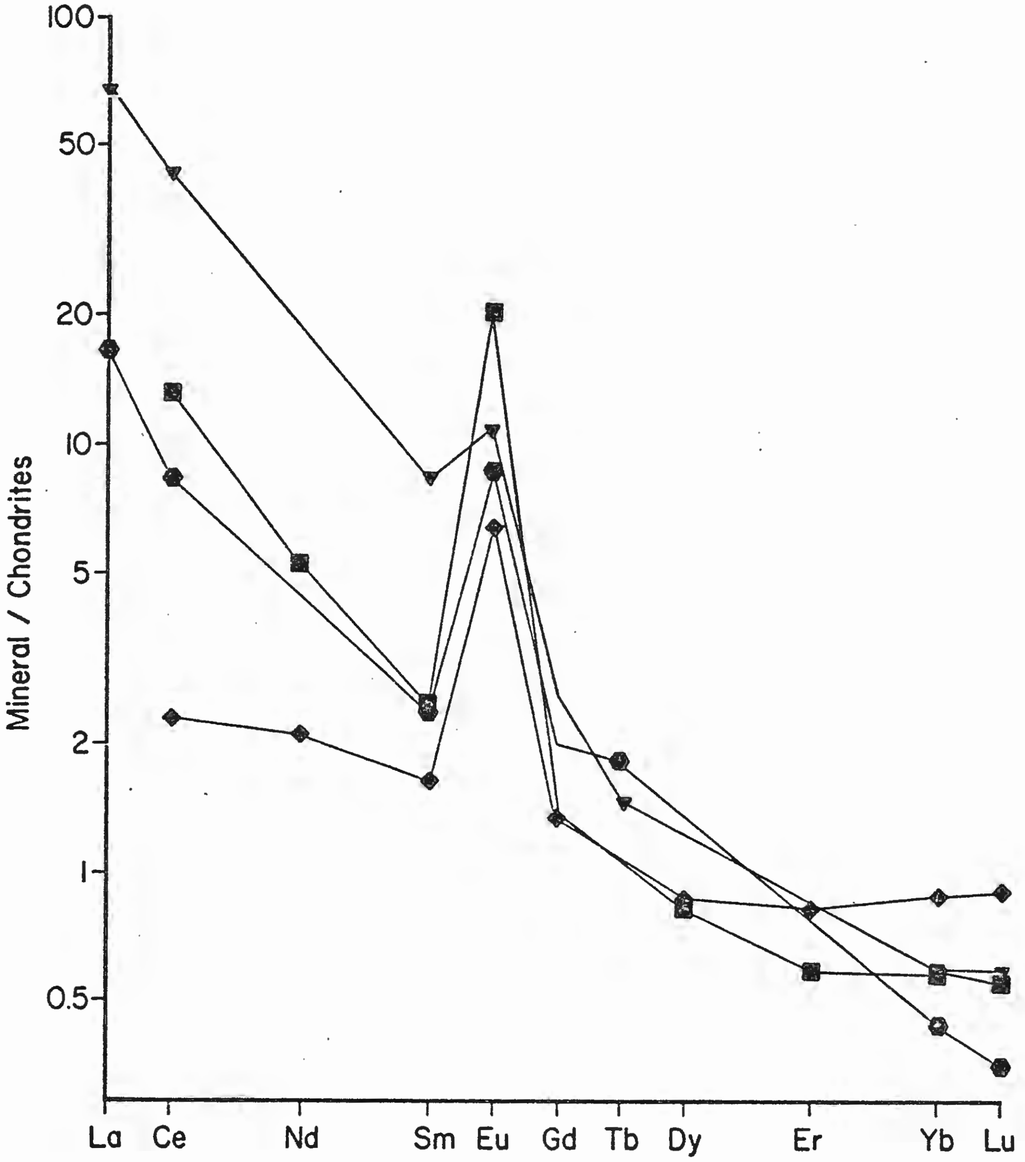


Fig. V-16 : Chondrite-normalized REE means for plagioclase from a granite (triangles), dacites (squares), Scourian granulites (hexagons) and basalt-andesites (diamonds).

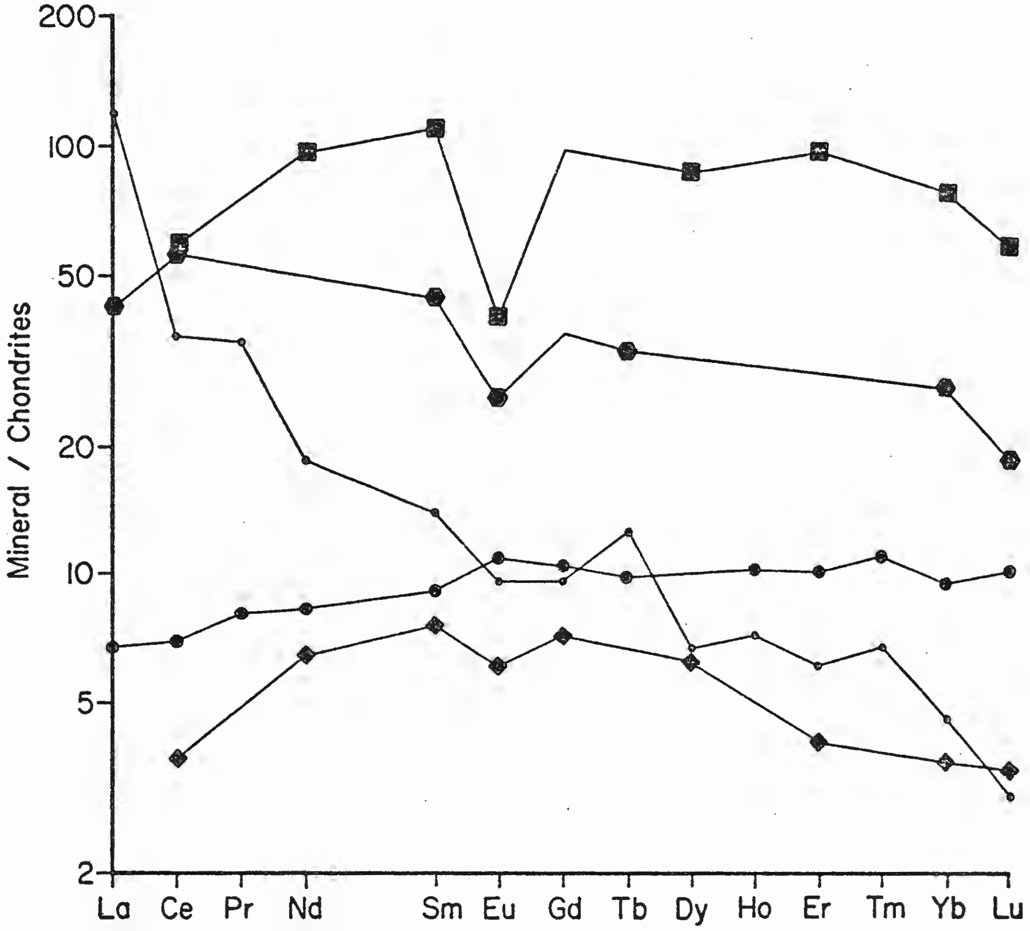


Fig. V-17 : Chondrite-normalized REE means for hornblendes from dacites (squares), Scourian granulites (hexagons), a lherzolite xenolith (small circles), basalt-andesites (diamonds) and the Lizard peridotite (large circles).

Eu anomalies. A hornblende mean from a lherzolite xenolith shows similar HRE abundances to the above two, but exhibits relative LRE enrichment. The dacite and Scourian hornblendes show very similar relative patterns, with slightly higher absolute concentrations for the dacite mean. Overall, the Scourian and dacite hornblendes have the highest absolute concentrations of REE.

Three garnet means are presented in Fig. V-18. The Scourian mean shows a pattern intermediate in absolute concentrations between the dacite and ultrabasic and eclogitic mean. The dacite means exhibits a large negative Eu anomaly versus a very small one for the Scourian garnet mean.

Thus, except for garnet, the Scourian minerals show REE distributions and abundances very similar to dacite phenocrysts (usually slightly lower in absolute abundances); but distinctly different from REE mineral patterns for basalt-andesites, rhyolites and ultrabasic rocks.

Mean REE K_D's of coexisting minerals from volcanic phenocrysts and ultrabasic rocks have been calculated, and are given in Appendix 4. They are compared to mean K_D's of coexisting Scourian minerals in Figures V-19 to V-23.

The patterns are very similar in general form for all rock types. In detail, the Scourian and dacite mineral pairs are usually very similar (e.g. Fig. V-19, V-20, V-21). The results for clinopyroxene-orthopyroxene pairs (Fig. V-20) show a striking similarity of patterns and abundances for the dacites, Scourian granulites and Lizard peridotite, with a maximum K_D at approximately Sm, and lower values for the LRE and HRE. Clinopyroxene-orthopyroxene pairs from basalt-andesites, however, show

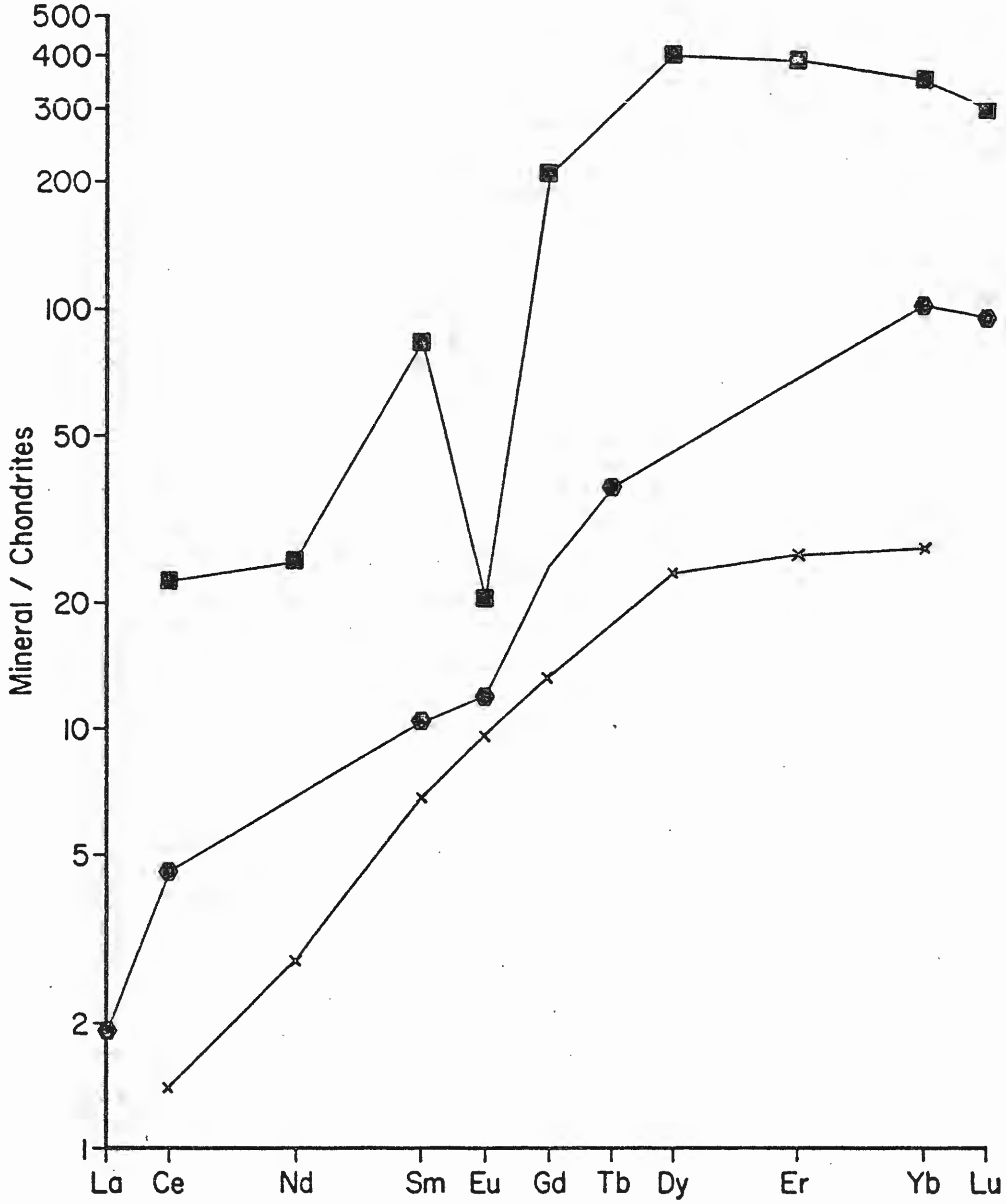


Fig. V-18 : Chondrite-normalized REE means for garnets from dacites (squares), Scourian granulites (hexagons) and ultrabasic and eclogitic inclusions (crosses).

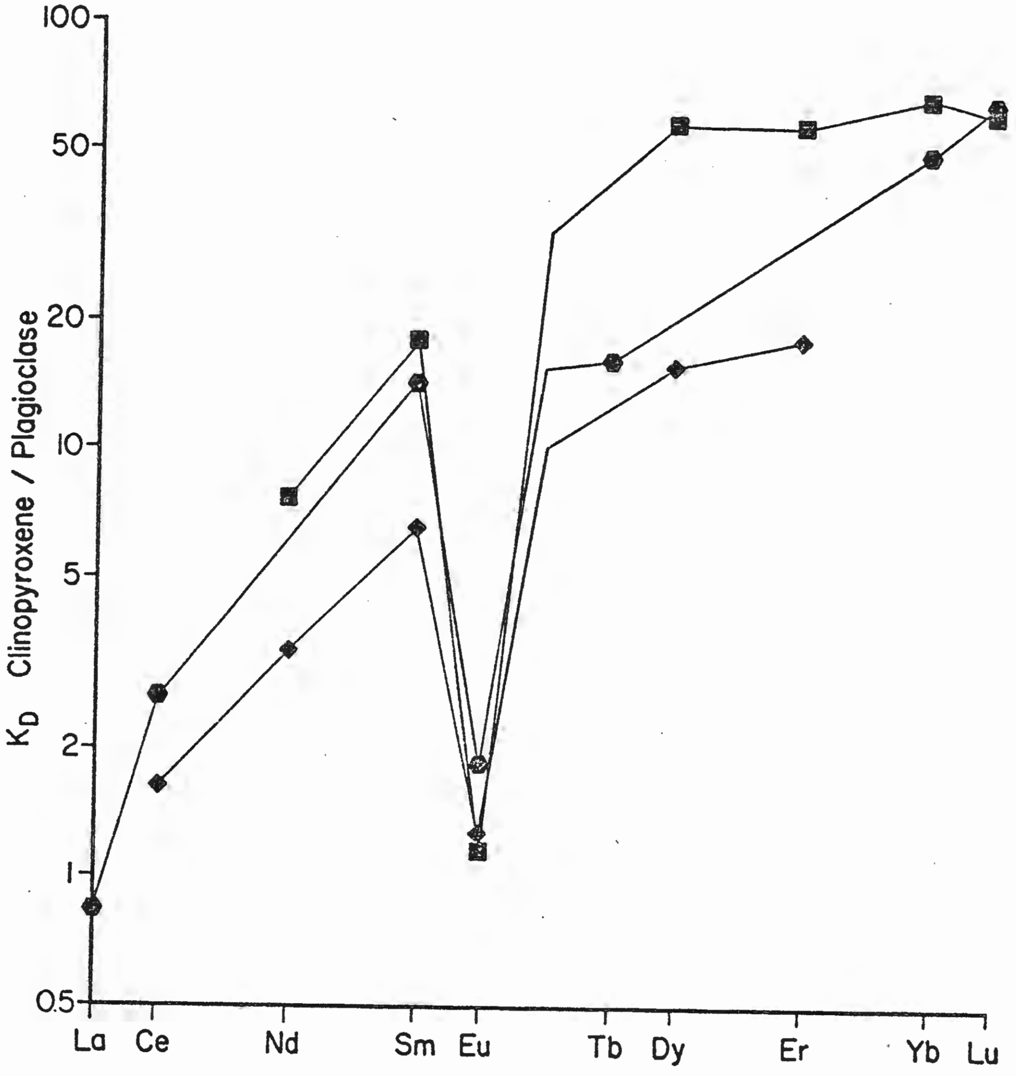


Fig. V-19 : Mean REE distribution coefficients for coexisting clinopyroxene/plagioclase pairs from dacites (squares), Scourian granulites (hexagons) and basalt-andesites (diamonds).

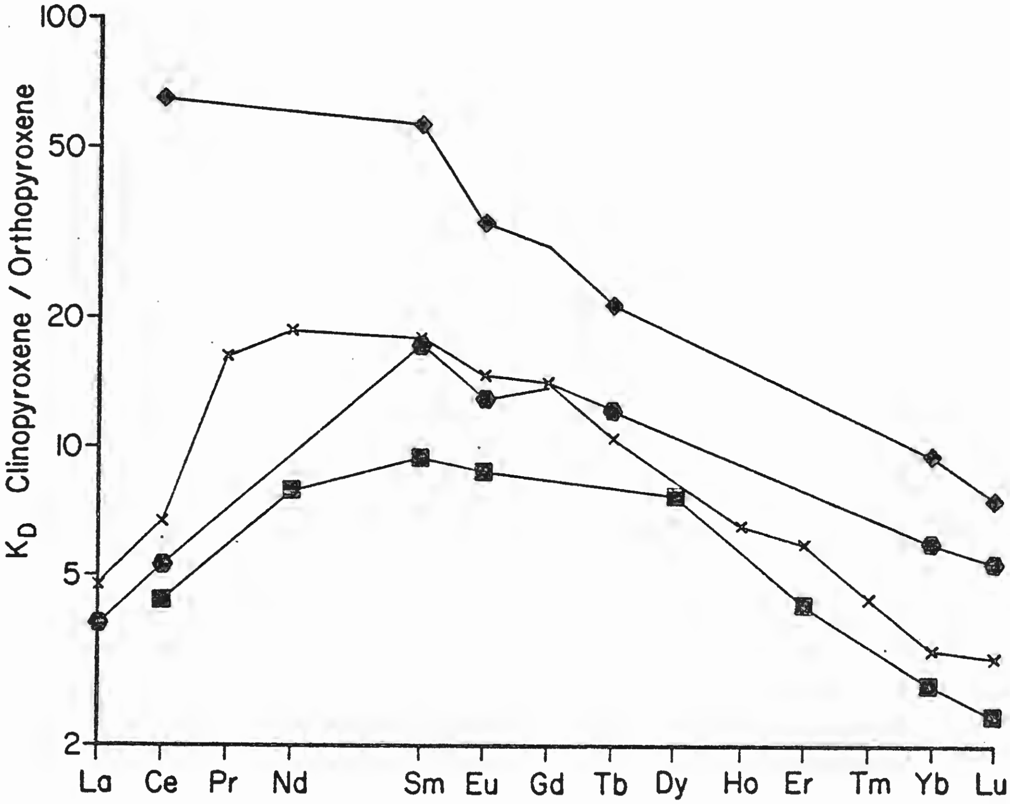


Fig. V-20 : Mean REE distribution coefficients for coexisting clinopyroxene/orthopyroxene pairs from basalt-andesites (diamonds), the Lizard peridotite (crosses), Scourian granulites (hexagons) and dacites (squares).

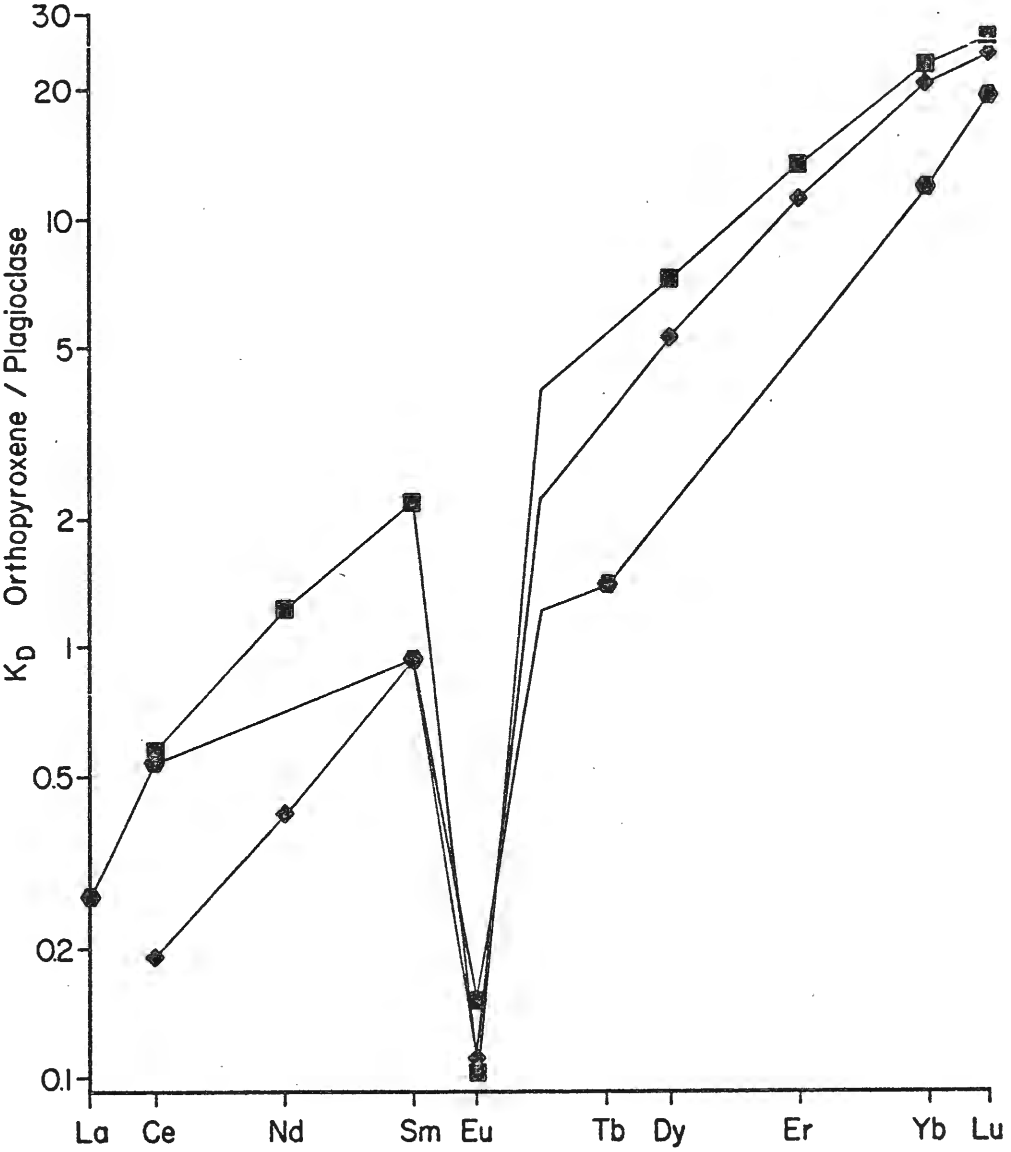


Fig. V-21 : Mean REE distribution coefficients for coexisting orthopyroxene/plagioclase pairs from dacites (squares) Scourian granulites (hexagons) and basalt-andesites (diamonds).

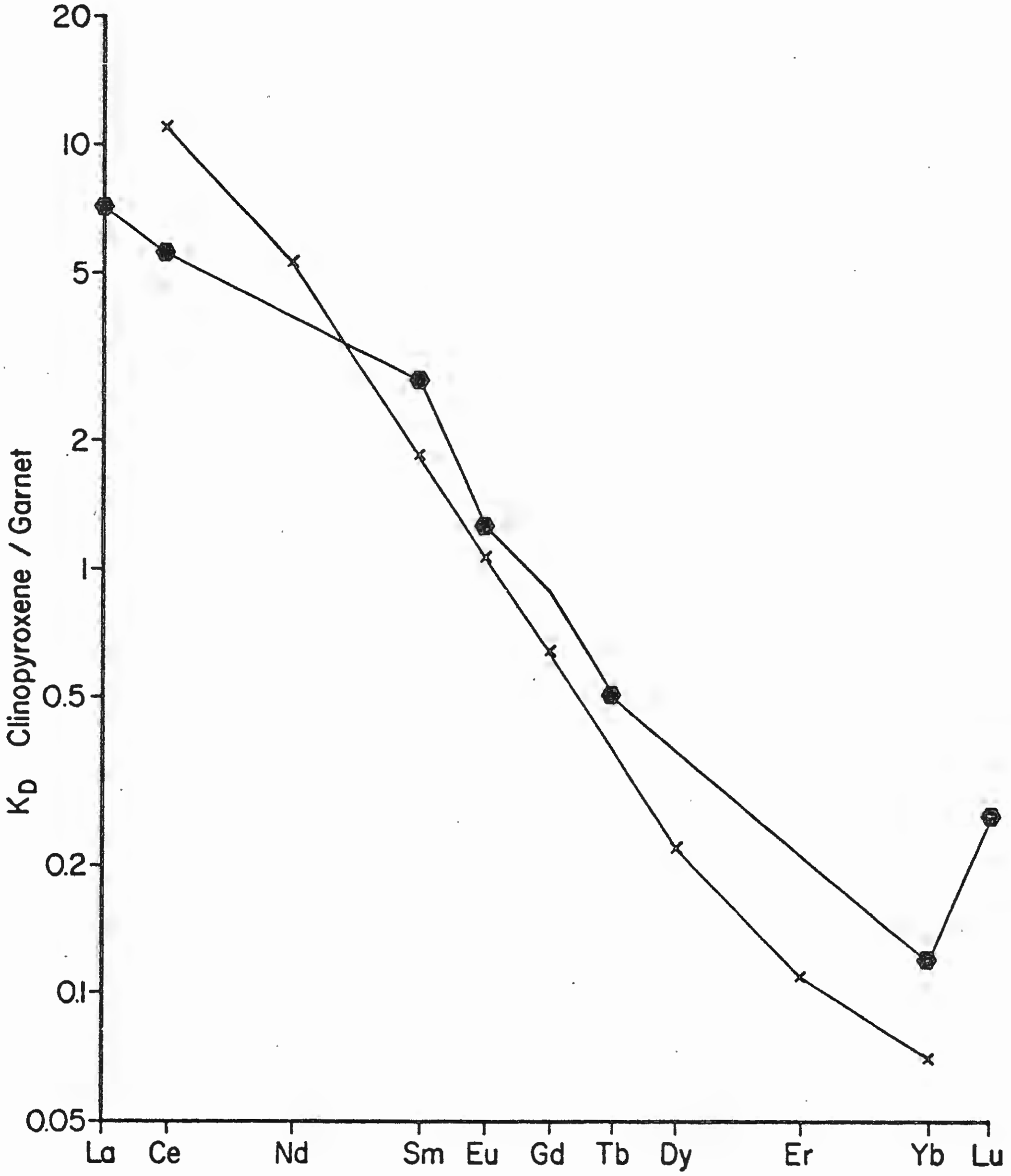


Fig. V-22 : Mean REE distribution coefficients for coexisting clinopyroxene/garnet pairs from the Scourian granulites (hexagons) and ultrabasic and eclogitic nodules (crosses).

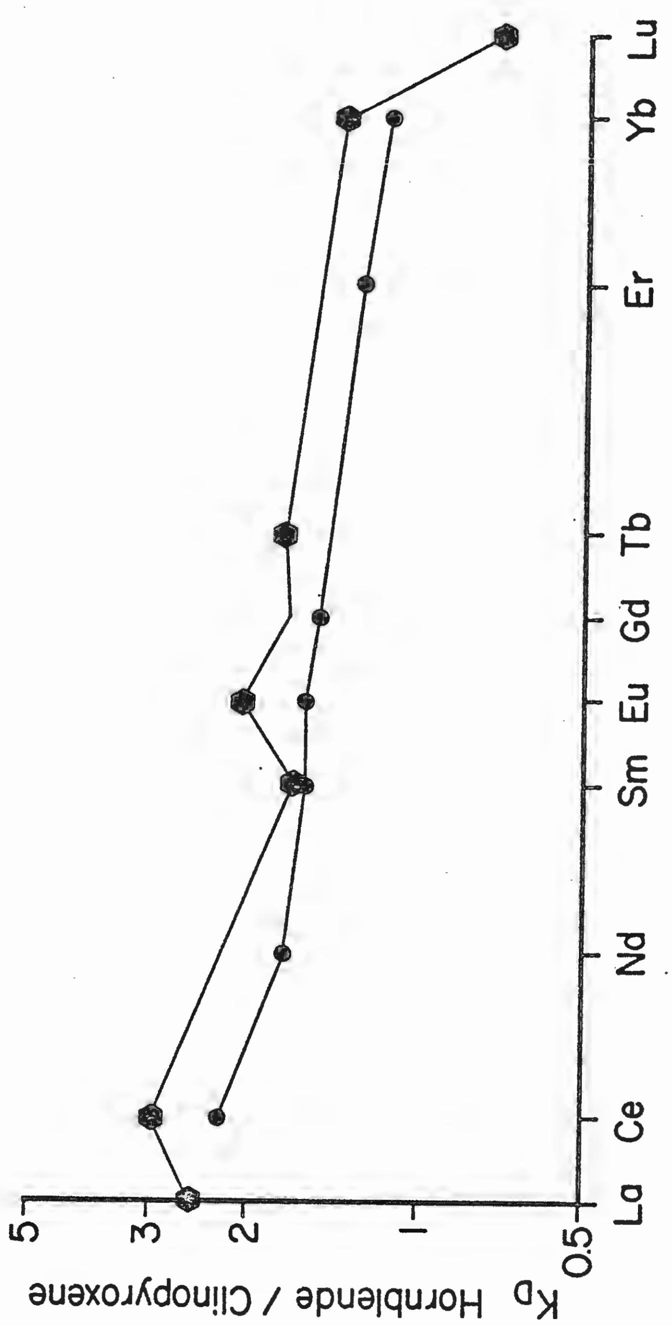


Fig. V-23 : Mean REE distribution coefficients for coexisting hornblende/clinopyroxene pairs from the Scourian granulites (hexagons) and lherzolite nodules (circles).

distinctly different patterns with maximum K_D values for the LRE, decreasing to Lu. The results of clinopyroxene-plagioclase (Fig. V-19) and orthopyroxene-plagioclase (Fig. V-21) pairs show the strong partitioning of Eu into the plagioclase structure for all rock types.

In considering the REE mineral data, the question arises as to whether the similarities in REE abundances, distributions and K_D's between dacites and granulite mineral phases are purely fortuitous or do they represent some form of genetic link? The REE results for the whole rock data (presented in the previous chapter) suggested the possibility that the Scourian complex may be the residuum after genesis of melts of the granodiorite to granite family. If such is the case, it might be expected that the Scourian mineral phases would show evidence of having equilibrated with a melt of approximately granodioritic composition. Since dacites are the extrusive equivalents of granodiorites, the Scourian mineral data are compatible with such an origin. There is also the possibility, however, that the observed Scourian REE patterns are mainly the result of "closed-system" metamorphic recrystallization and equilibration. These and other aspects will be treated at greater length in the concluding chapter of the thesis.

Summary of the REE Mineral Data

Several important conclusions may be derived from the Scourian REE mineral results:

1) The REE appear to be located in regular lattice sites in the Scourian minerals.
2) The bulk of the REE are located in the major rock-forming

minerals of the Scourian gneisses.

3) All of the major Scourian rock-forming minerals except plagioclase show negative Eu anomalies. Plagioclase exhibits a ubiquitous large positive Eu anomaly.

4) The Scourian REE mineral patterns are similar in relative and, to a lesser extent absolute, abundances to volcanic phenocrysts of dacitic rocks.

5) The REE K_D's between coexisting Scourian phases show consistent patterns indicative of equilibrium distributions, and are similar to K_D's from other rock types, most notably dacites.

6) In contrast to volcanic rock sequences, there is no strong correlation (and limited variation) in the Scourian complex between REE mineral content and rock type. The maximum observed variation for a given element in a given mineral phase is approximately a factor of 5 (versus variations of greater than 2 orders of magnitude in volcanic phenocrysts).

Other Trace Elements

The abundances of the trace elements Sc, Cr, Co, Hf and Th in the Scourian minerals are given in Table V-9.

1) Scandium

Sc occurs as the 3^+ ion in nature, which has an ionic radius of 0.83Å (in six-fold coordination). It generally shows a close geochemical coherence to Fe^{2+} and Fe^{3+}, and to a lesser extent Y, Al, Ti and the HRE (Frondel, 1970). It is thought to preferentially enter the six-fold coordination sites in garnet and the pyroxenes. As a result, it tends

Table V-9: Trace Elements Sc, Cr, Co, and Th in Scourian Minerals.

Sample #	Mineral	Sc (ppm)	Cr (ppm)	Co (ppm)	Th (ppm)
65-18	Clinopyroxene	124	389	46.5	n.d.*
64-12		126	306	34.9	n.d.
65-33		86	331	43.5	n.d.
65-41		73	524	60.7	n.d.
66-11		101	571	91.8	n.d.
67-109		59	250	51.5	n.d.
67-30		171	n.a.**	53.7	n.d.
65-18	Orthopyroxene	31	123	71.6	n.d.
65-33		35	141	132	n.d.
65-165		47	222	116	n.d.
64-12		33	135	86.8	n.d.
67-30		35	11	98.2	0.57
67-109		18	993	101	0.20
65-18	Plagioclase	0.1	n.d.	0.5	n.d.
64-12		1.0	n.d.	4.5	0.08
65-33		0.5	n.d.	3.6	0.14
65-41		0.2	n.d.	1.0	0.11
65-165		0.2	n.d.	0.5	0.12
66-11		0.1	n.d.	1.0	0.30
67-30		0.2	n.d.	0.2	0.23
67-109		0.3	n.d.	0.6	0.10
65-33	Garnet	119	422	59.6	n.d.
65-41		118	583	70.1	n.d.
67-109		111	1,103	73.2	n.d.
65-165		196	369	47.1	n.d.
67-30		768	n.a.	47.6	n.d.
64-12	Hornblende	112	389	70.0	n.d.
67-109		49	1,781	79.5	n.d.
66-11	Scapolite	1.5	11.2	70.0	0.65
Ca 63A		n.d.	2.3	n.d.	0.56
67-30	Quartz	0.4	0.8	0.6	0.12

* n.d. = not detected.
** n.a. = not analysed.

to be concentrated in pyroxenes, amphiboles and garnets, and relatively depleted in feldspathic minerals (Frondel, 1970). The observed abundances in the Scourian minerals are consistent with this behaviour. Sc is highest in the clinopyroxenes (mean of 106 ppm), garnets (mean of 262 ppm), hornblendes (mean of 81 ppm), and orthopyroxenes (mean of 33 ppm). It shows very low abundances in plagioclase (less than 1 ppm), scapolite and quartz.

K_D's have been calculated for Sc for coexisting clinopyroxene-orthopyroxene pairs of the Scourian complex (Table V-10). They show a tight grouping about a mean value of 3.76 (Table V-10). In Fig. V-24, they are shown on a log-log plot with data for coexisting pyroxenes from the granulite facies charnockitic rocks of Kondapalli, India (Leelanandam, 1967). The Scourian and Kondapalli results are very similar in both absolute concentrations of Sc in the pyroxenes and in the observed K_D's. Equilibrium distributions, on such log-log plots (if not affected by compositional variables), are generally reflected by elongated clusters of points that roughly define straight lines (Albee, 1965; Leelanandam, 1967). The observed trend for the Scourian and Kondapalli Sc values shows a close approach to an equilibrium distribution - although the rather narrow range of absolute Sc values for the pyroxenes and/or the limited number of data points prohibits a more accurate determination of the slope of the line.

2) Chromium

Cr^{3+} has an ionic radius of 0.70 Å and is known to readily substitute for Al^{3+}, Fe^{3+} and Fe^{2+} in ferromagnesium minerals (Matzat and Shiraki, 1970). The observed abundances in the Scourian minerals are

Table V-10: Distribution coefficients (K_D's) of Scourian clinopyroxene/orthopyroxene pairs for Sc, Cr and Co.

Sample No.	K_D (Sc)	K_D (Cr)	K_D (Co)
65-18	4.05	3.16	0.65
64-12	3.83	2.27	0.40
65-33	2.49	2.35	0.33
67-109	3.45	(0.25)*	0.51
67-30	4.96		0.55
Mean	3.76	2.59	0.49

* not used in mean calculation.

to 140 ppm range; whereas, in the plagioclases it is less than 5 ppm (Table V-9).

Co K_D's have been calculated for coexisting Scourian clinopyroxene-orthopyroxene pairs (Table V-10) and are compared to results from the Kondapalli and Madras charnockites in Fig. V-26. The Co K_D's do not show as strong a straight-line relationship as Sc or Cr on the log-log plot - probably due to the limited range of absolute concentrations in the pyroxenes. The Scourian K_D's show a strong clustering around a value of 0.49, suggestive of an equilibrium distribution.

Thus, the Sc, Cr, and Co K_D's for coexisting Scourian pyroxenes generally show a tight grouping, similar to isofacial charnockitic rocks of India. These results are consistent with the previously discussed REE distributions in indicating equilibration between the Scourian pyroxenes with respect to their trace elements.

4) Hafnium and Thorium

Hf was observed to be very low in abundance in the Scourian rocks (Chapter 4). The small observed fluctuations in the whole rock Hf concentrations were concluded to be the result of variable accessory zircon. Hf was not detected in any of the analysed Scourian minerals, confirming the above postulate.

Similarly, Th is very low in abundance in the Scourian rocks and was not detected in many of the Scourian minerals, except for 2 orthopyroxenes, plagioclase, scapolite and quartz (Table V-9). As with Hf, most of the observed whole rock Th is probably located in accessory phases such as zircon.

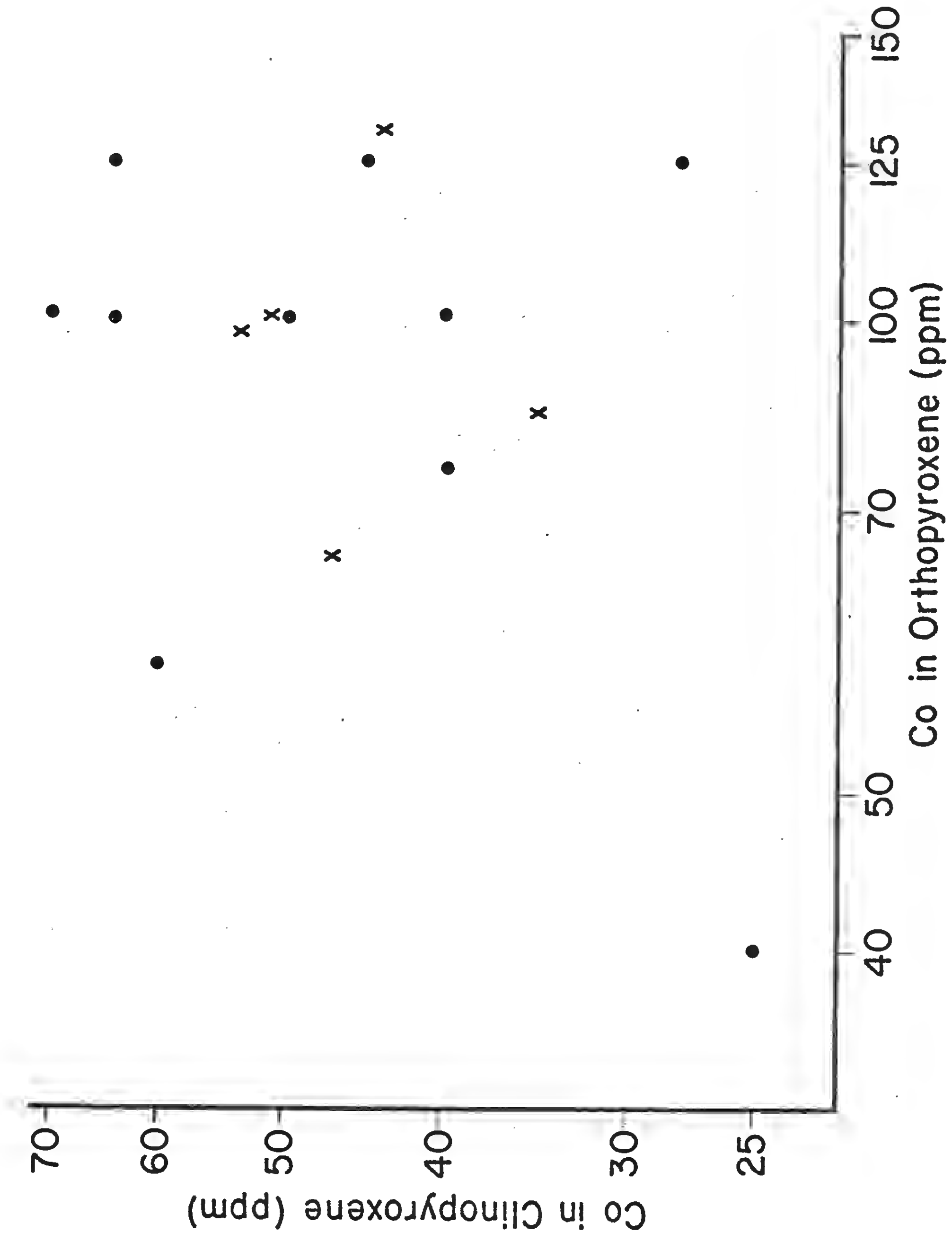


Fig. V-26 : Log-log plot of Co for coexisting clinopyroxene/orthopyroxene pairs from the Scourian complex (crosses) ,and the Kondapalli and Madras charnockites ,India (circles) (Leelanandam ,1967).

CHAPTER 6

Granitoid Rocks of the Scourian Complex

Introduction

As discussed in Chapter 2, rocks of the granite family are rare in medium-to high-pressure granulite facies terrains, possibly due to a previous history involving partial melting and extraction of melts which would particularly affect rocks of granitic composition. Nonetheless, granitic rocks have been reported from several medium-to high-pressure granulite facies terrains (e.g. Heier, 1973), including the Scourian complex (e.g. O'Hara, 1965; Muecke, 1969; Evans and Lambert, 1974; Holland and Lambert, 1975). In such cases, however, they usually make up only a small portion of the terrain, and because of this, they are often only briefly mentioned.

In this chapter, the results of a more detailed investigation of the Scourian granite sheets and pegmatites are presented. The origin of these granitic rocks is considered in terms of field relationships, petrology, and major and trace element chemistry including the REE.

Occurrence and Petrology of the Granite Sheets

The granites occur as generally concordant sheets, occasionally with 1 to 2 cm. wide off-shoot veins cross-cutting the surrounding gneisses. Although not a large part of the terrain by volume, they occur in all rock types of the Scourian complex, including the amphibolitized gneisses of the Inverian shear zones. The locations of the analysed sheets are given in Fig. V1-1.

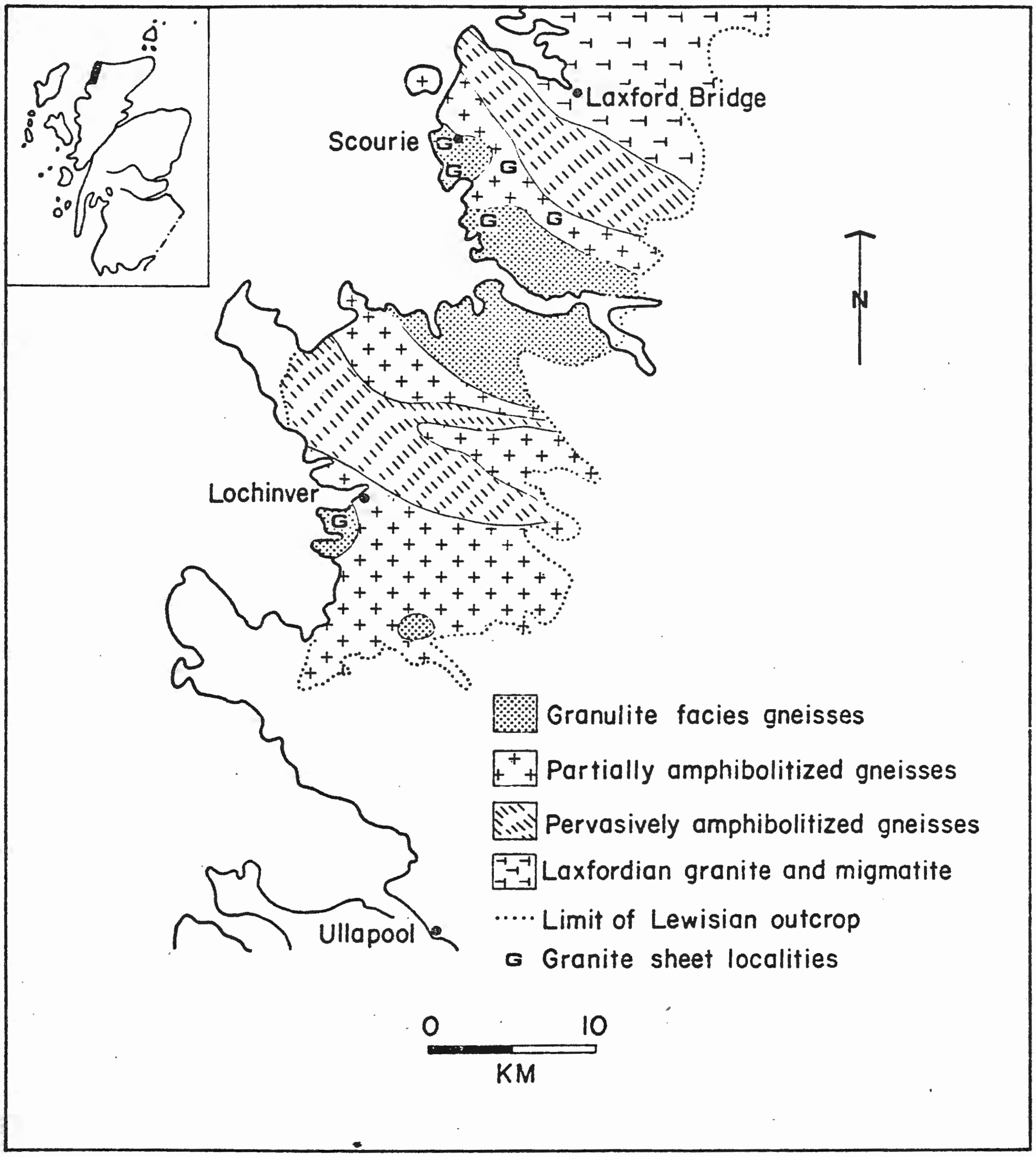


Fig. VI-1 : Location map of analyzed Scourian granite sheets.

They vary in width from a few metres to over 10 metres, and have been traced along strike several hundred metres. They are generally fine-to medium-grained pink rocks (although they may also be pegmatitic in places), containing occasional streaks of secondary chloritic material. They usually exhibit a granular texture. The granite sheets and the host pyroxene granulite gneisses exhibit a common planar fabric as defined by the presence of platy quartz. Contacts with the surrounding gneisses are generally sharp; however, a narrow transition zone is sometimes present.

The granites consist essentially of an anhedral mosaic of quartz and mesoperthite. The degree of exsolution observed in this mesoperthite phase is a function of the intensity of alteration. The feldspars form a distinct string perthite in the relatively unaltered pyroxene granulites. In slightly more altered gneisses, broad wavy interlayers of plagioclase and K-feldspar are observed. The granite sheets in the Inverian shear zones exhibit separate plagioclase and K-feldspar grains - apparently representing complete recrystallization. The presence of an exsolved ternary feldspar phase (Fig. V1-2) is indicative of a high temperature of formation ($>700^{\circ}C$) at low partial pressures of H_2O (O'Hara, 1965; Muecke, 1969). This feature, when combined with the common planar fabric of the granites and their hosts as defined by the presence of lenticular quartz, indicates their formation prior to or during granulite facies metamorphism.

Major Element Chemistry

Major element chemistry and CIPW norms of the 7 analysed granite sheets are presented in Table V1-1. They exhibit a strikingly uniform

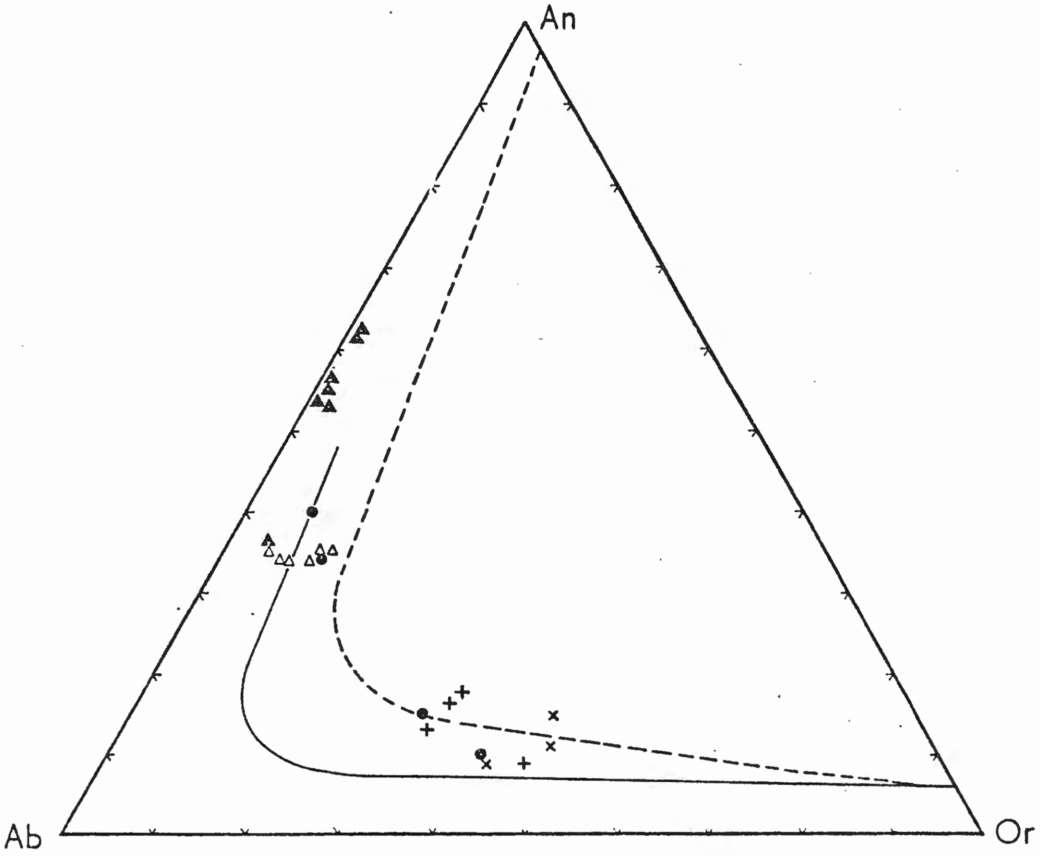


Fig. V1-2 : Plot of plagioclase and ternary feldspars on the Ab-Or-An diagram, including Scourian plagioclases (solid triangles), calculated Scourian plagioclase compositions (open triangles; Muecke, 1969), ternary feldspars from granite gneisses (solid circles; O'Hara, 1965), ternary feldspars from Langoy (vertical crosses; Heier, 1960), ternary feldspars from arendalites (oblique crosses; Heier and Taylor, 1959), ternary feldspar solvus at 900°C and 500 bars water pressure (solid line; Hamilton, 1966). From Muecke, 1969.

chemistry, although they occur in a wide variety of host rocks and come from widely scattered localities within the Scourian complex (Fig. Vl-1). They are notably enriched in K_2O (3.36 to 4.83%) compared to the felsic to mafic gneisses (which generally contain < 1% K_2O), and low in CaO--reflected in low anorthite in the norm (Table Vl-1).

On an albite-orthoclase-quartz diagram (Fig. Vl-3), they plot near the low pressure, water-saturated granite minimum in the haplogranite system, (i.e. no anorthite component). Increasing the anorthite component, moves the minimum away from the albite apex towards the quartz-orthoclase side. Increasing the partial pressure of H_2O moves the minimum towards the albite apex. For comparative purposes, two granite minima are presented in Fig. Vl-3 - the minimum in the haplogranite system at 2000 bars H_2O, and the minimum in the granite system with 5 per cent anorthite at 1000 bars H_2O. The Scourian sheets plot very close to the minimum at 2000 bars H_2O. If these granites had formed by partial melting under a different $P\text{-}T\text{-}P_{H_2O}$ regime than that of Scourian metamorphism during the progressive regional metamorphism of the Scourian complex (assuming the Scourian rocks had such a history), it is conceivable that they would plot in the low-pressure, water-saturated, granite minimum. If such were the case, however, it seems unlikely that they would have survived the subsequent severe conditions of Scourian granulite facies metamorphism without melting. On the other hand, if they formed by partial melting under conditions of granulite facies metamorphism, it seems curious that they plot in the low pressure, water-saturated granite minimum. This aspect will be discussed further in a later section.

Table Vl-1: Major Element Analyses and CIPW Norms of Scourian Granite Sheets

Sample No.	67-117	65-190	65-198	M-19	CRE 474	5	79	Mean of 7 Arkoses (Pettijohn, (1957).	Mean of 2 Meta-Arkoses (Barooah, 1970).
$Si0_2$	74.93	75.65	76.34	74.22	75.95	76.42	76.03	76.37	75.60
$Ti0_2$	0.08	0.07	0.15	0.11	0.06	0.21	0.12	0.41	0.00
Al_20_3	13.88	14.18	12.38	14.36	13.28	13.59	13.31	10.63	14.00
Fe_20_3	0.68	0.33	0.92	0.70	0.40	0.09	0.00	2.12	0.18
Fe0	0.00	0.13	0.29	0.29	0.12	0.39	0.42	1.22	0.33
Mn0	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.25	0.02
Mg0	0.30	0.25	0.28	0.37	0.20	0.17	0.19	0.23	0.17
Ca0	1.05	1.35	0.78	1.47	0.91	1.21	0.33	1.30	1.36
Na_20	4.31	4.54	3.65	3.85	3.96	3.46	3.81	1.84	3.46
K_20	4.31	3.36	4.65	4.30	4.55	4.23	4.83	4.99	3.95
P_20_5	0.02	0.02	0.02	0.03	0.01	0.01	0.01	0.83	0.01
H_20+	0.22	0.14	0.28	0.15	0.15	0.27	0.27	0.21	0.01
H_20-	0.07	0.13	0.19	0.07	0.12	0.14	0.06		
Total	99.86	100.21	99.95	99.93	99.72	100.21	99.39	100.40	100.09
Q	30.84	33.18	35.47	31.83	33.45	37.19	34.46		
Or	25.60	19.89	27.65	25.51	27.06	25.07	28.46		
Ab	36.62	38.44	31.04	32.67	33.69	29.33	32.54		
An	5.10	6.57	3.67	7.12	4.47	5.95	1.59		
Di	0.00	0.06	0.07	0.00	0.00	0.00	0.00		
Hy	0.75	0.62	0.67	0.92	0.50	0.76	1.07		
Mg	0.00	0.25	0.57	0.65	0.25	0.13	0.00		
Hm	0.68	0.21	0.53	0.25	0.23	0.00	0.00		
Il	0.02	0.13	0.29	0.21	0.11	0.40	0.23		
Ru	0.07	0.00	0.00	0.00	0.00	0.00	0.00		
Ap	0.05	0.05	0.05	0.07	0.02	0.02	0.02		
C	0.26	0.67	0.00	0.77	0.21	1.14	1.25		

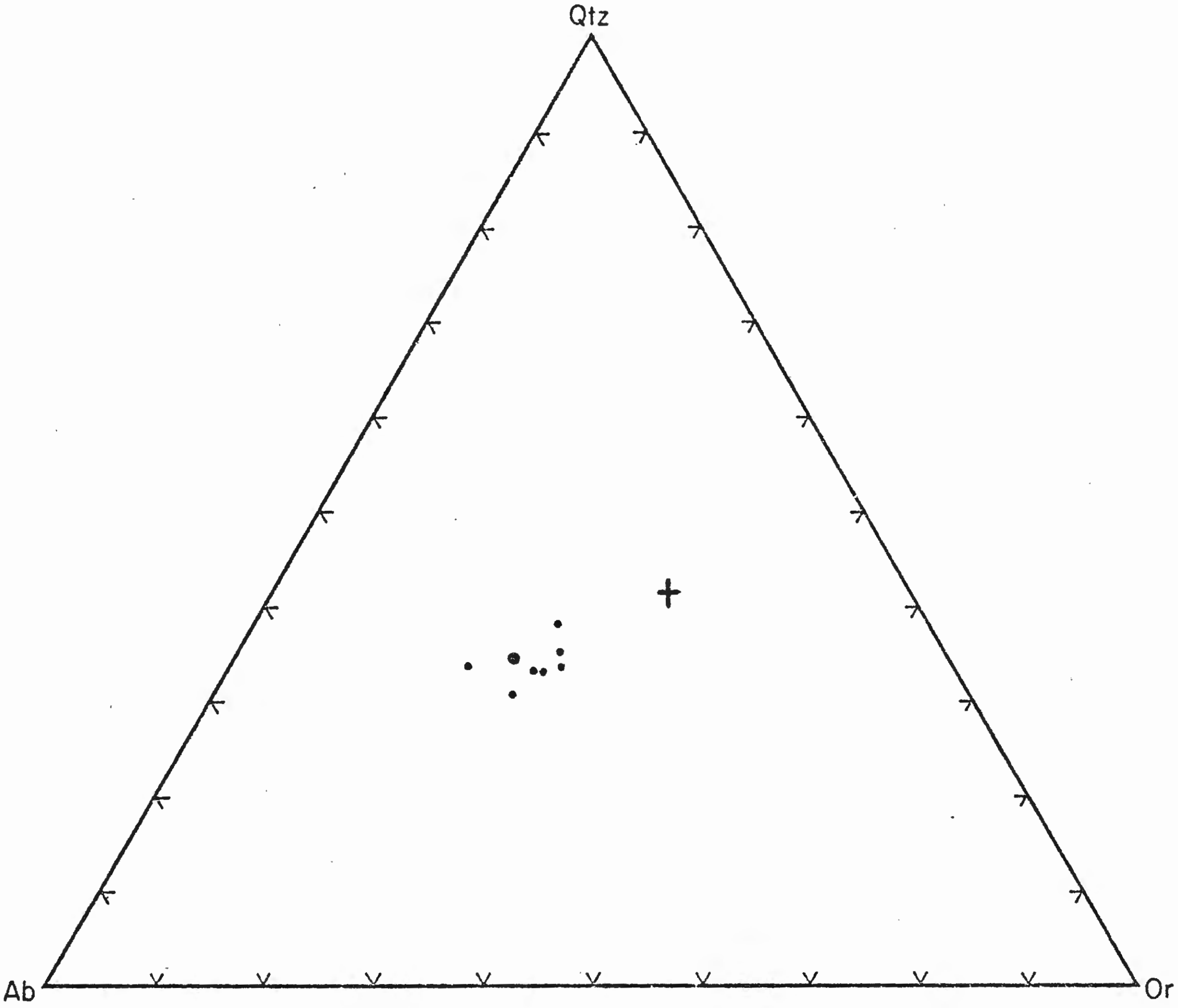


Fig. Vl-3 : Ab-Or-Qtz plot of Scourian granite sheets(small circles), the granite minimum(large circle) at $P_{H_2O} = 2000$ bars (Winkler, 1974), and the granite minimum (cross) at $P_{H_2O} = 1000$ bars and 5 per cent anorthite content (James and Hamilton, 1969).

K/Rb Ratios

K/Rb ratios for the granite sheets and the surrounding pyroxene granulites are presented in Fig. V1-4, together with Shaw's (1968) main trend for normal upper crustal igneous rocks.

The values for the granite sheets range from approximately 500 to 1400 - distinctly higher than the main trend (which includes "normal" granites), but similar to and overlapping the range of K/Rb ratios observed in the surrounding granulite facies gneisses, and indeed medium - to high pressure granulite facies terrains in general (see Chapters 2 and 3).

Heier and Brunfelt (1970) reported a similarly high K/Rb ratio (609) for a "young red granite" from a granulite facies terrain in Norway. It was interpreted as being formed by anatexis of the surrounding gneisses at a late stage in the granulite facies metamorphism (Heier and Brunfelt, 1970; Heier, 1960).

REE Geochemistry

REE results for the 7 granite sheets are presented in Table V1-2. Chondrite-normalized graphs (Fig. V1-5) exhibit low absolute concentrations of REE, LRE enrichment and large positive Eu anomalies, reflected by Eu/Eu* ratios of 2.51 to 11.3. The chondrite-normalized REE range for the granite sheets is shown in Fig. V1-6 along with the range of a granite composite based on three other granite composites given in Haskin et al, (1968). The Scourian granites are much lower in absolute concentrations of REE than normal granites, and are distinctive in having large positive Eu anomalies versus negative Eu anomalies for normal granites (Fig. V1-6; Koljonen and Rosenberg, 1974). In fact, their REE patterns are unique for granitic rocks with the exception of

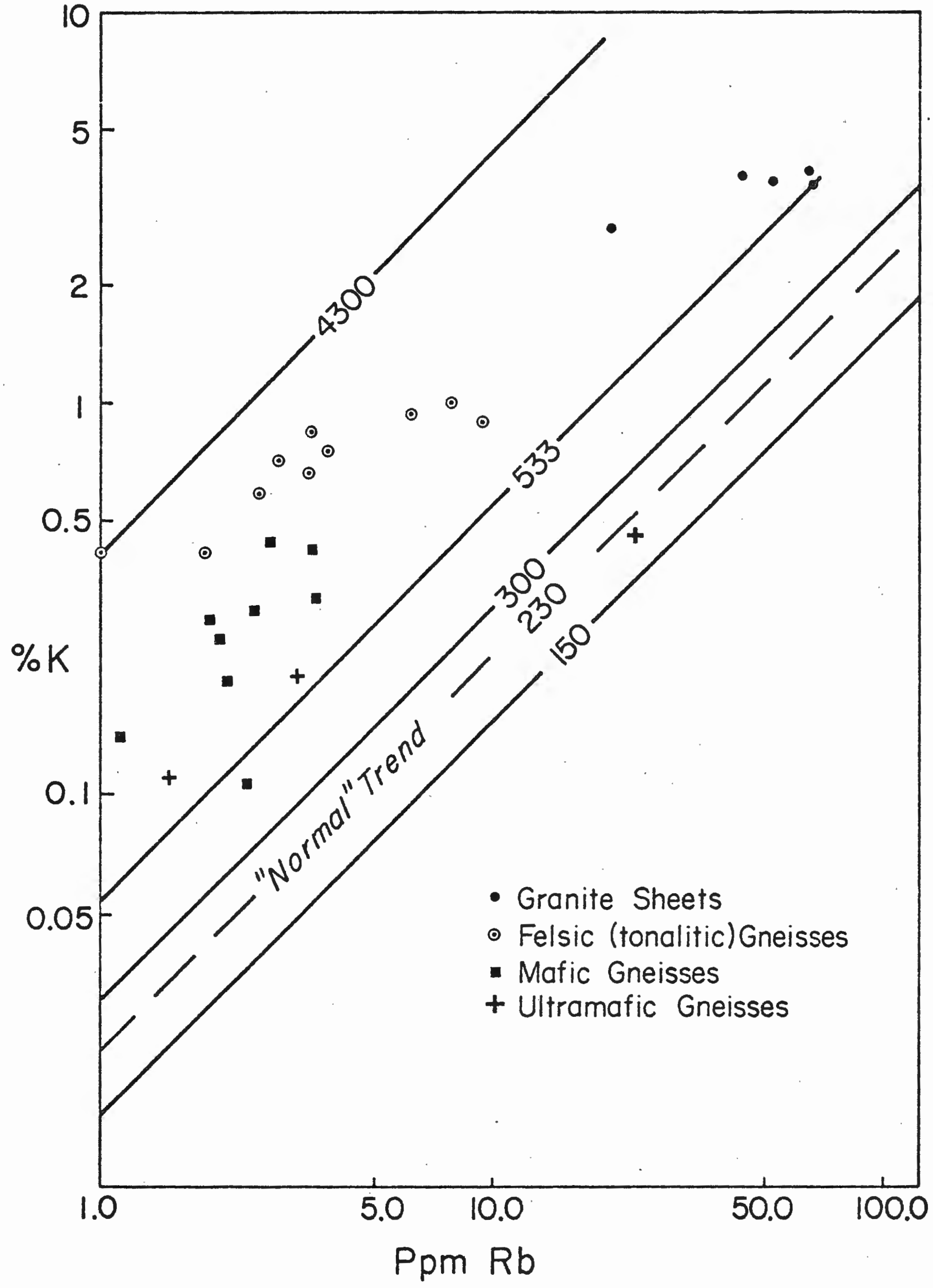


Fig. V1-4 : K versus Rb for Scourian gneisses and granite sheets. Normal trend is from Shaw (1968).

Table Vl-2: Trace Element Analyses of Scourian Granite Sheets

Sample No.	65-190	CRE 474	67-117	65-198	M-19	79	5
Ppm							
La	6.13	12.6	16.2	9.01	14.1	10.0	11.6
Ce	8.23	14.6	21.2	13.1	19.2	16.1	16.6
Sm	0.18	0.36	0.65	0.59	0.58	0.28	0.26
Eu	0.66	1.15	0.72	0.89	0.80	0.36	0.52
Tb	0.03	0.07	0.08	0.16	0.10	0.15	0.15
Yb	0.09	0.15	0.17	0.73	0.21	0.57	1.40
Lu	0.009	0.06	0.03	0.12	0.03	0.16	0.24
REE	15.3	29.0	38.9	24.6	35.0	27.6	30.8
Eu/Eu*	11.3	9.02	3.56	3.84	4.08	2.51	3.77
La/Yb	68	84	95	12	67	18	8.3
K/Rb***	1,357	864	533	605	660	n.a.*	n.a.
Sc	0.48	0.6	0.44	1.04	1.13	1.36	2.68
Cr	24.4	18.3	20.7	24.9	21.9	n.d.**	n.d.
Co	1.34	0.90	0.55	2.10	1.27	n.a.	n.a.
Hf	n.a.	2.4	1.9	1.40	1.9	n.d.	0.6
Th	n.a.	2.33	0.21	0.21	2.33	n.d.	2.06

* n.a. = not analysed

** n.d. = not detected

*** data from Muecke, 1969.

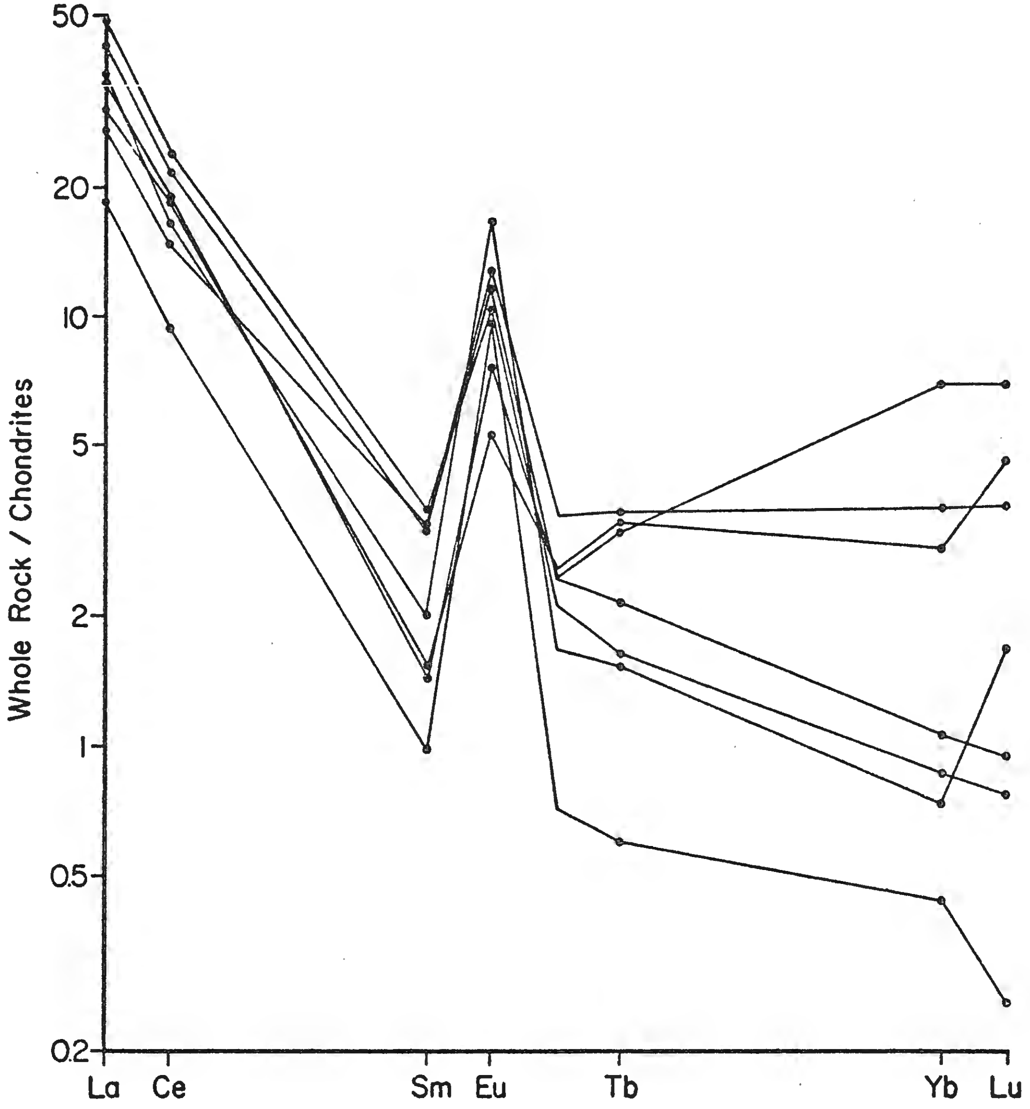


Fig. VI-5: Chondrite-normalized REE graphs of Scourian granite sheets.

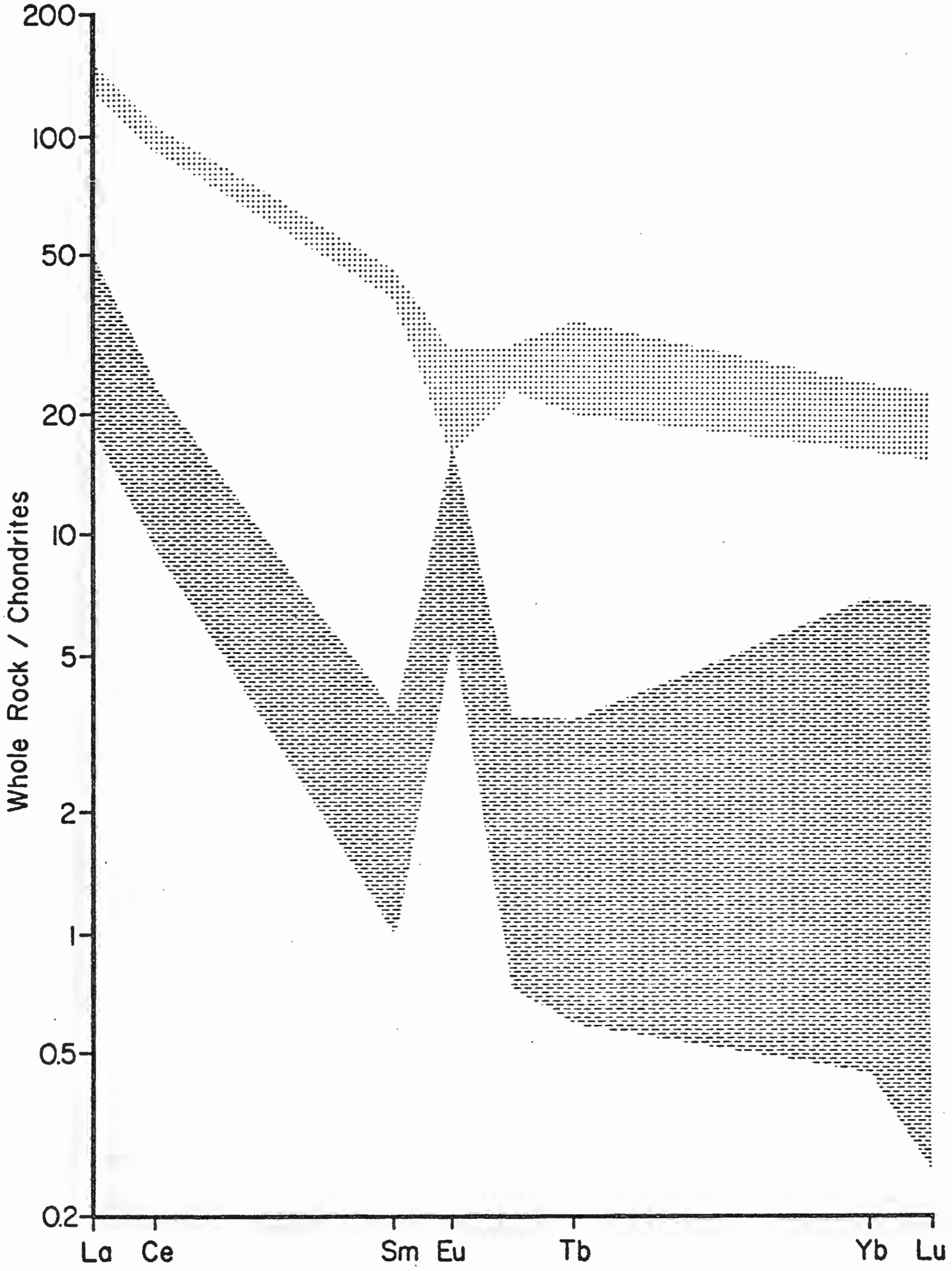


Fig. V1-6 : Chondrite-normalized REE range for the Scourian granite sheets (lower) compared to a granite composite (Haskin et al., 1968).

some granitic veins reported by Hanson (1975) from the Morton and Montevideo gneisses of the Minnesota River valley.

In Fig. V1-7, a mean plagioclase REE pattern from the pyroxene granulites (obtained from results in Chapter 5) is plotted with the REE range for the granite sheets. It appears, from this diagram, that the REE chemistry of the sheets reflects mainly the feldspar chemistry. The same is probably true for the K/Rb ratios. This last statement finds support in Shaw's (1968) review of K/Rb fractionation - where plagioclase was observed to have variable K/Rb ratios as high as 2100.

Compared to the felsic gneisses (Fig. V1-8), the granite sheets are depleted in REE, except Eu and possibly Yb and Lu.

Pegmatites

The pegmatites of the Scourian complex occur as dyke-like bodies, a few centimetres to a few metres in width, and up to several tens of metres long. They are coarse-grained rocks (1 to 2 cm) with a graphic granite texture, composed mainly of microcline and quartz, lesser plagioclase and biotite and very minor orthite and monazite (Evans and Lambert, 1974). Their major element chemistry is very similar to the granite sheets (Holland and Lambert, 1975). They clearly cross-cut Scourian structures but are deformed in the Inverian zones (Evans and Lambert, 1974).

Several workers have investigated the Sr^{87}/Sr^{86} ratios of these pegmatites (Holland and Lambert, 1975; Evans and Lambert, 1974; Evans, 1965, 1963; Giletti, et al., 1961). The isotopic data plot on 2 isochrons yielding ages of 2540 ± 20 m.y. and 2310 ± 40 m.y., and an initial ratio in both cases of approximately 0.7020 (Evans and Lambert, 1974). These ages are consistent

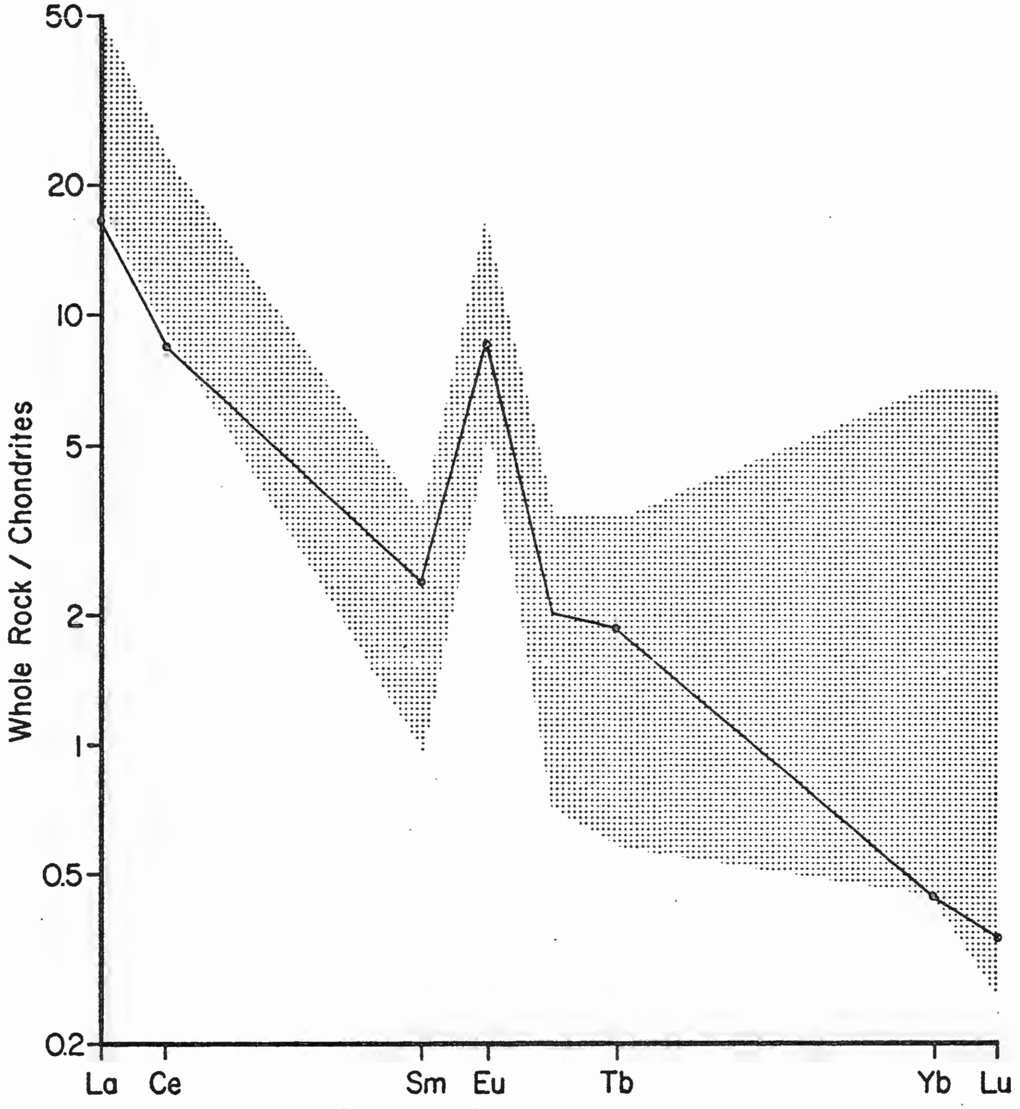


Fig. V1-7 : Mean plagioclase REE pattern from the Scourian pyroxene granulite gneisses compared to the REE range for the granite sheets.

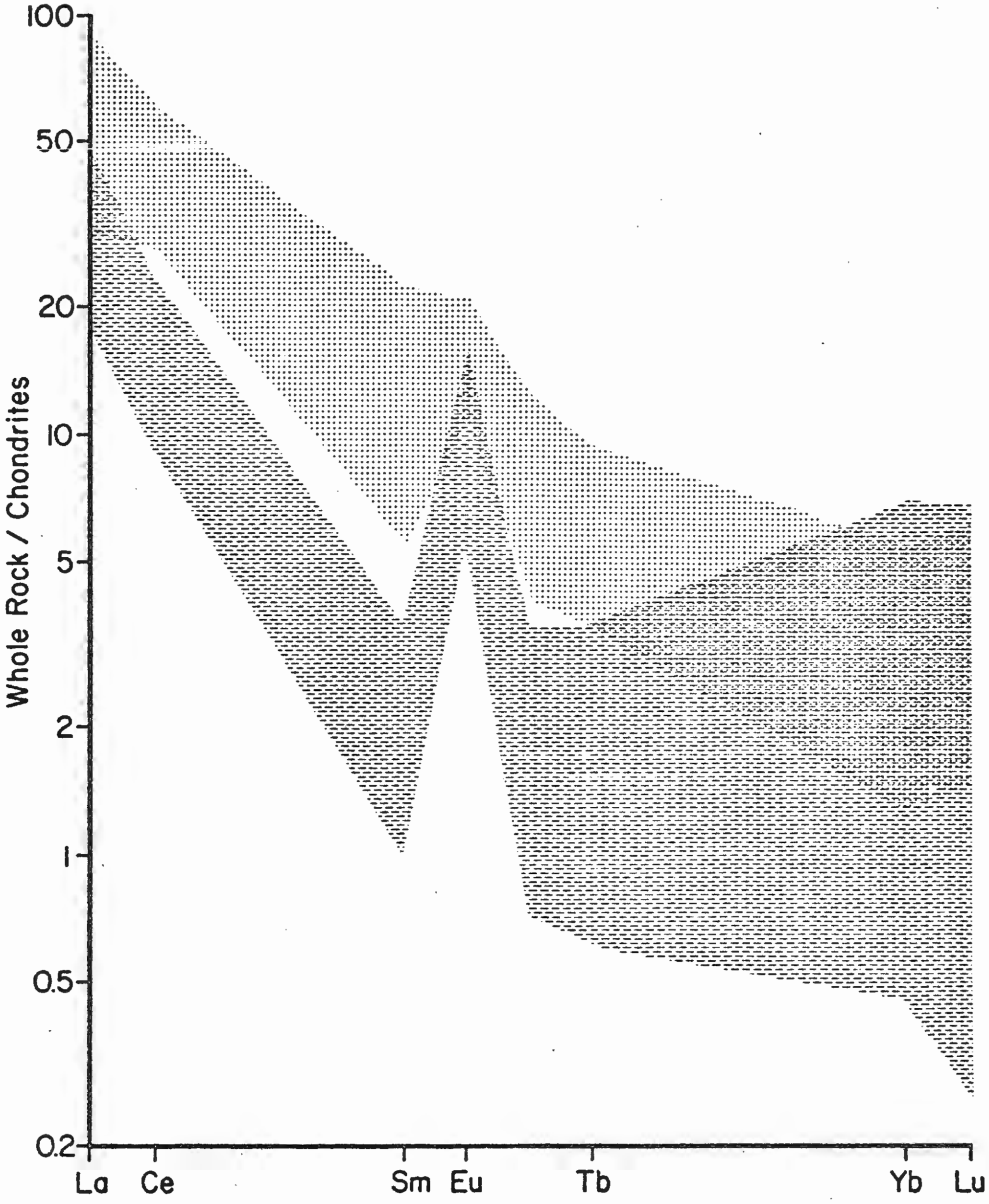


Fig. V1-8 : REE range for the Scourian granite sheets (lower) compared to the REE range for the Scourian felsic gneisses (upper).

with field evidence; that is, the pegmatites are post-Scourian (<2600 m.y.) and pre-Inverian (2310 to 2200 m.y.). Evans and Lambert (1974) noted that the low initial ratios are close to those of the Scourian gneisses (see Chapter 3), consistent with derivation of the pegmatites by anatexis of the Scourian gneisses. They also suggested that since the pegmatites plot on 2 isochrons, there were either 2 different periods of pegmatite intrusion or some of the pegmatites were affected by the Inverian event. Evans and Lambert (1974) noted the similarity with respect to Sr isotopes between a concordant granite gneiss and nearby pegmatite from the Loch Kirkaig area, which they thought may suggest a genetic link.

In an attempt to discover if a relationship exists between the conformable granite gneiss sheets and the latter cross-cutting pegmatites, 7 of the latter were analysed for the major elements and REE (Table Vl-3). With respect to the major elements, the pegmatites fall into two broad groups:

1. Potash-rich group: 4 of the pegmatites have K_2O greater than 7 per cent and K_2O/Na_2O ratios greater than 2.3.
2. Soda-rich group: 3 of the pegmatites have greater Na_2O than K_2O, with K_2O/Na_2O ratios less than 0.8.

Chondrite normalized REE graphs of the pegmatites are presented in Fig. Vl-9. The potash-rich group show REE patterns virtually indistinguishable from the concordant granite sheets, including the large positive Eu anomaly. The soda-rich group, however, yield quite different REE graphs. They have the highest absolute concentrations of REE (Table Vl-3) and either smaller positive Eu anomalies (80 and 65-196) than the potash-rich group, or a negative Eu anomaly (27). It is interesting to note here that the pegmatites exhibiting similar REE patterns to the granite

Table V1-3: Major and Trace Element
Data of Scourian Pegmatites

Sample No.	65-150	65-166	65-187	65-183	65-196	80	27
SiO_2	73.69	74.55	76.00	72.94	65.52	74.92	75.91
Al_2O_3	14.49	13.56	12.75	14.91	20.63	13.62	13.93
Fe_2O_3	0.00	0.00	0.00	0.00	0.21	0.76	0.17
FeO	0.11	0.24	0.26	0.17	0.31	0.59	0.47
MgO	0.01	0.06	0.11	0.08	0.33	0.17	0.23
CaO	0.20	0.36	0.29	0.23	2.08	1.17	1.22
Na_2O	2.45	3.11	2.06	2.45	8.39	4.20	4.43
K_2O	8.59	7.14	7.52	9.09	1.07	3.52	3.28
TiO_2	0.02	0.03	0.09	0.01	0.02	0.50	0.03
MnO	0.01	0.01	0.01	0.01	0.01	0.03	0.01
P_2O_5	0.01	0.01	0.01	0.01	0.01	0.18	0.01
CO_2	0.00	0.00	0.03	0.00	0.00	0.00	0.00
H_2O^+	0.47	0.60	0.55	0.51	0.98	0.77	0.65
H_2O^-	0.23	0.08	0.20	0.35	0.19	0.12	0.25
Total	100.27	99.75	99.88	100.76	99.75	100.55	100.59
Ppm							
La	7.45	8.90	11.0	10.2	30.1	39.2	17.3
Ce	8.00	11.5	10.6	11.3	44.7	79.5	37.5
Sm	0.25	0.44	0.22	0.34	0.90	3.98	1.78
Eu	1.39	0.94	2.63	1.59	1.19	1.52	0.33
Tb	0.02	0.06	0.14	0.06	0.13	0.36	0.41
Yb	0.10	n.a.*	0.38	0.23	0.35	0.74	2.00
Lu	0.02	0.02	0.04	0.04	0.03	0.14	0.33
Eu/Eu*	18.8	6.60	20.8	12.5	4.08	1.28	0.51
La/Yb	75	-	29	44	86	53	8.7
ΣREE	17	22	25	24	77	125	60
Sc	0.30	0.35	0.31	0.36	0.33	1.74	1.30
Cr	n.d.**	n.d.	3.35	n.d.	n.d.	4.41	n.d.
Hf	n.d.	n.d.	n.d.	n.d.	1.2	3.0	n.d.
Th	0.70	1.19	0.39	1.87	1.85	11.3	1.19

* n.a. = not analysed

** n.d. = not detected.

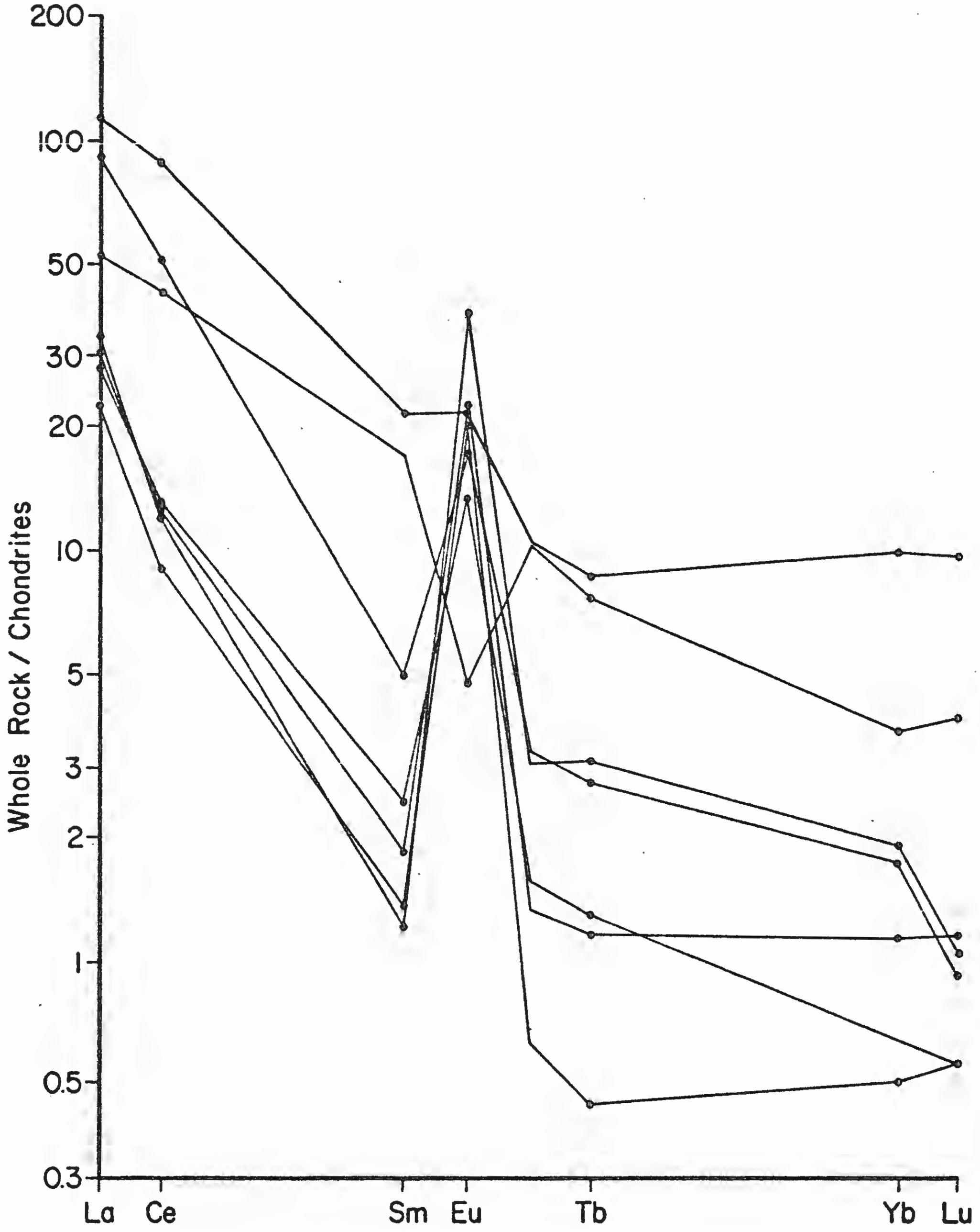


Fig. V1-9 : Chondrite-normalized REE graphs of Scourian pegmatites.

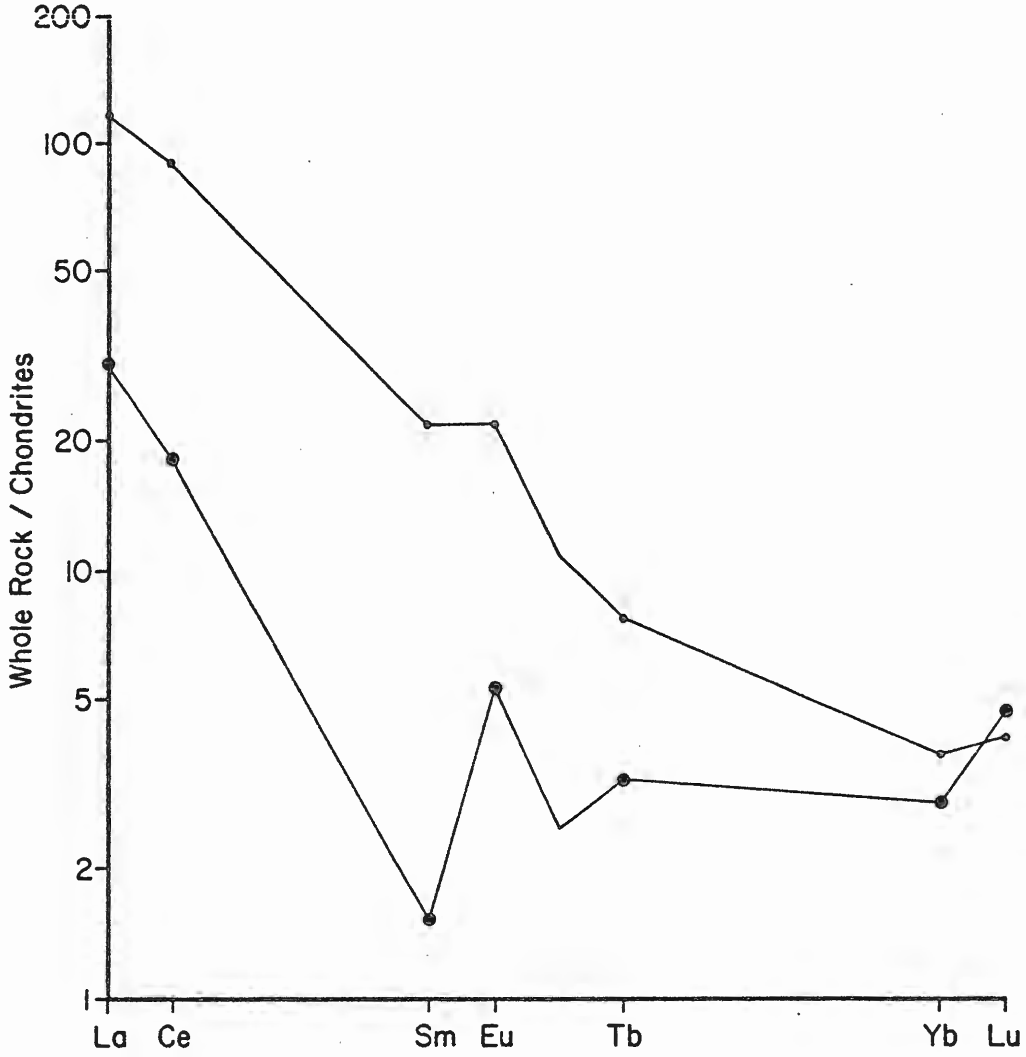


Fig. Vl-10 : Chondrite-normalized REE graphs of a concordant granite sheet (79; large circles) and a nearby cross-cutting pegmatite (80; small circles).

gneisses all come from the Loch Kirkaig area - the location with the isotopically similar pegmatite and granite gneiss mentioned earlier. The soda-rich pegmatites occur in the northern region around Scourie (Fig. V1-1).

These results strengthen the idea of Evans (Evans and Lambert, 1974) that there are at least 2 separate times of pegmatite intrusion, with perhaps different origins.

Discussion

The major features of the granite sheets may be summarized as follows:

1) They occur as concordant layers exhibiting a common planar fabric to the pyroxene-granulite hosts - an intimate part of a relatively dry, depleted granulite facies terrain.
2) K/Rb ratios are higher than normal upper crustal granites, but are similar to the surrounding granulites and to medium - to high-pressure granulite facies terrains in general.
3) The REE patterns are distinctive - much lower in absolute abundances than most granites, with large positive Eu anomalies versus negative Eu anomalies for other granitic rocks. Both the K/Rb ratios and REE chemistry of the granites resembles that of the feldspars in the surrounding gneisses.
4) The granites plot in the low pressure, water-saturated granite minimum.

Previous workers have interpreted these sheets as meta-arkoses (Barooah, 1970) and replacement pegmatites (Evans and Lambert, 1974). Barooah (1970) postulated a sedimentary origin for these rocks on the basis of a chemical similarity with Pettijohn's (1957) mean of 7 arkoses (Table Vl-1). Such evidence can hardly be considered relevant as virtually all rocks of the granite family show a similar resemblance to arkosic sediments which, by definition, are derived in large part from granites. Arkosic sediments have REE patterns similar in relative and absolute abundances to normal granites, including negative Eu anomalies (e.g. Nance and Taylor, 1976), and, therefore, are quite distinct from the granite sheets (e.g. sample 5, Table Vl-2, which is from Barooah's type locality). Furthermore, no other recognizable metasediments have been recorded from the Scourian complex.

The replacement pegmatite origin of the granite gneiss sheets proposed by Evans and Lambert (1974) is based on the previously mentioned isotopic similarity between the pegmatites and the granite gneisses, most notably in the Loch Kirkaig area. They propose that the granite sheets formed as replacement bodies (replacing the felsic gneisses) derived from the same source and at the same time as the potash pegmatites. The lack of any replacement textures in the granite gneisses, and their strong common planar fabric with the host pyroxene granulite gneisses rule against this hypothesis. The REE evidence, however, suggests that some of the pegmatites (those with low absolute concentrations of REE and large positive Eu anomalies) may have originated by later remobilization of the granite sheets. This mode of formation would also be compatible with the isotopic data.

Some form of metamorphic differentiation may be considered as another possible origin for these granite gneisses, since they are composed largely of the mobile components quartz and alkali feldspar. It might be expected, however, that the composition of metamorphic differentiation layers would be variable and a function of host rock composition (i.e. relative proportions of plagioclase, potash feldspar and quartz). However, the consistent major and trace element chemistry, and petrology observed in the granite sheets irrespective of host rock type, tend to rule against this mechanism of formation.

It is here proposed that the granite sheets have originated by anatexis of gneisses undergoing granulite facies metamorphism as suggested by Heier and Brunfelt for the Norwegian young red granite mentioned earlier. The granites thus represent a late melting fraction of rocks which were already essentially dry and depleted in incompatible elements. The very high temperatures and low partial pressures of water necessary for such a process would account for the presence of the ternary feldspars.

As mentioned earlier in the chapter, the granites plot in the low-pressure, water-saturated granite minimum. Under the relatively high temperatures and pressures previously estimated for Scourian metamorphism (Chapter 3) and under vapour-saturated conditions, minimum granite melts should be richer in anorthite than observed for the granite sheets and the minimum shifts more to the albite side of the Ab-Or-Qtz diagram (James and Hamilton, 1969). Recent work by Whitney (1975), however, has shown that anatexis at high pressure (greater than 8 Kb.) and low water contents should yield magmas poorer in anorthite than vapour-saturated equivalents, more similar to minimum melts at low pressure under vapour-saturated conditions. He noted that this is a result of the fact that plagioclase becomes the liquidus phase at 7 Kb (and higher pressures) for rocks of granitic composition versus alkali feldspar under vapour-saturated conditions. This would result in the formation of liquids poorer in plagioclase than vapour-saturated equivalents. Hence, the granite sheets may plot close to the granite eutectic expected under the conditions of Scourian granulite facies metamorphism.

The partial melting origin, however, is not without drawbacks or complications. Although it may explain the major element chemistry of the sheets and their consistent petrology and chemistry throughout the complex, partial melting alone does not explain the observed REE patterns and abundances. For equilibrium (or fractional) melting, the parental material for the granite sheets must have had lower REE abundances than the granite sheets since virtually all REE solid-liquid K_D's of the rock-forming minerals are less than 1 (e.g. Nagasawa and Schnetzler, 1971). If plagioclase were an important phase in the residuum (as it is in the Scourian complex), the parental material would have had an even greater positive Eu anomaly than the granite sheets. A rock type of such unusual REE chemistry has not been recorded from the Scourian complex or, to the author's knowledge, from any other region. Further, it is shown in a later section, that granitic liquids in equilibrium with the Scourian gneisses would have REE patterns and abundances similar to normal upper crustal granites--that is, high absolute concentrations of REE and negative Eu anomalies.

Thus, retention of the partial melting model for the origin of the granite sheets (a desirable model from the point of view of petrology and major element chemistry) requires that some other process or mechanism was operative during or after their formation. Two possibilities are:

1) Disequilibrium melting
2) Sub-solidus reequilibration of the granite sheets with the surrounding gneisses.

In the first of these models (disequilibrium melting), the mobile components of the parental gneisses, quartz and alkali feldspar, would melt and form the granite sheets. However, the granitic melts, once formed, would not equilibrate with the residual minerals in the gneisses. This lack of equilibration could be due to a) the length of time involved in the formation of the granite sheets (i.e. rapid, therefore not allowing equilibration) and/or b) the dry nature of the terrain at the time of formation of these last melts.

In the second model, it is envisioned that the granite sheets may have undergone a sub-solidus re-equilibration with the surrounding gneisses after the anatectic event. The resulting REE patterns would reflect the predominance of feldspar in the granite sheets. Such a mechanism has been proposed recently for the origin of migmatitic rocks of South-eastern Australia (Price and Taylor, 1977).

At this point, and with the data at hand, it is not possible to decide unequivocally between the above two possible mechanisms. However, there are now several examples cited in the literature of granitic and pegmatitic vein material from high grade, amphibolite facies metamorphic terrains, which show low absolute concentrations of REE and positive Eu anomalies (Price and Taylor, 1977; Chou et al., 1976, 1977; Hanson, 1975). If it is accepted that such material is derived by partial melting, the same problem exists with respect to the REE geochemistry of these rocks as with the granite sheets of the Scourian complex. These results may tend to lend support to the sub-solidus re-equilibration model presented above. It would be difficult to envisage disequilibrium melting due to a lack of sufficient time for equilibration in all of these examples. Further, these amphibolite facies terrains were certainly not as "dry" as the Scourian granulite facies complex, and hence this explanation for the lack of equilibration is also suspect. More work in this area should prove very rewarding. One possible suggestion is to study the REE geochemistry of granitic and pegmatitic bodies of varying sizes (widths) in a high grade terrain. If sub-solidus re-equilibration is the dominant process controlling the REE patterns of many of these rocks and presumably this would be accomplished via a diffusion mechanism, there should be a limit to the size of the body which could effectively re-equilibrate (since diffusion over large distances is hardly likely in most geological environments.)

REE and isotopic evidence is consistent with derivation of pegmatites by remobilization of the granite gneisses perhaps related to the Inverian amphibolitization. The soda-rich pegmatites, however, do not conform to this origin and require another process of formation.

Conclusions

The experimental evidence and major element data of the Scourian granite sheets suggest that water deficient melts generated during advanced stages of granulite facies metamorphism may be indistinguishable from their low-pressure, wet counterparts, on the basis of bulk rock chemistry alone. Their trace elements, particularly the REE, are however, distinct, and may lead to their recognition. The REE data further suggest that such melts a) may have undergone sub-solidus re-equilibration with their host gneisses with respect to the REE or b) have formed by a disequilibrium melting process, involving only the mobile components quartz and alkali feldspar. These granitic rocks of high grade terrains merit further investigation.

CHAPTER 7

Discussion and Conclusions

Introduction

Various aspects of the REE data have already been discussed in the previous three chapters. In this chapter, the REE results, combined with other relevant data and REE modelling, are used to consider the origin of the Scourian complex and discuss possible broader implications of the REE data.

Origin of the Scourian Complex

There are basically four hypothesis that have been postulated for the origin of medium - to high-pressure granulite facies terrains in general, and the Scourian complex in particular:

1) Essentially isochemical metamorphism of an upper crustal segment, in the case of the Scourian complex, an Archean volcanic series (Bowes *et al.*, 1971).
2) Granulite facies metamorphism of an upper crustal segment involving the release of an aqueous fluid phase (Heier, 1973), perhaps augmented by mantle degassing (e.g. Sheraton *et al.*, 1973).
3) Direct addition of material from the mantle and crystallization under conditions of the granulite facies (e.g. Holland and Lambert (1975).
4) Granulite facies metamorphism of an upper crustal segment involving the formation and removal of a melt phase (e.g. Fyfe, 1973).

1) Bowes et al., (1971) proposed that the Scourian complex originated by essentially isochemical metamorphism of an Archean volcanic series, based on some chemical similarities and similar differentiation trends to Archean volcanics. Holland and Lambert (1975), however, showed that many of the chemical parameters of the Scourian complex are not compatible with such an origin. They noted that the Scourian assemblage:

a) shows very little increase in K compared to Si or the Larsen factor, versus the distinct trend of increasing K with Si and the Larsen factor observed in Archean volcanics,

b) exhibits quite different trends of variation of Na, Zr, Sr, Zn and Cr with the Larsen factor compared to Archean volcanics, and

c) shows distinctly different abundances of Ti, Fe, Mn, Ba and Ni versus the Larsen factor compared to Archean volcanic rocks.

The REE data also rule against this hypothesis. Individual rock type REE patterns show some distinct differences from most upper crustal rocks of equivalent major element chemistry, including Archean volcanics. Taken as a group, some of the REE trends (e.g. increasing Eu/Eu* with increasing SiO_2) are the opposite of those observed in Archean volcanics (e.g. Condie and Baragar, 1974).

The low Rb/Sr ratios of the gneisses (less than 0.02) also rule against this hypothesis. If the rocks were derived by partial melting of mantle material, the Rb/Sr values imply a source more depleted than that of mid-ocean ridge basalts, which conflicts with the LRE enriched REE patterns and high Ba concentrations observed in the Scourian gneisses (Tarney and Windley, 1977). Therefore, if the gneisses are metamorphosed

Archean volcanics, some post-eruptive process(es) has modified their chemistry.

2) Granulite facies metamorphism of an upper crustal segment involving the release of an aqueous fluid phase may account for some of the observed incompatible element depletions (Rb, U,Cs , etc.) in medium-to high-pressure granulite facies assemblages, as discussed in Chapter 3. Although there are no indesputable sedimentary relics in the mainland Scourian complex (metasediments are observed in the high-grade rocks of the Lewisian of the Outer Hebrides, reported by Dearnley, 1963), the presence of recognizable metasediments in some depleted granulite facies complexes requires that at least some granulite facies rocks were at one time in the upper crust and presumably then had normal crustal trace element abundances and ratios. Subsequent granulite facies metamorphism undoubtedly involved the release of an aqueous phase. The depletion of the REE via such an aqueous phase, however, poses a volume problem. That is, since the REE partition only weakly into an aqueous fluid from silicate phases (Cullers et al., 1973), very large amounts of fluid are required to effectively reduce the REE content of the rocks during granulite facies metamorphism, when available water from dehydration reactions is decreasing compared to that of lower metamorphic grades. To overcome this volume problem, it has been proposed that the excess fluid required for this mechanism to become important is derived by mantle outgassing (Sheraton et al., 1973). However, if such outgassing can take place and is (or was) an important process in the lower crust (for which there is little evidence), and at the temperatures envisioned for the lower crust, it would undoubtedly cause widespread melting. Hence the removal of the

melts produced would be the mechanism responsible for the observed incompatible element depletions (see discussion of hypothesis 4, below).

Fluid inclusion studies of granulite facies rocks (e.g. Touret, 1971) have shown that the fluid produced during granulite facies metamorphism may be relatively enriched in CO_2 compared to that produced at lower metamorphic grades, which generally contains mostly H_2O. Thus, the formation of carbonate REE complexes might be invoked to account for some of the observed REE and other incompatible element depletions. It appears, however, that very high alkali and fluoride contents are required to effectively complex the REE and such concentrations are not typical of normal igneous rocks (Bandurkin, 1961; Mineyev, 1963). Such fluids also appear to selectively concentrate the HRE (Mineyev, 1963) and no selective depletion of HRE is observed in the Scourian rocks. Further, it is unlikely that complexes would be stable at the high temperatures of Scourian metamorphism.

3) Holland and Lambert (1975) proposed that the Scourian complex originated by direct addition of mantle dioritic and gabbroic material into the base of the crust via an underplating mechanism. The depleted nature of the Scourian rocks was considered to be inherited from the mantle source region and/or the result of crystallization under granulite facies conditions with escape of enriched, late-stage melts to higher crustal levels. Their model calls for water-undersaturated, low-percentage partial fusion of the upper mantle, yielding an andesitic (or gabbroic) melt, with accessory more mafic and ultramafic melts from time to time. Their hypothesis is largely based on the results of factor analysis of the Scourian gneisses, which yield cogenetic, igneous-like trends. They envisioned this process

as a major shield-forming mechanism, in which granodiorites represent the differentiated upper parts of the accreting material.

Tarney and Windley (1977) proposed a somewhat similar model for the origin of depleted granulite facies assemblages. They regard the dominant process as similar to that giving rise to modern Cordilleran granodioritic and tonalitic batholiths. Both the more mafic lower crust and the upper crustal batholiths would be produced at approximately the same time by partial melting of the oceanic crust during subduction. The mafic magmas, being more dense, would not rise to such high levels in the crust. They would, however, have the geochemical character of calc-alkaline igneous rocks, with LRE enriched REE patterns and high Ba/Sr ratios. As they cool from igneous temperatures, they would equilibrate under the P-T conditions of the lower crust; that is, under those of the granulite facies. This model has the added feature of allowing the granulite facies metamorphism to closely follow crustal generation - as indicated by the isotopic evidence (e.g. Moorbath, 1975; Moorbath et al., 1969). Their model differs from that of Holland and Lambert in the lack of a direct link between the lower crustal rocks and upper crustal granodiorites. In their model, both represent separate initial magma types; whereas in the Holland and Lambert model, one is derived from the other by magmatic differentiation.

Probably the main drawback of the above mentioned underplating models for the origin of granulite facies terrains in general, is the presence of recognizable metasediments in many such terrains. Furthermore, these metasediments may even fall on the igneous-like trends observed for the other rock types (Heier, 1960). To explain the presence of such obvious upper crustal rocks, Tarney and Windley (1977) suggested that they represent oceanic supracrustals tectonically emplaced in the lower crust during subduction. There is, however, no structural evidence for this kind of mechanism in exposed granulite facies terrains. Further, the dominant sediment types of granulite facies terrains are carbonate and quartzite (e.g. Heier, 1973)-sediments of stable platform environments and not important sediment types of oceanic plates in such tectonically active regions as continent-oceanic plate boundaries. For example, the metasediments observed in the granulite facies terrains of Sri Lanka and India have been interpreted as being derived from a sandstone-shale-limestone-evaporite sequence, implying shallow water sedimentation in a shelf or intracratonic basin (Katz, 1976). Individual marble units can be traced for hundreds of kilometres along strike. One continuous unit 20 Km thick and 150 Km in length has been mapped (Katz, 1976) - hardly to be expected if these sediments represent a series of tectonic thrust sheets emplaced in the lower crust.

In the case of the Scourian complex, however, no indesputable metasediments have been observed and therefore, the Holland and Lambert hypothesis cannot be rejected on these grounds. In their model, the various gneiss types of the Scourian complex represent a cogenetic, igneous rock sequence. The absolute and relative REE abundances of phenocryst phases in volcanic sequences is a strong function of rock type, and variations in absolute concentrations for a particular phase of greater than 2 orders of magnitude are observed between basalts and dacites (Nagasawa and Schnetzler, 1971). It might therefore be expected that the absolute and relative abundances of the Scourian mineral phases would show similar variations with rock type (and hence "melt" composition). There is no such strong correlation of mineral REE content with rock type in the analysed Scourian minerals. The maximum observed variation for a given mineral phase is only a factor of 5, in spite of a range of rock composition from ultramafic to felsic.

4) The prefered hypothesis of this work is that the Scourian complex is the residuum, left after generation and removal of granitic melts as suggested by Brown and Fyfe (1970, 1972) and Fyfe (1973) for the origin of many granulite facies complexes. A wide range of features of the Scourian complex, including the REE data, suggests an origin fundamentally distinct from normal upper crustal igneous and metamorphic processes. Although each line of evidence supporting this model may be explained in terms of some other process(es); taken together, a formidable case can be made for the residual nature of the Scourian complex.

a) Anhydrous nature of the Scourian complex:
Brown and Fyfe (1970) argued that the formation of a melt phase was the natural consequence of the breakdown of hydrous phases, such as the micas and hornblende, during prograde metamorphism. The anhydrous nature of many granulite facies complexes would thus be a result of the strong partitioning of water into the melt.

b) Incompatible element depletions: The incompatible elements, such as Rb, U and Th, are known to be strongly partitioned into a melt phase, thus providing an effective mechanism for removal of these elements from the Scourian complex, and their concentration in the upper crust.

c) Mineralogy: The Scourian minerals show a very narrow range of composition in spite of a wide range of rock types (Muecke, 1969). Such a feature is in accord with the minerals having been in equilibrium with a melt phase.

d) Estimated conditions of Scourian metamorphism: Fyfe and Brown (1970) showed that maximum melt production under conditions $P_{load} > P_{H_2O}$ would occur in the 750°C to 950°C temperature range. The estimated temperature of Scourian metamorphism of 916°C occurs within this interval.

e) Major element chemistry: Major element trends suggest that the Scourian gneisses are cogenetic (Holland and Lambert, 1975), but are unlike those observed in upper crustal igneous rock sequences. The gneisses, even the acid varieties, exhibit very low potash levels, generally less than 1 per cent. Profound modification involving partial melting could account for both of these features. Removal of potash-rich granitic melts would lead to a potash depletion in the residual gneisses. The cogenetic nature of the various gneiss types could be accounted for by equilibration of the gneisses with a melt(s) of granitic composition. The various rock types would thus represent varying proportions of the residual mineral phases, probably controlled by the original (pre-melting) rock composition.

f) REE whole rock data: The relatively low absolute concentrations of REE in the gneisses compared to upper crustal estimates is consistent with the tendency of the REE to be preferentially partitioned into a melt phase. The overall positive Eu anomaly would be a result of plagioclase enrichment of the residual gneisses during melting. As discussed in the previous chapter, experimental data indicate that plagioclase is probably an important residual phase during anatexis under the estimated conditions of Scourian metamorphism.

g) REE mineral data: Several features of the Scourian mineral REE data are consistent with equilibration with a melt phase:
   - i) There is no strong correlation of mineral REE content with rock type.
   - ii) The relative and absolute mineral REE abundances and distribution coefficients between coexisting phases show strong similarities to data for mineral phenocrysts that have equilibrated with LRE enriched melts of dacitic (granodioritic) composition.

The proposed model differs from that of Holland and Lambert (1975) essentially only to the extent of requiring a previous upper crustal history for the Scourian precursor. The model thus becomes applicable to metasediment-bearing, depleted granulite facies complexes in general. The low present day Sr^{87}/Sr^{86} ratios of the Scourian complex require that this previous upper crustal history was less than approximately 50 to 100 m.y. It has been shown, in modern and ancient tectonically active zones, that such a constraint is well within the time frame of major tectonic events (e.g. Moorbath, 1975). For example, Arth (1975) proposed, as an origin for quartz monzonites from the Archean granite-greenstone complex of N.E. Minnesota, 20 to 50 per cent partial melting of metagraywacke, leaving a residue of plagioclase, amphibole, garnet and pyroxene - that is, a granulite facies assemblage. Low initial Sr^{87}/Sr^{86} ratios for the monzonites suggests that the sediments would have to be buried and melted within 50 m.y. This constraint is consistent with the 50 m.y. history suggested for the entire tectonothermal event in this region.

Trace Element Modelling

1) Residua

Using either the model of Holland and Lambert (1975) or the model presented here, it may be possible to estimate the amount of granitic material that has been extracted from the Scourian complex. Several assumptions are, however, required:

a) The Scourian precursor or initial melt had normal Eu abundances (i.e. Eu/Eu* = 1).

b) the partial melt or residual granitic liquid had REE abundances similar to the 60-70% SiO_2 granite composite of Haskin _et al_. (1968).

Such a calculation has been performed and the results are presented in Table VII-1. These data indicate that approximately 14% granite could have been derived from the Scourian precursor.

To test the partial melting hypothesis further, trace element modelling of partial melting has been performed. The starting assumptions were as follows:

a) The Scourian gneisses are the residuum after partial melting.

b) The equation of Shaw (1970) for equilibrium partial melting is applicable. It is:

$$C^L = \frac{C^I}{Do + F - FD_o}$$

where C^L = concentration of the trace element in the liquid
C^I = initial concentration of the trace element prior to melting
D_o = bulk distribution coefficient

Table VII-1: REE content of Scourian precursor
assuming Eu/Eu* = 1
(14% granite + 86% Scourian)

	Scourian Complex (ppm)	Granite of 60-70% SiO_2 (ppm)	Scourian Precursor (ppm)
La	14.4	43	18.4
Ce	28.4	83	36.1
Sm	2.6	8.5	3.44
Eu	0.93	2.0	1.08
Gd	2.40*	7.4	3.09
Yb	0.92	3.25	1.25
Lu	0.17	0.54	0.22
Eu/Eu*	1.12	0.76	1.00

** Gd value obtained by linear interpolation between Tb and Eu.

$$= P^{\alpha}K^{\alpha/l} + P^{\beta}K^{\beta/l} + P^{\gamma}K^{\gamma/l} \ldots .$$

where P^{α} = weight fraction of mineral α in residuum

$K^{\alpha/l}$ = distribution coefficient for trace element between phase α and melt.

F = weight fraction of melt produced.

The residual concentration is given by:

$$C^S = \frac{C^I - F\,C^L}{1 - F}$$

where C^S = the concentration of the trace element in the residuum.

c) The mineral/liquid distribution coefficients for rhyolitic rocks, summarized by Arth and Hanson (1975), are applicable.

d) The trace element content of the starting material (pre-melting) is known.

For assumption d), the average trace element content of the Belvue Road graywackes of the Archean Fig Tree Group, South Africa were used (Wildeman and Condie, 1973). A graywacke was chosen as the starting material as melting experiments have shown that crustal anatexis of such rocks may produce melts of granitic composition (Winkler and von Platen, 1958; von Platen, 1965). The actual absolute trace element concentrations of the starting material are not critical, as the trends produced should be the same for any reasonable starting material.

The residual mineralogy was estimated from the modal analyses of the various gneiss types reported by Muecke (1969). Three models were attempted - each one differing in residual mineralogy. For model A, an estimate of the mineralogy for the whole Scourian complex was used, assuming 80% felsic gneisses, and 20% intermediate, mafic and ultramafic gneisses (weighted equally). For model B, this same estimate less garnet was used, since a small error in the garnet estimate would have a pronounced effect on the behavior of the HRE during melting. Due to the generally low abundance (or absence) of garnet in many of the Scourian gneisses, it is difficult to arrive at a reliable estimate for this mineral in the Scourian complex as a whole. For model C, only the felsic gneisses were considered as having taken part in the melting process.

The trace elements used were Ba, Sr, Rb and the REE, as distribution coefficient data applicable to granitic rocks are available for these elements. The residual mineralogy and calculated bulk distribution coefficients for each model, and the mineral / liquid distribution coefficients used are given in Table VII-2.

The results of the modelling are presented in Tables V11-3, V11-4 and V11-5, along with initial concentrations and observed residual concentrations (i.e. abundances in the Scourian gneisses). Also presented are several critical element ratios, which are less dependent on initial concentrations than absolute values.

Chondrite-normalized REE graphs of the residual results for each model are presented in Fig. VII-1, VII-2 and VII-3, along with the Scourian REE estimate. The best fit is clearly for model B, especially at 20% partial melting. Increasing the degree of partial melting beyond 20% yields an increasing positive Eu anomaly in the residual gneisses - too large compared to that observed in the Scourian gneisses. (Fig. VII-2). The absolute concentrations of the REE are all slightly on the high side

Table. V11-2 : Trace Element Modelling Parameters

1. Mineral/liquid distribution coefficients for rhyolitic rocks (from Arth and Hanson, 1975).

	Clinopyroxene	Orthopyroxene	Hornblende	Plagioclase	Garnet*	K-feldspar
Ce	0.50	0.15	1.52	0.27	0.35	0.044
Sm	1.67	0.27	7.77	0.13	2.66	0.018
Eu	1.56	0.17	5.14	2.15	1.50	1.13
Tb**	1.89	0.40	11.5	0.081	19.6	0.0085
Yb	1.58	0.86	8.38	0.049	39.9	0.012
Lu	1.54	0.90	5.50	0.046	29.6	0.006
Ba	0.0029	0.0026	0.044	0.31	0.017	6.12
Rb	0.032	0.0027	0.014	0.041	0.0085	0.366
Sr	0.516	0.085	0.022	4.4	0.015	3.87

* from dacitic rocks
** by linear extrapolation between Gd and Dy

2. Residual Mineralogy (weight %) of the Scourian complex and felsic gneisses, calculated from the modal data of Muecke (1969) and the known densities of the minerals.

	Model A	Model B	Model C
Hornblende	2.0	2.1	0
Plagioclase	60.4	62.2	67.0
Garnet	2.9	0	1.2
K-feldspar	1.5	1.6	1.8
Quartz	14.8	15.2	18.2
Clinopyroxene	8.2	8.4	3.5
Orthopyroxene	10.2	10.5	8.3

Model A = whole Scourian complex
Model B = whole Scourian complex, less garnet (recalculated to 100%).
Model C = Scourian felsic gneisses only.

3. Calculated Bulk Distribution Coefficients (solid/liquid) for each model.

	Model A	Model B	Model C
Ce	0.26	0.26	0.22
Sm	0.48	0.41	0.20
Eu	1.61	1.61	1.55
Tb	1.04	0.49	0.39
Yb	1.57	0.43	0.64
Lu	1.21	0.37	0.51
Ba	0.28	0.29	0.32
Rb	0.034	0.034	0.036
Sr	2.77	2.85	3.04

Table VII-3: Model A results for equilibrium melting, where C^L is the concentration in the melt, C^S is the concentration in the residuum, C^I is the initial concentration and F is the fraction of partial melting.

	C^L				C^S				C^I	Whole Scourian Complex
F	0.1	0.2	0.3	0.4	0.1	0.2	0.3	0.4		
Ba	1778	1476	1262	1102	498	413	353	309	626	643**
Rb	689	396	278	214	23	13	9	7	90	9**
Sr	137	147	158	172	378	406	438	476	354	495**
Ce	157	128	109	94.1	40.7	33.3	28.2	24.5	52.3	28.4
Sm	7.51	6.85	6.29	5.81	3.61	3.29	3.02	2.79	4.0	2.66
Eu	0.69	0.72	0.75	0.78	1.11	1.16	1.21	1.26	1.07	0.93
Tb	0.49	0.49	0.50	0.50	0.51	0.51	0.52	0.52	0.51	0.34
Yb	1.03	1.08	1.14	1.17	1.63	1.69	1.78	1.84	1.57	0.92
Lu	0.22	0.22	0.23	0.23	0.26	0.27	0.27	0.28	0.26	0.17
Rb/Sr	5.0	2.7	1.8	1.2	0.06	0.03	0.02	0.01	0.25	0.02
Ba/Rb	2.6	3.7	4.5	5.1	22	32	39	44	7.0	71
Ba/Sr	12.9	10.0	8.0	6.4	1.3	1.0	0.8	0.6	1.8	1.3
Eu/Eu*	0.32	0.36	0.41	0.45	0.95	1.07	1.18	1.31	0.85	1.12
Ce/Yb	152	119	96	80	25	20	16	13	33	31

** Values from Holland and Lambert, 1975.

Table VII-4: Model B results for equilibrium melting, where C^L is the concentration in the melt, C^S is the concentration in the residuum, C^I is the initial concentration, and F is the fraction of partial melting.

	C^L				C^S				C^I	Whole Scourian Complex
F	0.1	0.2	0.3	0.4	0.1	0.2	0.3	0.4		
Ba	1734	1449	1244	1091	503	420	361	316	626	643**
Rb	689	396	278	214	23	13	9	7	90	9**
Sr	133	143	154	168	379	407	440	478	354	495**
Ce	157	128	109	94.1	40.7	33.3	28.2	24.5	52.3	28.4
Sm	8.53	7.58	6.81	6.19	3.50	3.11	2.79	2.54	4.0	2.60
Eu	0.69	0.72	0.75	0.78	1.11	1.16	1.21	1.26	1.07	0.93
Tb	0.94	0.86	0.79	0.73	0.46	0.42	0.39	0.36	0.51	0.34
Yb	3.22	2.89	2.61	2.39	1.39	1.24	1.12	1.03	1.57	0.92
Lu	0.60	0.52	0.47	0.42	0.22	0.19	0.17	0.15	0.26	0.17
Rb/Sr	5.2	2.8	1.8	1.3	0.06	0.03	0.02	0.01	0.25	0.02
Ba/Rb	2.5	3.7	4.5	5.1	22	32	40	45	7.0	71
Ba/Sr	13.0	10.1	8.1	6.5	1.3	1.0	0.8	0.7	1.8	1.3
Eu/Eu*	0.26	0.31	0.35	0.40	1.00	1.16	1.34	1.53	0.85	1.12
Ce/Yb	49	44	42	39	29	27	25	24	33	31

** Values are from Holland and Lambert, 1975.

Table VII-5: Model C_L results for equilibrium melting, where C^L is the concentration in the melt, C^S is the concentration in the residuum, C^I is the initial concentration, and F is the fraction of partial melting.

			C^L				C^S		C^I	Scourian Felsic Gneisses
F	0.1	0.2	0.3	0.4	0.1	0.2	0.3	0.4		
Ba	1613	1372	1195	1057	516	439	382	338	626	623**
Rb	680	393	277	213	24	14	10	8	90	5**
Sr	125	134	146	159	379	409	443	484	354	477**
Ce	176	139	115	98.3	38.6	30.6	25.3	21.6	52.3	32.7
Sm	14.3	11.1	9.09	7.69	2.86	2.22	1.82	1.54	4.0	2.75
Eu	0.72	0.74	0.77	0.80	1.11	1.15	1.20	1.25	1.07	1.02
Tb	1.13	1.00	0.89	0.80	0.44	0.39	0.35	0.31	0.51	0.30
Yb	2.32	2.21	2.10	2.00	1.49	1.41	1.34	1.28	1.57	0.57
Lu	0.47	0.43	0.40	0.37	0.24	0.22	0.20	0.19	0.26	0.14
Rb/Sr	5.4	2.9	1.9	1.3	0.06	0.03	0.02	0.02	0.25	0.01
Ba/Rb	2.4	3.5	4.3	5.0	22	31	38	42	7.0	125
Ba/Sr	12.9	10.2	8.2	6.6	1.4	1.1	0.9	0.7	1.8	1.3
Eu/Eu*	0.17	0.22	0.28	0.34	1.18	1.52	1.89	2.30	0.85	1.21
Ce/Yb	76	63	55	49	26	22	19	17	33	57

** Values are from Holland and Lambert, 1975.

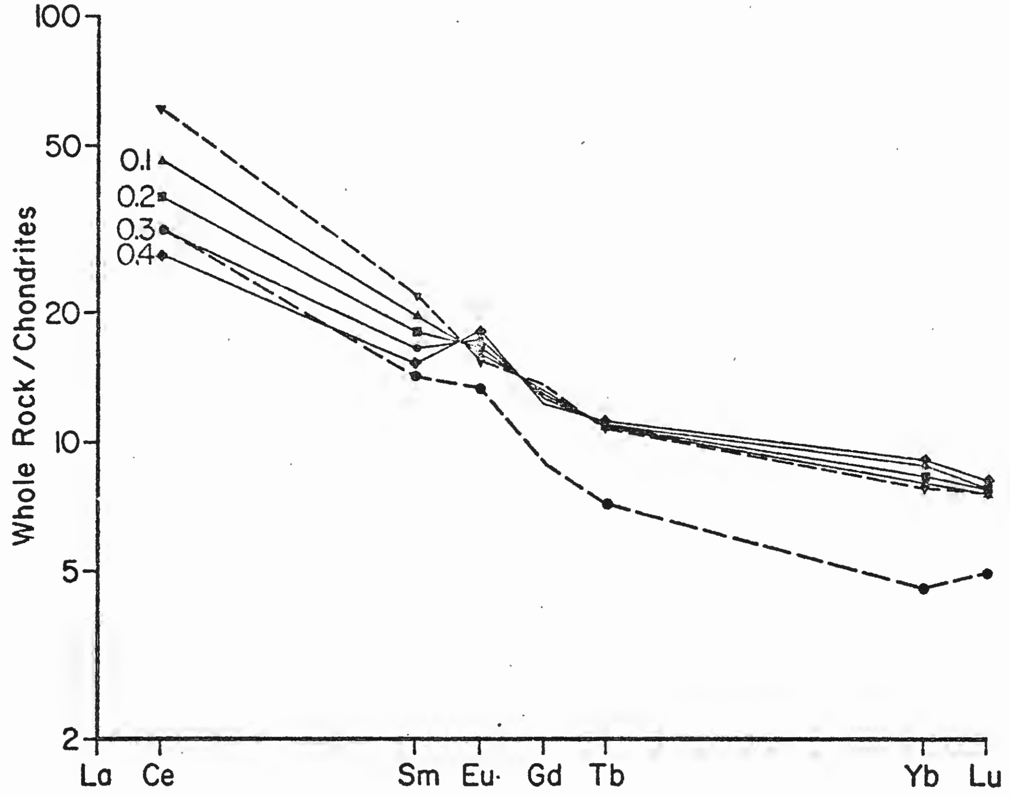


Fig. VII-1 : Model A residual REE results for partial melting of graywacke (f = 0.1,0.2,0.3,0.4) ,compared to observed Scourian values (dashed line ,circles) and the pre-melting graywacke composition (dashed line ,triangles).

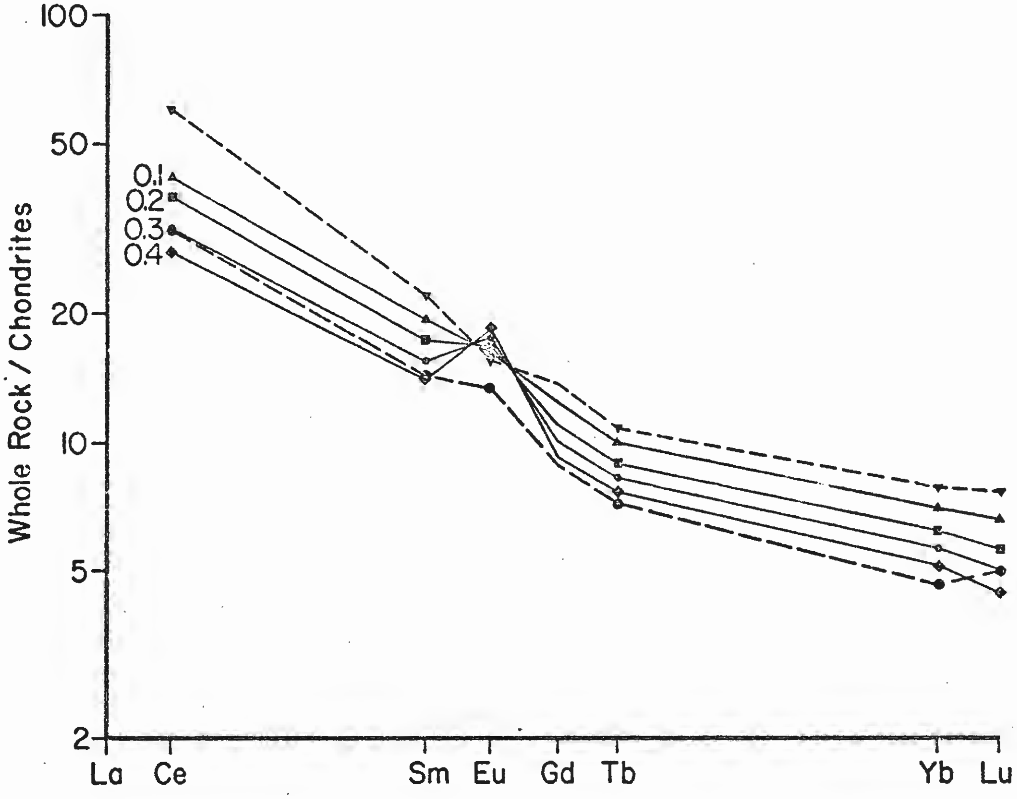


Fig. VII-2 : Model B residual REE results for partial melting of graywacke (f = 0.1,0.2,0.3,0.4) ,compared to observed Scourian values (dashed line ,circles) and the pre-melting graywacke composition (dashed line ,triangles).

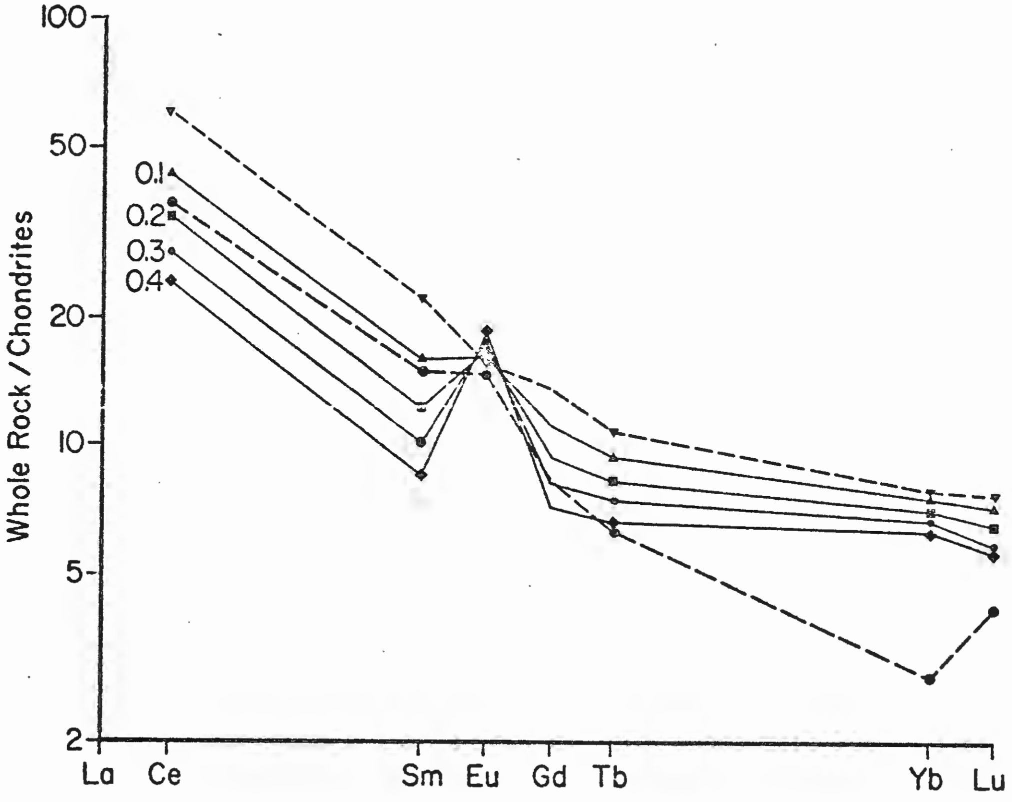


Fig. VII-3 : Model C residual REE results for partial melting of graywacke (f = 0.1,0.2,0.3,0.4) ,compared to the observed Scourian values (dashed line ,circles) and the pre-melting graywacke composition (dashed line ,triangles).

(Fig. VII-2) in model B. The model A results are all relatively too high with respect to the HRE due to the presence of garnet (Fig. VII-1). This result indicates that if the partial melting model is correct, very little modal garnet was present during melting. In model C, the calculated REE patterns are quite different from that observed in the felsic gneisses (Fig. VII-3). The HRE are much higher in the felsic gneisses due to the minor garnet present, but more seriously, all the model patterns show much larger positive Eu anomalies than observed in the felsic gneiss mean. It would appear from this discussion, that the best fit is for approximately 20% partial melting for model B.

2) Granites

The model REE results for the granitic melts from Tables VII-3,4,5 are presented as chondrite-normalized graphs in Fig. VII-4, VII-5 and VII-6. For comparison, the range of REE abundances observed in Archean granitic rocks from the Barberton Mountain Land, South Africa (Condie and Hunter, 1976) is also given with each of the model results (these granitic rocks are intrusives from essentially the same location as the graywacke starting material). All three models produce granitic REE abundances, with LRE enriched patterns and negative Eu anomalies. They plot, for the most part, within the range of observed REE abundances of the Archean granites, generally towards the lower part of this range (Fig. VII-4, VII-5, VII-6).

The modelling results for the other elements (Ba, Rb, Sr) are also compatible with the partial melting model. The results for 20% partial melting using model B will be discussed, as this model gave the best fit for the REE data. Examining the results presented in Table VII-4, it is

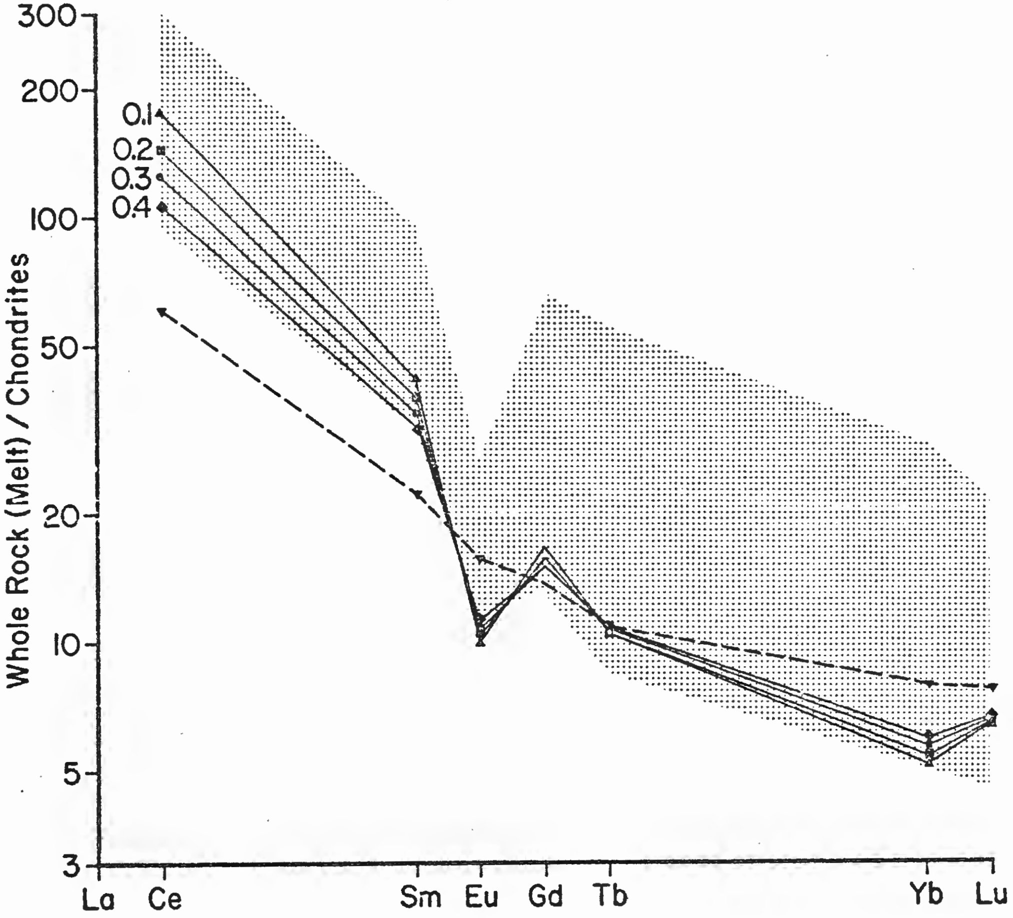


Fig. VII-4 : Model A liquid REE results for partial melting of graywacke (f = 0.1,0.2,0.3,0.4) ,compared to the observed REE range of Archean granitic rocks from the Barberton Mountain Land ,S. Africa .Dashed line represents the graywacke starting material.

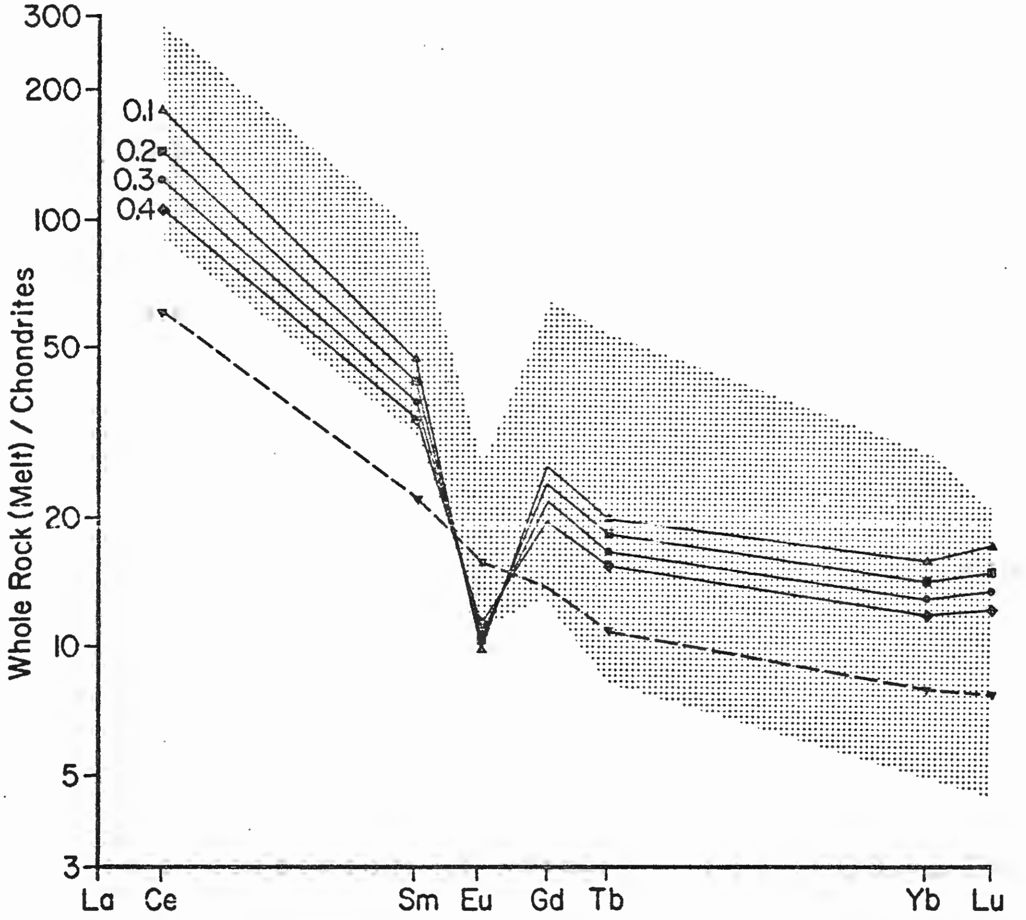


Fig. VII-5 : Model B REE liquid results for partial melting of graywacke (f = 0.1,0.2,0.3,0.4) ,compared to observed REE range of Archean granitic rocks from the Barberton Mountain Land , S. Africa .Dashed line represents the graywacke starting material.

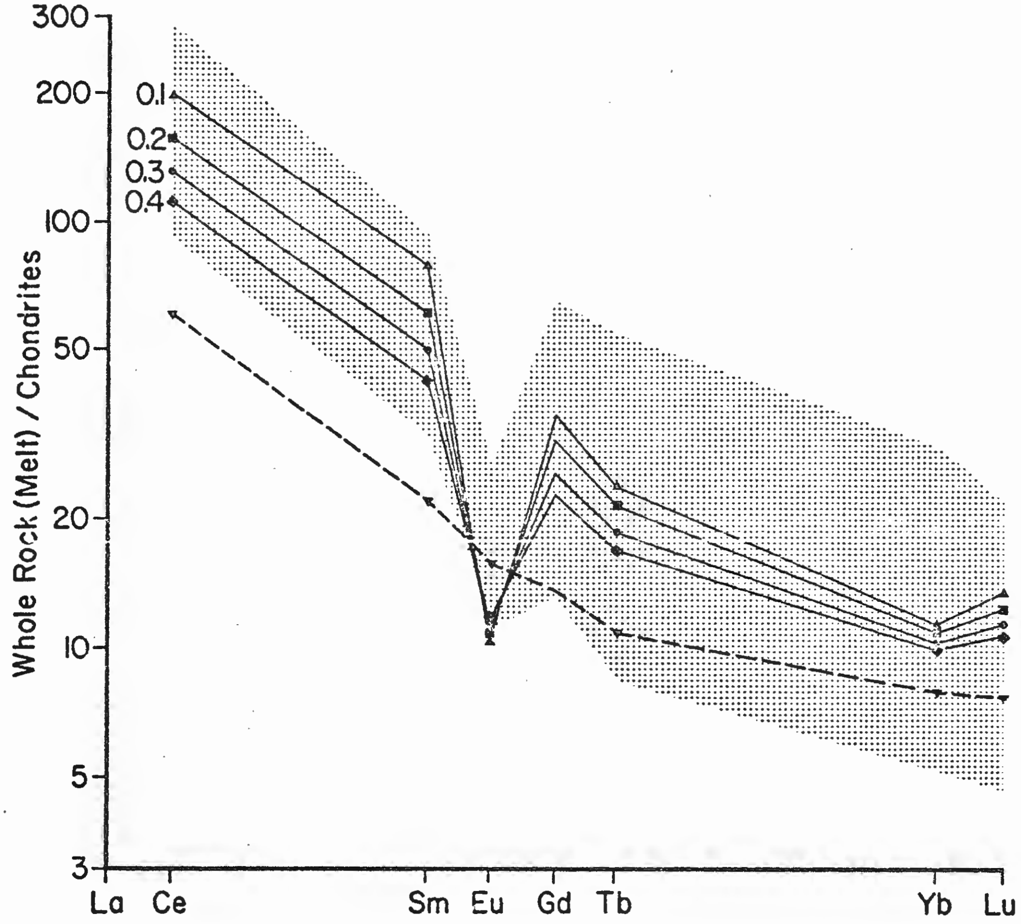


Fig. VII-6 : Model C liquid REE results for partial melting of graywacke (f = 0.1,0.2,0.3,0.4) ,compared to observed REE range of Archean granitic rocks from the Barberton Mountain Land , S. Africa.The dashed line represents the graywacke starting material.

observed that the residual gneisses are strongly depleted in Rb (13 ppm) compared to the starting (pre-melting) concentrations (90 ppm) - very similar, even in absolute concentrations, to the value of 9 ppm Rb observed in the Scourian gneisses. Compared to the initial concentrations, Sr has increased slightly (407 vs. 354 ppm) and Ba decreased slightly (420 vs. 626) in the calculated residuum. The Rb/Sr ratio of the model residuum of 0.03 is very close to the Scourian value of 0.02, and to those of many granulite facies terrains which usually have Rb/Sr ratios of 0.02 or less (Tarney and Windley, 1977). The Ba/Rb ratio of the residual gneisses has increased from a value of 7.0 in the graywacke to a value of 32 (vs. 71 in the Scourian gneisses). This result is very similar in general form to the observed differences between amphibolite facies and granulite facies gneisses (10 vs. 60; Tarney and Windley, 1977). The Ba/Sr ratio of the residuum (1.0), on the other hand, has not been significantly changed from that of the graywacke parent (1.8) - again, similar to results from amphibolite and granulite facies terrains, in general, where this ratio is observed to be approximately constant (Tarney and Windley, 1977). This is an important observation as Tarney and Windley (1977) ruled out partial melting as the main cause of granulite facies depletions because it would result in a significant lowering of the Ba/Sr ratio. Clearly, this is not the case with the model presented here.

The calculated results for Ba, Rb, and Sr for the granitic melt, at 20% partial melting (model B), are within the range of observed concentrations of granitic rocks in general. The Ba value of 1449 ppm is close to the mean Ba content of quartz monzonites of 1605 given by Fisher and Puchelt (1970). The Rb value of 396 ppm falls well within the range of 170-910 ppm given for low-Ca granites by Heier and Billings (1970). Similarly, the Sr value of 143 falls within the range of 17-692 observed in the Archean granitic rocks reported by Condie and Hunter (1976).

Thus, the trace element modelling results are compatible with the residual nature of the Scourian complex. Approximately 20% partial melting of upper crustal material (metasediments, for example) with subsequent removal of the melts, could account for virtually all of the observed geochemical features of the Scourian gneisses. It would appear that the Scourian precursor was slightly higher in Ba and Sr than the graywacke used in the melting model, in order to produce a better modelling fit with the observed abundances in the Scourian gneisses. Using either the model presented here or that of Holland and Lambert (1975), the Scourian precursor must have been LRE enriched (more so than observed in the Scourian gneisses at present) and high in Ba. A calc-alkaline source (or sediments derived largely from calc-alkaline rocks) may be indicated by the high Ba contents. Such rocks generally have LRE enriched REE patterns (e.g. Nance and Taylor, 1976) and high Ba contents (e.g. Tarney and Windley, 1977).

Broader Implications

It may be of interest at this point to discuss some of the possible broader implications of the REE data. There are, however, two main problems in interpreting these results in a wider context:

a) the lack of REE data for other medium - to high-pressure granulite facies terrains.

b) the difficulty in assessing how representative the Scourian complex is of the lower crust.

Regarding point b) above, it was shown in Chapter 2 and 3 that the Scourian complex does conform to models of lower crustal composition based on evidence from seismology, heat flow, geochemistry and experimental petrology. Further, the observed depletions of certain elements in the Scourian complex are similar in general form to observations in other granulite facies complexes - perhaps more extreme in the case of the Scourian complex, however. In order to overcome point a) above, further work is required, although the 5 granulite facies gneisses reported by Green *et al*. (1969, 1972) show positive Eu anomalies as do the lower crustal granulite xenoliths from the Lesotho kimberlites reported by Rogers and Nixon (1975).

The uniqueness of the REE as geochemical indicators is perhaps best exemplified by Eu. Because the REE generally form a very coherent group, the anomalous behaviour of Eu takes on a special significance. Eu has apparently decreased in relative abundance (relative to Sm and Gd) in the upper crust since the Archean, as reflected in the changing REE content of clastic sediments (discussed in Chapter 1) whereas the other REE have remained approximately constant in relative and absolute abundances (perhaps increasing slightly in absolute abundances). Wildeman and Haskin (1973) examined several possible mechanisms to account for this relative decrease in Eu with time, including igneous, metamorphic and sedimentary processes. They concluded that none of these possible mechanisms appeared convincing. Assuming a lower crust of approximately Scourian composition, however, derived at least in part by granite genesis (and subsequent upward movement of these melts), it may be possible to balance the observed relative Eu depletion in the upper crust by a relative Eu enrichment in the lower crust yielding an overall continental crust with normal Eu abundances. This is a desirable result as all evidence to date indicates the vast majority of material added to the crust directly from the mantle has normal Eu abundances (e.g. oceanic tholeiites, island arc volcanics).

To test this idea further, a continental crustal balancing has been attempted for the REE, using the following assumptions:

a) The Scourian complex is representative of the lower crust with respect to REE abundances.

b) REE averages for clastic sediment composites (e.g. NASC) are representative of upper crustal REE abundances.

c) The crust as a whole has normal or chondritic Eu abundances (i.e. Eu/Eu* = 1).

Initially, it was assumed that the NASC (a Phanerozoic shale composite) is representative of the REE abundances of the upper crust. The results of this calculation (Table VII-5a) indicate that, for Eu/Eu* equal to 1, 84% of the continental crust must be "Scourian-like" lower crust versus 16% "NASC-like" upper crust. If it is assumed that the Conrad discontinuity is the boundary between the lower and upper crust (located at approximately 20 Km. depth), there should be approximately 50% upper and 50% lower crust. Therefore, the percentage of lower crust indicated by the above calculation is too high.

To explain this apparent imbalance, one (or more) of the following must be valid:

a) NASC is relatively too depleted in Eu compared to the true upper crust.

b) The lower crust is relatively more enriched in Eu compared to

Table VII-5: Whole-crust REE abundances calculated from
(a) 84% Scourian + 16% NASC* and
(b) 62% Scourian + 38% Archean** graywacke.

Ppm	(a)	(b)
La	17.2	16.0
Ce	35.5	37.5
Sm	3.1	3.14
Eu	0.98	0.98
Tb	0.42	0.40
Yb	1.26	1.17
Lu	0.22	0.20
Eu/Eu*	1.0	1.0

* NASC values from Haskin et al., 1968.

** Archean graywacke values from Wildeman and Condie, 1973.

the Scourian gneisses.

c) The model is wrong, and the continental crust as a whole has a negative Eu anomaly.

d) The lower and upper crust have evolved with time (with respect to their REE abundances) and hence the above calculation would not be valid as the Scourian complex may represent the Archean lower crust, and NASC the Phanerozoic upper crust.

Point a) above is not a likely possibility. As noted by Veizer (1977), shales are, if anything, more basic than the average upper crust. The real or true upper crustal REE average would, therefore, have a greater granitic contribution and hence an even larger negative Eu anomaly which would tend to increase, not decrease, the calculated percentage of lower crust.

Point b), that is, a larger positive Eu anomaly in the lower crust than observed in the Scourian complex could be valid, but at present (due to a lack of data) is difficult to assess. Even using a lower crust composed exclusively of the felsic gneisses (the gneiss type with the largest positive Eu anomaly), still yields 74% lower crust.

Therefore, assuming the initial assumptions are correct (or approximately so), point d) above may be part of the answer. It is possible to test this point further using REE data for Archean clastic sediments as the Archean upper crustal estimate and the Scourian REE data, again, as the lower crustal estimate. The Archean clastic sediment estimate used is that of Wildeman and Condie (1973) - their REE average of Archean graywackes. The results of the calculation (Table VII-4b) indicate 62% lower crust and 38% upper crust - a much more realistic split. Thus, the results are not incompatible with the concept of a lower crust with a positive Eu anomaly complementary to the observed upper crustal negative Eu anomaly, at least for the Archean continental crust. If the model is valid, the larger negative Eu anomaly of the Phanerozoic upper crust, as represented by NASC, requires a larger positive Eu anomaly (than observed in the Scourian complex) in the Phanerozoic lower crust, if the two are so simply related. It may be possible to test this hypothesis further by examining lower crustal rocks of different ages. This may be complicated by two factors, however:

a) the scarcity of medium-to high-pressure granulite facies terrains of any age, but especially Phanerozoic.

b) the contribution of granitic rocks (with negative Eu anomalies) to the material being melted. If the starting or pre-melting material already contains a negative Eu anomaly, the resulting residuum will be less relatively enriched in Eu compared to Sm and Gd.

Although it is difficult to critically evaluate lower crustal evolution, there is much evidence supporting the theory that the continental upper crust has evolved with time, from basic to more acidic in character. For example, Veizer (1973) proposed that although recycling is the dominant process responsible for the formation, preservation, destruction and composition of sedimentary masses during geological time, superimposed on this is an evolutionary trend. He suggested that the majority of these evolutionary trends were the result of 2 or 3 variables such as evolution of the crust, P_{O_2} and perhaps P_{CO_2}. He showed that the continental crust developed from a more mafic one in the Archean to a more felsic one in younger geological periods. One may then ask what mechanism was responsible for this change in composition? One possibility suggested by the "Eu problem" is the reworking of crustal material (via sediments?) in active orogenic belts, involving partial melting. The granodiorite to granite melts produced would move upwards, yielding a depleted, stable residuum in the lower crust with a relative Eu enrichment due to the predominance of plagioclase. Thus, the increasing importance of this process with time may account for the observed upper crustal Eu decrease since the Archean as suggested by Nance and Taylor (1976).

Thus, in the model preferred here, the Archean granulite facies complexes may represent deeper, complementary levels of the granite-greenstone belts, typical of Archean terrains (e.g. Shackleton, 1975; Glikson, 1975). Glikson (1972, 1975) noted that the earliest "granitic" rocks observed are the so-called Na-granites which intrude early simatic crust in the form of large batholiths. They have very low Sr^{87}/Sr^{86} initial ratios (indicating a mantle origin) and are LRE enriched with normal or chondritic Eu abundances. He considers these large batholiths to represent the proto-continents. Later in the development of these terrains, the first true granites (K-rich) appear, which have the characteristic negative Eu anomaly observed in virtually all subsequent granitic rocks. Glikson (1975) interpreted these rocks as forming by crustal anatexis.

These general trends in crustal evolution may be related to the changing thermal regime of the crust. There is considerable evidence that the geothermal gradient was much steeper in the Archean (e.g. Moorbath, 1975), especially the early Archean (>3000 m.y.). Thus, deep crustal reworking may have been more complete, as a rule, in the early Archean than in late Archean times and subsequent geological periods, when selective reworking became the rule (Watson, 1973).

One can envisage several lines of active crustal evolution in a classical geosynclinal sequence or orogenic belt. Starting with relatively dry material, such as basalt, prograde regional metamorphism would probably result in a stable granulite facies assemblage with normal REE abundances early in the tectonic history of a crustal segment. Such might also be the case if the basaltic material were emplaced directly into the deep crust from the mantle. On the other hand, if the starting material were a relatively wet mixture of sediments, the resulting evolution would, of necessity, be more complex. Under upper amphibolite facies conditions, metamorphism and magmatism merge (Heier, 1973). Partial melting of such a sequence of sediments would yield granitic melts on the one hand, and a depleted residuum in the granulite facies on the other.

Clearly, the above two extremes are not mutually exclusive. The lower continental crust is, therefore, probably composed of both residual material after granite genesis and basic material that has either been added directly from the mantle or has been through a tectonic cycle involving a period of residence in the upper crust. The REE, especially the presence or absence of a Eu anomaly, may be particularly useful in assessing the relative importance that anatexis has played in a given segment of lower crust.

Conclusions

The following sequence of events for the Scourian complex is suggested by the results of this study:

1) Initial formation of a crustal segment at greater than 2800 to 2900 m.y. - the precursor to the Scourian complex.
2) Profound modification of that segment during granulite facies metamorphism at approximately 2600 to 2900 m.y. Granitic melts were produced which moved to higher crustal levels, leaving behind the observed depleted Scourian assemblages.
3) Some post-granite, late-stage adjustment of this residuum, involving the formation of the depleted granite gneiss sheets.

It is further suggested, although tentatively at this stage, that such a history may not be unique to the Scourian complex, but may be the mechanism responsible for the observed upward concentration of incompatible elements in the continental crust and the relative depletion of Eu in the upper continental crust since the Archean. Assuming a deep crust of Scourian composition, the continental crust may be stratified with respect to the REE as has been documented for many of the other incompatible elements.

The REE provide a potentially powerful tool for intracrustal studies - particularly in high grade metamorphic terrains. More elaborate and detailed models await a larger data base, particularly for high grade metamorphic rocks, and a more accurate knowledge of the mineral/liquid REE distribution coefficients and the effects of varying P and T on them.

REFERENCES

Ahrens, L. H.: Aspects of the geochemistry of the rare earths. In: Progress in the science and technology of the rare earths, Vol. 1, (L. Eyring, ed.), New York: Pergamon 1964.

Albee, A. L.: Phase equilibria in three assemblages of Kyanite-zone pelitic schists, Lincoln Mountain quadrangle, central Vermont. J. Petrol. 6, 246-301 (1965).

Albuquerque, C. A. R. de: Geochemistry of the tonalitic and granitic rocks of the Nova Scotia southern plutons. Geochim. Cosmochim. Acta 41, 1-13 (1977).

Allen, J. C., Boettcher, A. L., Marland, G.: Amphiboles in andesite and basalt: I. Stability as a function of P-T-fO_2. Amer. Mineral. 60, 1069-1085 (1975).

Arth, J. G.: A model for the origin of the early Precambrian greenstone-granite complex of North-eastern Minnesota. In: The early history of the earth, (B. F. Windley, ed.). London-New York-Sydney-Toronto: Wiley, 1975.

Arth, J. G., Hanson, G. N.: Geochemistry and origin of the early Precambrian crust of northeastern Minnesota. Geochim. Cosmochim. Acta 39, 325-362 (1975).

Balashov, Y. A., Kremenetskiy, A. A., Shvets, V. M.: Geochemical criteria of the nature of Precambrian amphibolites. Geochem. Int. 1973, 918-931 (1973).

Bandurkin, G. A.: Behaviour of the rare earths in fluorine-bearing media. Geochemistry 2, 159-167 (1961).

Barooah, B. C.: Significance of calc-silicate rocks and meta-arkose in the Lewisian complex south-east of Scourie. Scott. J. Geol. 6, 221-225 (1969).

Beach, A.: Amphibolitization of Scourian granulites. Scott. J. Geol. 10, 35-44 (1974).

Berckhemer, H.: Direct evidence for the composition of the lower crust and the Moho. Tectonophysics 8, 97-105 (1969).

Birch, F.: The velocity of compressional waves in rocks to 10 Kilobars, 2. J. Geophys. Res. 66, 2199-2224 (1961).

Bowes, D. R.: Geochemistry of Precambrian crystalline basement rocks, north-west Highlands of Scotland. Proc. 24th Int. Geol. Congr. 1, 97-103 (1972).

Bowes, D. R., Barooah, B. C., Khoury, S. G.: Original nature of Archean rocks of north-west Scotland. Geol. Soc. Aust. Spec. Publ. 3, 77-92 (1971).

Broecker, W., Oversby, V.: Chemical equilibria in the earth. Toronto: McGraw-Hill 1974.

Brooks, C. K.: The concentrations of zirconium and hafnium in some igneous and metamorphic rocks and minerals. Geochim. Cosmochim. Acta 34, 411-416 (1970).

Brown, G. C., Fyfe, W. S.: The production of granitic melts during ultra metamorphism. Contrib. Mineral. Petrol. 28, 310-318 (1970).

Brown, G. C., Fyfe, W. S.: The transition from metamorphism to melting: the status of the granulite and eclogite facies. 24th Int. Geol. Congr. 2, 27-34 (1972).

Brune, J. N. : Surface waves and crustal structure. In : The earth's crust and upper mantle, (P. J. Hart, ed.), Am. Geophys. Mon. 13, 1969.

Brunfelt, A. O., Steinnes, E. : Instrumental activation analysis of silicate rocks with epithermal neutrons. Anal. Chim. Acta 48, 13-24 (1969).

Bullard, E., Everett, J. E., Smith, A. G. : The fit of the continents around the Atlantic. Phil. Trans. Roy. Soc. Lond. A 258, 41-52 (1965).

Buma, G., Frey, F. A., Wones, D. R. : New England granites : trace element evidence regarding their origin and differentiation. Contrib. Mineral. Petrol. 31, 300-320 (1971).

Burns, R. G., Burns, V. M., Turekian, K. K. : Cobalt. In : Handbook of geochemistry, (K. H. Wedepohl, ed.), Berlin-Heidelberg-New York : Springer 1969.

Carmichael, I. S. E., Turner, F. J., Verhoogen, J. : Igneous Petrology. 739 pp. McGraw-Hill 1974.

Chou, C. L., Hamud, A. J., Harris, N. B. W., Goodwin, A. M. : Abundances of rare earth and other trace elements in Archean granitic and gneissic rocks from the eastern Lac Seul region of the English River gneiss belt. Proc. 1976 Geotraverse Conf., 80-86 (1976).

Chou, C. L. Harris, N. B. W., Goodwin, A. M. : Abundances of rare earth and other elements in Archean granitic and gneissic rocks from the English River gneiss. Proc. 1977 Geotraverse Conf., 80-93 (1977).

Christensen, N. I., Fountain, D. M.: Constitution of the lower continental crust based on experimental studies of seismic velocities in granulite. Geol. Soc. Am. Bull. 86, 227-236 (1975).

Compton, R. R.: Charnockitic rocks of Santa Lucia Range, California. Am. J. Sci. 258, 609-636 (1960).

Condie, K. C., Baragar, W. R. A.: Rare earth distributions in volcanic rocks from Archean Greenstone Belts. Contrib. Mineral. Petrol. 45, 237-246 (1974).

Condie, K. C., Hunter, D. R.: Trace element geochemistry of Archean granitic rocks from the Barberton region, South Africa. Earth Planet. Sci. Lett. 29, 389-400 (1976).

Condie, K. C., Lo, H. H.: Trace element geochemistry of the Louis Lake batholith of early Precambrian age, Wyoming. Geochim. Cosmochim. Acta 35, 1099-1119 (1971).

Cullers, R. L., Medaris, L. G., Haskin, L.: Experimental studies of the distribution of rare earths as trace elements among silicate minerals and liquids and water. Geochim. Cosmochim. Acta 37, 1499-1512 (1973).

Cullers, R. L., Yeh, L. T., Chaudhuri, S.: Rare earth elements in Silurian pelitic schists from N. W. Maine. Geochim. Cosmochim. Acta 38, 389-400 (1974).

Davis, B. T. C., Boyd, F. R.: The join $Mg_2Si_2O_6$- $CaMgSi_2O_6$ at 30 Kilobars pressure and its application to pyroxenes from Kimberlites. J. Geophys. Res. 71, 3567-3576 (1966).

Dearnley, R.: The Lewisian complex of South Harris. Quart. J. Geol. Soc. Lon. 119, 243-307 (1963).

Deer, W. A., Howie, R. A., Zussman, J.: Rock-forming minerals. London: Longmau Group (1971).

den Tex, E.: Metamorphic lineages of orogenic plutonism. Geol. Mijnbouw 44, 105-132, (1965).

Dostal, J.: The origin of garnet-cordierite-sillimanite bearing rocks from Chandos Township, Ontario. Contrib. Mineral. Petrol. 49, 163-175 (1975).

Drake, M. J.: The oxidation state of europium as an indicator of oxygen fugacity. Geochim. Cosmochim. Acta 39, 55-64 (1975).

Drake, M. J., Weill, D. F.: Partition of Sr, Ba, Ca, Y, Eu^{2+}, Eu^{3+}, and the other REE between plagioclase feldspar and magmatic liquid: an experimental study. Geochim. Cosmochim. Acta. 39, 689-712 (1975).

Eade, K. E., Fahrig, W. F.: Geochemical evolutionary trends of continental plates - a preliminary study of the Canadian shield. Geol. Survey Canada Bull. 179, 51 pp. (1971).

Emmermann, F., Daieva, L., Schneider, J.: Petrologic significance of rare earth distribution in granites. Contrib. Mineral. Petrol. 52, 267-283 (1975).

Evans, B. W., Shaw, D. M., Haughton, D. R.: Scapolite stoichiometry. Contrib. Mineral. Petrol. 24, 293-305 (1969).

Evans, C. R.: Geochronology of the Lewisian basement near Lochinver, Sutherland. Nature 207, 54-56 (1965).

Evans, C. R.: Geology of the Lochinver district, Sutherland. Ph.D. thesis, Oxford University (1963).

Evans, C. R., Lambert, R. St. J.: The geology of the Lochinver district, Sutherland, the type area of the Inverian metamorphism. J. Geol. Soc. London 130, 125-150 (1974).

Ferrara, G., Treuil, M.: Petrological implications of trace element and Sr Isotope distributions in basalt-pantellerite series. Bull. Volcanol. 38, 548-574 (1975).

Fisher, K., Puchett, H.: Barium. In: Handbook of geochemistry, (K. H. Wedepohl, ed.), Berlin-Heidelberg-New York: Springer 1970.

Flanagan, F. J.: 1972 values for international geochemical reference samples. Geochim. Cosmochim. Acta 37, 1189-1200 (1973).

Frey, F. A.: Rare earth abundances in alpine ultramafic rocks. Phys. Earth Planet. Interiors 3, 323-330 (1970).

Frey, F. A., Bryan, W. B., Thompson, G.: Atlantic ocean floor: geochemistry and petrology of basalts from Leg 2 and 3 of the Deep Sea Drilling Project. J. Geophys. Res. 79, 5507-5527 (1974).

Frey, F. A., Green, D. H.: The mineralogy, geochemistry and origin of lherzolite inclusions in Victorian basanites. Geochim. Cosmochim. Acta 38, 1023-1059 (1974).

Frey, F. A., Haskin, L. A., Haskin, M. A.: Rare-earth abundances in some ultramafic rocks. J. Geophys. Res. 76, 2057-2070 (1971).

Frey, F. A., Haskin, M. A., Poetz, J. A., Haskin, L. A.: Rare earth abundances in some basic rocks. J. Geophys. Res. 73, 6085-6098 (1968).

Frondel, C.: Scandium. In: Handbook of geochemistry (K. H. Wedepohl ed.). Berlin-Heidelberg-New York: Springer 1969.

Fryer, B. J.: Rare earth evidence in iron formations for changing Precambrian oxidation states. Geochim. Cosmochim. Acta 41, 361-367 (1977).

Fyfe, W. S.: The granulite facies, partial melting and the Archean crust. Phil. Trans. Roy. Soc. Lond. A 273, 457-461 (1973).

Gilbert, M. C.: Reconnaissance study of the stability of amphiboles at high pressures. Carnegie Inst. Wash. Yearbook 67, 167-169 (1968).

Gilbert, M. C.: Synthesis and stability relations of the hornblende ferropargasite. Am. J. Sci. 264, 698-742 (1966).

Gilletti, B. J., Moorbath, S., Lambert, R. St. J.: A geochronological study of the metamorphic complexes of the Scottish Highlands. Quart. J. Geol. Soc. Lond. 117, 233-272 (1961).

Glikson, A. Y.: Early Precambrian evidence of a primitive ocean crust and island nuclei of sodic granite. Bull. Geol. Soc. Am. 83, 3323-3344 (1972).

Glikson, A. Y.: Stratigraphy and evolution of primary and secondary greenstones: significance of data from the shields of the southern hemisphere. In: The early history of the earth (B. F. Windley, ed.) London-New York-Sydney-Toronto: Wiley, 1975.

Glikson, A. Y.: Trace element geochemistry and origin of early Precambrian acid igneous series, Barberton Mountain Land, Transvaal. Geochim. Cosmochim. Acta 40, 1261-1280 (1976).

Gordon, G. E., Randle, K., Goles, G., Corliss, J., Beeson, M., Oxley, S.: Instrumental activation analysis of standard rocks with high resolution gamma ray detectors. Geochim. Cosmochim. Acta 32, 369-396 (1968).

Graham, A. L., Nicholls, G. D.: Mass spectrographic determinations of lanthanide element contents in basalts. Geochim. Cosmochim. Acta 33, 555-568 (1969).

Green, D. H., Ringwood, A. E.: An experimental investigation of the gabbro to eclogite transformation and its petrological applications. Geochim. Cosmochim. Acta 31, 767-833 (1967).

Green, T. H.: High pressure experimental studies on the mineralogical constitution of the lower crust. Phys. Earth Planet. Interiors 3, 441-450 (1970).

Green, T. H., Brunfelt, A. O. Heier, K. S: Rare-earth element distribution and K/Rb ratios in granulites, mangerites and anorthosites, Lofoten-Vesteraalen, Norway. Geochim. Cosmochim. Acta 26, 241-257 (1972).

Green, T. H., Brunfelt, A. O., Heier, K. S.: Rare earth element distribution in anorthosites and associated high grade metamorphic rocks, Lofoten-Vesteraalen, Norway. Earth. Planet. Sci. Lett. 7, 93-98 (1969).

Hamilton, D. L.: The ternary feldspar solvus. Abst. I. M. A. Meeting, Cambridge (1966).

Hanson, G. N.: REE analyses of the Morton and Montevideo gneisses from the Minnesota River Valley. Geol. Soc. Am. Abstr. 7, 1099 (1975).

Haskin, L. A., Frey, F. A.: Dispersed and not-so-rare earths. Sci. 152, 299-314 (1966).

Haskin, L. A., Frey, F. A., Schmitt, R. A., Smith, R. H.: Meteoric, solar and terrestrial rare-earth distributions. Phys. Chem. Earth 7, 169-321 (1966).

Haskin, L. A., Haskin, M. A., Frey, F. A., Wildeman, T. R.: Relative and absolute terrestrial abundances of the rare earths. In: Origin and distribution of the elements, (L. H. Ahrens, ed.), 889-912, New York: Pergamon 1968.

Heier, K. S.: Geochemistry of granulite facies rocks and problems of their origin. Phil. Trans. Roy. Soc. Lon. A273, 429-442 (1973).

Heier, K. S.: Metamorphism and the chemical differentiation of the crust. Geol. For. Stockh. Forh. 87, 249-256 (1965).

Heier, K. S.: Petrology and geochemistry of high-grade metamorphic and igneous rocks on Langoy, Northern Norway. Norg. Geol. Unders. 207, 1-246 (1960).

Heier, K. S.: Rubidium-strontium and strontium 87/strontium 86 ratios in deep crustal material. Nature 202, 477-478 (1964).

Heier, K. S., Billings, G. K.: Rubidium. In: Handbook of geochemistry, (K. H. Wedepohl, ed.), Berlin-Heidelberg-New York: Springer, 1970.

Heier, K. S., Brunfelt, A. O.: Concentration of cesium in high grade metamorphic rocks. Earth. Planet. Sci. Lett. 9, 416-420 (1970).

Heier, K. S., Taylor, S. R.: Distribution of Li, Na, K, Rb, Cs, Pb and Tl in southern Norwegian pre-Cambrian alkali feldspars. Geochim. Cosmochim. Acta 15, 284-305 (1959).

Heier, K. S., Thoresen, K.: Geochemistry of high grade metamorphic rocks, Lofoten-Vesteraalen, N. Norway. Geochim. Cosmochim. Acta 35, 89-99 (1971).

Hellman, P. L., Henderson, P.: Are the rare earth elements mobile during zeolitization? Nature 267, 38-40 (1977).

Herrmann, A. G., Potts, M. J., Knoke, D.: Geochemistry of the rare earth elements in spilites from the oceanic and continental crust. Contrib. Mineral. Petrol. 44, 1-16 (1974).

Herrmann, A. G., Wedepohl, K. H.: Untersuchungen an spilitischen Gesteinen der variskischen Geosynkline in Nord west deutschland. Contrib. Mineral. Petrol. 29, 225-274 (1970).

Hewins, R. H.: Pyroxene geothermometry of some granulite facies rocks. Contrib. Mineral. Petrol. 50, 205-209 (1975).

Holland, J. G.: Geochemical studies in the Lewisian. Ph.D. thesis, Oxford University (1966).

Holland, J. G., Lambert, R. St. J.: Chemical petrology and K-Ar ages of the Lewisian gneisses of Rona, Near Skye, Scotland. Geol. Mag. 109, 339-347 (1972a).

Holland, J. G., Lambert, R. St. J.: Comparative major element geochemistry of the Lewisian of the mainland of Scotland. In: The early Precambrian of Scotland and related rocks of Greenland (R. G. Park, J. Tarney, eds.) Univ. of Birmingham Press, 1973.

Holland, J. G., Lambert, R. St. J.: Major element composition of the shields and the continental crust. Geochim. Cosmochim. Acta 36, 373-384 (1972a).

Holland, J. G., Lambert, R. St. J.: The chemistry and origin of the Lewisian gneisses of the Scottish mainland: the Scourie and Inver assemblages and sub-crustal accretion. Precambrian Res. 2, 161-188 (1975).

Holland, J. G., Lambert, R. St. J.: The geochemistry of lithium in the mainland Lewisian of Scotland. Proc. 24th Int. Geol. Congr. 10, 169-178 (1972b).

Holloway, J. R.: The system pargasite - H_2O - CO_2: a model for melting of a hydrous mineral with a mixed-volatile fluid - I. Experimental results to 8 Kbar. Geochim. Cosmochim. Acta 37, 651-666 (1973).

Holloway, J. R., Ford, C. E.: Fluid-absent melting of the fluorohydroxy amphibole pargasite to 35 Kilobars. Earth Planet. Sci. Lett. 25, 44-48 (1975).

Hyndman, R. D., Lambert, I. B., Heier, K. S., Jaeger, J. C., Ringwood, A. E.: Heat flow and surface radioactivity measurements in the Precambrian shield of Western Australia. Phys. Earth Planet. Interiors 1, 129-135 (1968).

Irving, A. J., Frey, F. A.: Effects of composition on the partitioning of rare earth elements, Hf, Sc and Co between garnet and liquid; experimental and natural evidence. EOS 57, 339 (1976).

Ito, K., Kennedy, G. C.: An experimental study of the basalt-garnet granulite-eclogite transition. Am. Geophys. Union Mon. 14, 303-314 (1971).

Ito, K., Kennedy, G. C.: The fine structure of the basalt-eclogite transition. Min. Soc. Am. Sp. Pap. 3, 77-83 (1970).

Jakes, P., Taylor, S. R.: Excess europium content in Precambrian sedimentary rocks and continental evolution. Geochim. Cosmochim. Acta 38, 739-745 (1974).

James, R. S., Hamilton, D. L.: Phase relations in the system $NaAlSi_3O_8$-$KAlSi_3O_8$-$CaAl_2Si_2O_8$-SiO_2 at 1 kilobar water vapour pressure. Contrib. Mineral. Petrol. 21, 111-141 (1969).

Katz, M. B.: Tectonic evolution of the Archean granulite facies belt of Sri Lanka and South India. 25th I.G.C. 1, 13-14 (1976).

Kay, R. W., Gast, P. W.: The rare earth content and origin of alkali-rich basalts. J. Geol. 81, 653-682 (1973).

Kay, R. W., Hubbard, N. J., Gast, P. W.: Chemical characteristics and origin of oceanic ridge volcanic rocks. J. Geophys. Res. 75, 1585-1613 (1970).

Kay, R. W., Senechal, R. G.: The rare earth geochemistry of the Troodos ophiolite complex. J. Geophys. Res. 81, 964-970 (1976).

Khoury, S. G.: The structural geometry and geological history of the Lewisian rocks between Kylesku and Geisgeil, Sutherland, Scotland. Krystalinikum 6, 41-78 (1968).

Koljonen, T., Rosenberg, R. J.: Rare earth elements in granitic rocks. Lithos 7, 249-261 (1974).

Lachenbruch, A. H.: Crustal temperature and heat production: implications of linear heat flow relation. J. Geophys. Res. 75, 3291-3300 (1970).

Lambert, I. B., Heier, K. S.: Estimates of the crustal abundances of thorium, uranium and potassium. Chem. Geol. 3, 233-238 (1968a).

Lambert, I. B., Heier, K. S.: Geochemical investigations of deep-seated rocks in the Australian shield. Lithos 1, 30-53 (1968b).

Leelanandam, C.: Chemical study of pyroxenes from the charnockitic rocks of Kondapalli (Andhra Pradesh), India, with emphasis on the distribution of elements in coexisting pyroxenes. Min. Mag. 36, 153-179 (1967).

Lewis, J. D., Spooner, C. M.: K/Rb ratios in Precambrian granulite terrains. Geochim. C smochim. Acta 37, 1111-1118 (1973).

Loubet, M., Shimizu, N., Allegre, C. J.: Rare earth elements in alpine peridotites. Contrib. Mineral. Petrol. 53, 1-12 (1975).

MacGregor, I. D.: The system MgO-Al_2O_3-SiO_2: solubility of Al_2O_3 in enstatite for spinel and garnet peridotite compositions. Am. Mineral. 59, 110-119 (1974).

Manghnani, M. H., Ramananantoandro, R., Clark, S. P.: Compressional and shear wave velocities in granulite facies rocks and eclogites to 10 Kbar. J. Geophys. Res. 79, 5427-5446 (1974).

Masuda, A., Nakamura, N., Tanaka, T.: Fine structures of mutually normalized rare-earth patterns of chondrites. Geochim. Cosmochim. Acta 37, 239-248 (1973).

Masuda, A., Nakamura, N., Tanaka, T.: Rare earth elements in metagabbros from the Mid-Atlantic ridge and their possible implications for the genesis of alkali olivine basalts as well as the Lizard peridotite. Contrib. Mineral. Petrol. 32, 295-306 (1971).

Matzat, E., Shiraki, K.: Chromium. In: Handbook of geochemistry (K. H. Wedepohl, ed.). Berline-Heidelberg-New York: Spring 1969.

McGetchin, T. R., Silver, L. T.: A crustal-upper mantle model for the Colorado Plateau based on observations of crystalline rock fragments in the Moses Rock Dike. J. Geophys. Res. 77, 7022-7037 (1972).

Mineyev, D. A.: Geochemical differentiation of the rare earths. Geochemistry 12, 1129-1149 (1963).

Montigny, R., Bougault, H., Bottinga, Y., Allegre, C. J.: Trace element geochemistry and genesis of the Pindos ophiolite suite. Geochim. Cosmochim. Acta 37, 2135-2147 (1973).

Moorbath, S.: The geological significance of early Precambrian rocks. Proc. Geol. Assoc. 86, 259-279 (1975).

Moorbath, S., Park, R. G.: The Lewisian chronology of the southern region of the Scottish mainland. Scottl. J. Geol. 8, 51-74 (1972).

Moorbath, S., Welke, H., Gale, N. W.: The significance of lead isotope studies in ancient, high-grade metamorphic basement complexes, as exemplified by the Lewisian rocks of northwest Scotland. Earth Planet. Sci. Lett. 6, 245-256 (1969).

Morris, R. V.: Electron paramagnetic resonance study of the site preference of Gd^{3+} and Eu^{2+} in polycrystalline silicate and aluminate minerals. Geochim. Cosmochim. Acta. 39, 621-634 (1975).

Morrison, G. H., Gerard, J. T., Travesi, A., Currie, R. L., Peterson, S. F., Potter, N. M.: Multielement neutron activation analyses of rock using chemical group separations and high resolution gamma spectrometry. Anal. Chem. 41, 1633-1637 (1969).

Muecke, G. K.: Petrogenesis of granulite-facies rocks from the Lewisian of North-West Scotland. Ph.D. Thesis, Oxford University (1969).

Muecke, G. K., Pride, C., Sarkar, P.: Rare earth element geochemistry of regional metamorphic rocks: In: Origin and Distribution of the Elements 2, in press, 1978.

Mueller, S., ed.: The structure of the earth's crust based on seismic data. 391 pp., Amsterdam: Elservier, 1974.

Mysen, B. O.: Rare earth partitioning between crystals and liquid in the upper mantle. Carn. Inst. Wash. Year Book 75, 656-659 (1976).

Nagasawa, H., Schnetzler, C. C.: Partitioning of rare earth, alkali and alkaline earth elements between phenocrysts and acidic igneous magma. Geochim. Cosmochim. Acta 35. 953-968 (1971).

Nance, W. B., Taylor, S. R.: Rare earth element patterns and crustal evolution - I. Australian post-Archean sedimentary rocks. Geochim. Cosmochim. Acta 40, 1539-1551 (1976).

Nance, W. B., Taylor, S. R.: Rare earth element patterns and crustal evolution - II. Archean sedimentary rocks from Kalgoorlie, Australia. Geochim. Cosmochim. Acta 41, 189-193 (1977).

Nur, A., Simmons, G.: The effect of saturation on velocity in low-porosity rocks. Earth Planet. Sci. Lett. 7, 189-193 (1969).

O'Hara, M. J.: A garnet-hornblende-pyroxene rock from Glenelg, Inverness-shire. Geol. Mag. 97, 145-156 (1960).

O'Hara, M. J.: Great thicknesses and high geothermal gradient of Archean crust: the Lewisian of Scotland. Abstracts, Int. Conf. Geotherm. Geobarom., Penn. State U., October, (1975).

O'Hara, M. J.: Mineral facies in ultrabasic rocks. In: Ultramafic and related rocks, (P. J. Wyllie, ed), New York: Wiley and Sons, 1967.

O'Hara, M. J.: Origin of ultrabasic and basic gneiss masses in the Lewisian. Geol. Mag. 102, 296-314 (1965).

O'Hara, M. J.: Thermometry and barometry of Scourie gneisses. I.G.C.P. Archean geochemistry meeting, Geol. Soc. Lon. (1976).

O'Hara, M. J.: Zoned ultrabasic and basic gneiss masses in the early Lewisian metamorphic complex at Scourie, Sutherland. J. Petrol. 2, 248-276 (1961).

Oliver, R. L.: Some observations on the distribution and nature of granulite-facies terrains. Spec. Publ. Geol. Soc. Australia 2, 259-268 (1969).

Onuma, N., Higuchi, H., Wakita, H., Nagasawa, H.: Trace element partition between two pyroxenes and the host volcanic rocks. Earth Planet. Sci. Lett. 5, 47-51 (1968).

Orso, V. I., Yeliseyeva, G. D., Kazantseva, A. I.: Rare earth assemblages in the accessory minerals of the ancient crystalline rocks of the Middle Dnepr region. Geochem. Int. 1967, 170-173 (1967).

Pakiser, L. C., Zietz, I.: Transcontinental crustal and upper-mantle structure, Rev. Geophys. 3, 505-520 (1965).

Peach, B. N., Horne, J., Gunn, W., Clough, C. T., Hinxman, L. W.: The geological structure of the North-West Highlands of Scotland. Mem. Geol. Surv. Great Britain. (1907).

Pettijohn, F. J.: Sedimentary rocks. 718 pp. New York: Harper and Row, 1957.

Philpotts, J. A.: Redox estimation from a calculation of Eu^{+2} and Eu^{+3} concentrations in natural phases. Earth Planet. Sci. Lett. 9, 257-268 (1970).

Philpotts, J. A., Schnetzler, C. C., Hart, S. R.: Submarine basalts: some K, Rb, Sr, Ba, rare-earth, H_2O and CO_2 data bearing on their alteration, modification by plagioclase, and possible source materials. Earth Planet. Sci. Lett. 7, 293-299 (1969).

Philpotts, J. A., Schnetzler, C. C., Thomas, H. H.: Petrogenetic implications of some new geochemical data on eclogitic and ultrabasic inclusions. Geochim. Cosmochim. Acta 36, 1131-1166 (1972).

Piper, D. Z.: Rare earth elements in the sedimentary cycle: a summary. Chem. Geol. 14, 285-304 (1974).

Poldervaart, A.: Chemistry of the earth's crust. In: Crust of the earth (A. Poldervaart, Ed.), Geol. Soc. Am. Sp. Paper 62, 119-144 (1955).

Powell, M., Powell R.: Plagioclase-alkali feldspar geothermometry revisited. Min. Mag. 41, 253-256 (1977).

Price, R. C., Taylor, S. R.: The rare earth element geochemistry of granite, gneiss, and migmatite from the Western Metamorphic Belt of South-Eastern Australia. Contrib. Mineral. Petrol. 62, 249-263 (1977).

Puchett, H., Emmermann, R.: Bearing of rare earth patterns of apatites from igneous and metamorphic rocks. Earth Planet. Sci. Lett. 31, 279-286 (1976).

Raheim, A., Green, D. H.: Experimental determination of the temperature and pressure dependence of the Fe-Mg partition coefficient for coexisting garnet and clinopyroxene. Contrib. Mineral. Petrol. 48, 179-203 (1974).

Raheim, A., Green, D. H.: P, T paths of natural eclogites during metamorphism - a record of subduction. Lithos 8, 317-328 (1975).

Randle, K.: Some trace element data and their interpretation for several new reference samples obtained by neutron activation analysis. Chem. Geol. 13, 237-256 (1974).

Reitan, P. H., Roelandts, I.: Rare earth partioning: coexisting metamorphic pyroxenes. Geol. Soc. Am. Abstr. 5, 778-779 (1973).

Rey, P., Wakita, H., Schmitt, R. A.: Radiochemical neutron activation analysis of indium, cadmium, yttrium and the 14 rare earth elements in rocks. Anal. Chim. Acta 51, 163-178 (1970).

Ringwood, A. E., Green, D. H.: An experimental investigation of the gabbro-eclogite transformation and some geophysical implications. Tectonophysics 3, 383-427 (1966).

Roaldset, E.: Rare earth element distributions in some Precambrian rocks and their phyllosilicates, Numedal, Norway. Geochim. Cosmochim. Acta 39, 455-469 (1975).

Rogers, N., Nixon, P. H.: Geochemistry of lower crustal granulite xenoliths from Lesotho Kimberlites. 19th Ann. Rep. Res. Inst. Afr. Geol. University of Leeds, 38-41 (1975).

Ronov, A. B., Balashov, Y. A., Girin, Y. P.: Regulations of rare earth element distribution in the sedimentary shell and in the crust of the earth. Sedimentology 21, 171-193 (1974).

Ronov, A. B., Balashov, Y. A., Migdisov, A. A.: Geochemistry of the rare earths in the sedimentary cycle. Geochem. Int. 4, 1-17 (1967).

Routi, J. T.: Sampo, a fortran IV program for computer analysis of gamma spectra from Ge (Li) detectors and other spectra with peaks. Am. Gov. Rept. UCRL - 19452, 31 pp. (1969).

Schilling, J. G.: Sea floor evolution: rare earth evidence. Phil. Trans. Roy. Soc. Lond. A268, 663-706 (1971).

Schmitt, R. A., Smith, R. H., Lash, J. E., Mosen, A. W., Olehy, D. A., Vaselevskis, J.: Abundances of the fourteen rare-earth elements, scandium and yttrium in meteoritic and terrestrial matter. Geochim. Cosmochim. Acta 27, 577-622 (1963).

Schnetzler, C. C., Philpotts, J. A.: Partition coefficients of rare-earth elements and barium between igneous matrix material and rock-forming mineral phenocrysts - I. In: Origin and distribution of the elements (L. H. Ahrens, ed.), 929-938. Pergamon, 1968.

Schnetzler, C. C., Philpotts, J. A.: Partition coefficients of rare-earth elements between igneous matrix material and rock-forming mineral phenocrysts - II. Geochim. Cosmochim. Acta 34, 331-340 (1970).

Shackleton, R. M.: Shallow and deep-level exposures of the Archean crust in India and Africa. In: The early history of the earth, (B. F. Windley, ed.) London-New York-Sydney-Toronto: Wiley, 1975.

Shaw, D. M.: A review of K-Rb fractionation trends by covariance analysis. Geochim. Cosmochim. Acta 32, 573-601 (1968).

Shaw, D. M.: Trace element fractionation during anatexis. Geochim. Cosmochim. Acta 34, 237-243 (1970).

Shaw, D. M., Dostal, J., Keays, R. R.: Additional estimates of continental surface Precambrian Shield composition in Canada. Geochim. Cosmochim. Acta 40, 73-83 (1976).

Shaw, D. M., Reilly, G. A., Muysson, J. R., Pattenden, G. E., Campbell, F. E.: The chemical composition of the Canadian Precambrian shield. Can. J. Earth Sci. 4, 829-854 (1967).

Sheraton, J. W., Skinner, A. C., Tarney, J.: The geochemistry of the Scourian gneisses of the Assynt district. In: The Early Precambrian of Scotland and related rocks of Greenland (R. G. Park, J. Tarney, eds.), Univ. of Birmingham Press, 1973.

Sighinolfi, G. P.: Beryllium in deep-seated crustal rocks. Geochim. Cosmochim. 37, 702-706 (1972).

Sighinolfi, G. P.: Investigations into deep crustal levels: fractionating effects and geochemical trends related to high-grade metamorphism. Geochim. Cosmochim. Acta 35, 1005-1021 (1971).

Sighinolfi, G. P.: K-Rb ratio in high grade metamorphism: a confirmation of the hypothesis of a continental crustal evolution. Contrib. Mineral. Petrol. 21, 346-356 (1969).

Sighinolfi, G. P., Sakai, T.: Uranium and thorium in Archean granulite facies terrains of Bahia, Brazil. Geochem. J. II., 33-39, (1977).

Smewing, J. D., Potts, P. J.: Rare-earth abundances in basalts and meta-basalts from the Troodos massif, Cyprus. Contrib. Mineral. Petrol. 57, 245-258 (1976).

Smithson, S. B., Brown, S. K.: A model for lower continental crust. Earth Planet. Sci. Lett. 35, 134-144 (1977).

Smithson, S. B., Shive, P. N.: Field measurements of compressional wave velocities in common crystalline rocks. Earth Planet. Sci. Lett. 27, 170-176 (1975).

Sollogub, V. B., Prosen, D.: Crustal structure of central and southeastern Europe by data of explosion seismology. In: The structure of the earth's crust based on seismic data. (S. Mueller, ed.) 1-33, Amsterdam: Elsevier 1974.

Spooner, C. M.: Sr^{87}/Sr^{86} initial ratios, K/Rb ratios and rare-earth element abundances in pyroxene granulites. Ph.D. thesis, M.I.T. (1969).

Stormer, J. C.: A practical two-feldspar geothermometer. Amer. Mineral. 60, 667-674 (1975).

Sun, S. S., Hanson, G. N.: Origin of Ross Island basanitoids and limitations upon the heterogeneity of mantle sources for alkali basalts and nephelinites. Contrib. Mineral. Petrol. 52, 77-106 (1975).

Sutton, J.: The first three-quarters of the geological record in Britain. In: The early Precambrian of Scotland and related rocks of Greenland (R. G. Park, J. Tarney, eds.) 9-12, University of Keele: Newcastle, England, 1973.

Sutton, J., Watson, J.: The pre-Torridonian metamorphic history of the Loch Torridon and Scourie areas in the North-West Highlands and its bearing on the chronological classification of the Lewisian. Quart. J. Geol. Soc. London 106, 241-296 (1951).

Tarney, J., Skinner, A. C., Sheraton, J. W.: A geochemical comparison of major Archean gneiss units from Northwest Scotland and East Greenland. Proc. 24th Int. Geol. Congr. 1, 162-174 (1972).

Tarney, J., Windley, B. F.: Chemistry, thermal gradients and evolution of the lower continental crust. J. Geol. Soc. Lond. 134, 153-172 (1977).

Taylor, S. R.: Abundances of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta 28, 1273-2185 (1964b).

Taylor, S. R.: The application of trace element data to problems in petrology. In: Physics and chemistry of the earth, VI, Pergamon Press, 133-213, 1965.

Taylor, S. R.: Trace element abundances and the chondritic earth model. Geochim. Cosmochim. Acta 28, 1989-1998 (1964a).

Touret, J. : Le facies granulite en Norvege meridionale. II. Les inclusions fluides. Lithos 4, 423-436 (1971).

Turner, F. J. : Metamorphic petrology; mineralogical and field aspects. 403 pp. New York-London-Toronto-Sydney : McGraw-Hill 1968.

Urey, H. C. : The abundances of the elements. Phys. Rev. 88, 248-252 (1952).

Varne, R., Graham, A. L. : Rare earth abundances in hornblende and clinopyroxene of a hornblende lherzolite xenolith. Implications for upper mantle fractionation processes. Earth Planet. Sci. Lett. 13, 11-18 (1971).

Veizer, J. : Secular variations in chemical and isotopic composition of sediments : A review. 2nd Symp. Origin. Distr. Elements. Abst., 75, (1977).

Veizer, J. : Sedimentation in geological history : recycling vs evolution or recycling with evolution. Contrib. Mineral. Petrol. 38, 261-278 (1973).

von Platen, H. : Kristallisation granitischer Schmelzen. Contrib. Mineral Petrol. II, 334-381 (1965).

Watson, J. : Concluding remarks : the evolution of a polycyclic gneiss complex. In : The early Precambrian of Scotland and related rocks of Greenland. (R. G. Park, J. Tarney, eds.) 191-194, University of Keele : Newcastle, England 1973.

Wells, P. R. A. : Pyroxene thermometry in simple and complex systems. Contrib. Mineral. Petrol. 62, 129-139 (1977).

Whitney, J. A.: The effects of pressure, temperature, and X_{H_2O} on phase assemblages in four synthetic rock compositions. J. Geol. 83, 1-31 (1975).

Whittaker, E. J. W., Muntus, R.: Ionic radii for use in geochemistry. Geochim. Cosmochim. Acta 34, 945-956 (1970).

Wildeman, T. R., Condie, K. C.: Rare earths in Archean graywackes from Wyoming and from the Fig Tree Group, South Africa. Geochim. Cosmochim. Acta 37, 439-453 (1973).

Wildeman, T. R., Haskin, L. A.: Rare earths in Precambrian sediments. Geochim. Cosmochim. Acta 37, 419-439 (1973).

Winkler, H. G. F.: Petrogenesis of metamorphic rocks. 320 pp. Berlin-Heidelberg-New York: Springer 1974.

Winkler, H. G. F., von Platen, H.: Experimentelle gesteins metamorphose - II. Bildung von anatektischen granitischen Schmelzen bei der Metamorphose von NaCl - fuhrenden Kalkfreien Tonen. Geochim. Cosmochim. Acta 15, 91-112 (1958).

Wood, B. J.: Samarium distribution between garnet and liquid at high pressure. Carn. Inst. Wash. Year Book 75, 659-662 (1976).

Wood, B. J., Banno, S.: Garnet-orthopyroxene and orthopyroxene-clinopyroxene relationships in simple and complex systems. Contrib. Mineral. Petrol. 42, 109-124 (1973).

Wood, D. A., Gibson, I. L., Thompson, R. N.: Elemental mobility during zeolite facies metamorphism of the Tertiary basalts of eastern Iceland. Contrib. Mineral. Petrol. 55, 241-254 (1976).

Woolard, G. P. : Evaluation of the isostatic mechanism and role of minerological transformations from seismic and gravity data. Phys. Earth Planet. Interiors 3, 484-498 (1970).

Zayats, A. P., Kuts, V. P. : Rare earth elements in the accessory minerals of gneisses of the Ukranian crystalline shield. Geochem. Int. 1964, 1126-1127 (1964).

Zielinski, R. A., Frey, F. A. : Gough Island: evaluation of a fractional crystallization model. Contrib. Mineral. Petrol. 29, 242-254 (1970).

APPENDIX I

Experimental Method

The major analytical technique employed in this study was instrumental neutron activation analysis (INAA). This method has been described in detail by Gordon et al. (1968) and, therefore, only a brief summary will be given here, followed by a discussion of accuracy and precision.

Theory

Samples are irradiated in a neutron flux which induces (n,γ) reactions. The product nuclide (s) of interest decays at a known half-life ($t_{\frac{1}{2}}$) giving off γ-rays of known energy. In the comparator method, samples and standards are irradiated together, to limit errors due to variable neutron flux (a flux monitor further reduces such errors). By choosing standards chemically similar to the samples of interest and by rigid control of the sample counting geometry, errors due to matrix effects, counting geometry, and different peak to background ratios can be minimized.

Samples counted at different times are corrected for decay using the radioactive decay equation:

$$N(0) = \frac{N(t)}{e^{-\lambda t}}$$

where $N(o)$ = no. of daughter products at time 0

$N(t)$ = no. of daughter products at time t

λ = decay constant of nuclide of interest.

Laboratory Facilities

The activation laboratory in the Geology Department at Dalhousie University consists of two Ortec 48 cm^3 Ge (Li) coaxial detectors, complete with NIM standard modular instrumentation, yielding two independent counting systems. The detectors are encased in a divided lead castle 90 cm by 160 cm., with a height of 115 cm. The castle is surrounded by 5 cm. of lead shielding, and a graded shielding of Cd, Cu and Al. The resolution of the detectors is approximately 2.2 KeV at 1332 KeV and the efficiency is approximately 10% of the 3 x 3 inch NaI (Tl) detector at 1332 KeV.

Amplifier signals are stored and analysed in a 4096 channel Nuclear Data model 50/50 pulse-height analyser with a PDP - 8/L as the on-line computer. Spectra are collected over the energy range 60 to 1660 KeV on 2048 channels. A PDP-12 computer is used for data transfer to the University CDC 6400 computer for off-line data processing.

Sample Preparation and Irradiation

Approximately 0.1 to 0.2 grams of powdered sample was weighed out, packed and sealed in clean, pure silica ampoules. (In the case of the mineral separates, each sample was hand-picked under the microscope with an estimated purity of greater than 99.5%). A weighed portion of Fe wire was wrapped around each sample to act as a flux monitor. Each group of 10 samples (including 3 standards) was then packed in an aluminum canister and sent to the McMaster Nuclear Reactor (Hamilton, Ontario) for irradiation. Irradiations were of approximately four hours duration at a flux of

10^{12} n/cm.^{2} sec. to 10^{14} n/cm.^{2} sec. After irradiation, the canisters were allowed to cool for three to four days at the reactor centre prior to shipment.

Counting Procedure and Data Processing

Samples were counted at three intervals after irradiation - chosen to maximize total counts above backround and minimize interferences. The short half-life ($t_{\frac{1}{2}}$) elements La and Sm were analysed on arrival (approximately one week after irradiation). Lu was analysed two weeks after irradiation, and all other elements, approximated six weeks after irradiation. The particulars for each element, such as photopeak used, interferences, $t_{\frac{1}{2}}$ etc., are given in Table A-1. The length of the counting interval was generally chosen to obtain a minimum of 10,000 counts above background yielding a counting error of 1%. This was not always possible, however, as on long counts it was observed that detector drift may become a serious problem and hence an upper limit of 20 to 25 hours was established for the counting interval.

Spectral data were punched out on paper tapes, converted onto a magnetic tape via the PDP-12 computer, and transferred to a library file in the CDC 6400 computer for off-line data processing. Peak areas were calculated by one of the following methods, depending on the complexity of the peak involved:

1) For singlet peaks (e.g. La, 1596 KeV) with an approximately linear continuum, the peak area was calculated using a simple linear background.

Table A-1: Element photopeaks, half-lives, interferences, and optimum counting time after irradiation.

Element	Target Nuclide	Product Nuclide	KeV	$t_{\frac{1}{2}}$	Interferences	Optimum counting time after irradiation
La	^{139}La	^{140}La	1596	40.2 hours		1 week
Sm	^{152}Sm	^{153}Sm	103	47 hours		1 week
Lu	^{176}Lu	^{177}Lu	208	6.7 days		2 weeks
Eu	^{151}Eu	^{152}Eu	122	12.7 years	Ba (124 KeV) - separated by SAMPO	1 to 2 months
Tb	^{159}Tb	^{160}Tb	299	72.1 days	Pa (300 KeV) - treated as singlet, Pa contribution corrected from singlet Pa(311KeV)	"
Ce	^{140}Ce	^{141}Ce	145	33 days	Fe (142 KeV) - separated by SAMPO or corrected from Fe (192 KeV)	"
Yb	^{168}Yb	^{169}Yb	177	32 days	Ta (179 KeV) - corrected from Ta (1221 and 1231 KeV)	"
Sc	^{45}Sc	^{46}Sc	889	83.9 days		"
Cr	^{50}Cr	^{51}Cr	320	27.8 days		"
Hf	^{180}Hf	^{181}Hf	482	42.5 days	Ba (487 KeV) - separated by SAMPO	"
Co	^{59}Co	^{60}Co	1173	5.26 years		"
Th	^{232}Th	^{233}Pa	311	27.0 days		"

2) For doublet peaks and those on the edge of the Compton continuum, the program SAMPO (Routi et al., 1969) was used. This program separates complex peaks, calculates a quadratic continuum and the peak area.

Resulting areas were corrected for differential decay, different sample weights and flux variations. The corrected areas were then compared directly to the standard for the result in ppm.

Precision and Accuracy

U.S.G.S. AGV-1 was the standard used throughout the study as it has a γ-ray spectrum very similar to many of the samples analysed, and its REE content is known to a fair degree of accuracy. Each group of 10 samples irradiated included 2 AGV-1's and a USGS G-2 standard. The duplicate AGV-1's allow an assessment of intra-group precision, and the G-2 standards allow an assessment of inter-group precision and some comparison in absolute terms to results reported by other workers. The values for the unknown Scourian samples were obtained from the mean of the results from the two AGV-1's.

The limiting factor in the accuracy of the results is the accuracy of the AGV-1 values used, which are those of Flanagan (1973). The results for the duplicate AGV-1 samples are presented in Table A-2a. The precision is best for the elements La, Sm, Ce and Eu (±7, ±7, ±11 and ±12%, respectively), followed by Tb and Lu (±14%). Yb shows the poorest precision of all the REE determined (±18%). Of the other elements determined, Sc, Th, Co and Hf are the most precise (< ± 20%), whereas Cr

Table A-2: a) Duplicate AGV-1 results and
b) G-2 results, for all elements

a) Duplicate AGV-1 Results

	Values Used* (ppm)	1	2	3	4	5	6	7	8	9	10	Mean	σ
La	35	35	36	34	32	35	34	36	35	n.a.**	n.a.	35	2.5
Ce	63	60	62	62	59	56	58	62	64	60	65	61	7.0
Sm	5.9	6.0	6.0	5.6	-	5.9	5.8	6.2	5.8	n.a.	n.a.	5.9	0.4
Eu	1.7	1.7	1.6	1.7	1.6	1.3	1.6	1.6	1.6	1.6	1.7	1.6	0.2
Tb	0.70	0.74	0.68	0.69	0.70	0.59	0.71	0.78	0.70	0.73	0.68	0.70	0.10
Yb	1.7	1.7	1.5	1.7	1.6	1.4	1.8	1.8	1.9	1.7	1.7	1.7	0.3
Lu	0.28	0.26	0.28	0.30	0.27	0.33	0.26	0.27	0.28	0.27	0.28	0.28	0.04
Co	14.1	14.7	13.9	13.1	13.0	12.9	13.3	14.5	15.3	13.1	14.5	13.8	2.4
Sc	13.4	13.6	13.3	13.0	12.7	13.2	13.5	13.4	13.2	12.9	13.7	13.3	0.8
Hf	5.2	5.3	5.4	5.6	4.9	-	6.0	-	-	5.0	5.5	5.4	0.7
Cr	12.2	9.5	11.6	12.1	10.0	12.9	12.7	-	10.1	13.4	14.9	11.9	4.3
Th	6.41	6.30	6.21	6.10	6.20	-	-	6.16	6.29	5.95	6.66	6.23	0.39

b) Results for G-2 (using average obtained from both AGV-1's)

	1	2	3	4	5	6	7	8	9	10	Mean	σ
La	83	84	78	78	79	73	82	79	83	78	80	8
Ce	128	146	160	149	147	143	144	150	156	150	147	18
Sm	7.8	7.7	7.4	7.1	n.a.	7.0	7.7	7.1	n.a.	n.a.	7.4	0.8
Eu	1.6	1.5	1.6	1.7	1.4	1.4	1.4	1.6	1.6	1.6	1.5	0.3
Tb	0.62	0.54	0.57	0.58	0.49	0.55	0.71	0.52	0.57	0.50	0.57	0.14
Yb	0.89	0.53	0.84	0.67	0.84	0.87	0.83	0.94	0.77	0.91	0.81	0.29
Lu	0.12	0.13	0.13	0.15	0.16	0.13	0.12	0.13	0.12	0.13	0.13	0.025
Co	4.6	4.0	4.0	4.2	4.4	4.2	3.8	4.0	4.1	4.4	4.2	0.60
Sc	4.0	3.8	4.1	4.0	3.8	3.9	3.7	3.7	4.0	3.7	3.9	0.4
Hf	8.6	9.1	8.7	8.0	n.a.	10.4	n.a.	n.a.	8.4	7.9	8.7	1.5
Cr	8.6	9.8	9.4	12.0	9.0	8.8	n.a.	10.8	10.3	8.9	9.7	2.6
Th	25.6	25.2	26.3	25.8	n.a.	n.a.	24.1	23.7	24.5	23.8	24.9	2.4

* Flanagan, 1973

** Not analysed.

shows very poor precision. The precision and accuracy is worst for the elements with the poorest cross-sections and those with the most difficult interferences. The counting times were generally chosen to maximize the REE results - hence, the generally poorer results for the other elements.

The results for G-2 (Table A-2b.) show a similar trend to the above results, but generally are less precise. This is to be expected as the G-2 values refer to inter-group precision and the G-2 spectrum differs considerably from that of AGV-1, adding to possible sources of errors. The mean REE values obtained for G-2 compare favourably with results reported by other workers using a variety of methods (Table A-3).

The poorest results for the Scourian samples analysed are probably for some of the minerals with distinctly different spectra (very high or very low peak/background ratios) and/or very low or high abundances of a particular element resulting in large extrapolations from the standard value (e.g. Yb and Lu values for garnet, discussed in Chapter 5).

From the preceding discussion, the accuracy of the results presented in this study may be taken as follows (the mineral results may be slightly less accurate):

Element	Accuracy	Element	Accuracy
La	± 7 to 10%	Lu	± 14 to 19%
Ce	± 11 to 12%	Sc	± 7 to 10%
Sm	± 7 to 11%	Cr	± 27 to 35%
Eu	± 12 to 20%	Co	± 14 to 17%

Table A-3: Comparison of G-2 REE results from this study with other workers.

Source	This Study	Arth and Hanson, 1975	Rey *et al.*, 1970	Morrison *et al.*, 1969	Green *et al.*, 1972	Gordon *et al.*, 1968	Buma *et al.*, 1971	Randle, 1974	Brunfelt and Steinnes, 1969	Flanagan (1973)
La	80	-	93	78	100	81	85	90	-	96
Ce	147	165	170	110	177	144	168.5	154	-	150
Sm	7.4	6.93	7.3	7.0	7.2	8.7	7.4	7.4	6.87	7.3
Eu	1.5	1.35	1.53	1.3	1.51	1.37	1.29	1.18	-	1.5
Tb	0.57	-	0.30	0.5	0.44	0.52	0.40	-	0.48	0.54
Yb	0.81	0.543	0.72	0.90	0.76	0.8	0.56	<1	0.9	0.88
Lu	0.13	0.0775	0.13	0.13	0.11	0.18	0.10	0.113	-	0.11
Method*	INAA	I.D.		G.S.	INAA	INAA	INAA	INAA	E.A.	

* INAA = instrumental neutron activation analysis

I.D. = isotope dilution

G.S. = group separation

E.A. = epithermal activation analysis

Element	Accuracy	Element	Accuracy
Tb	± 14 to 25%	Hf	± 13 to 17%
Yb	± 18 to 30%	Th	± 6 to 10%

APPENDIX 2

REE Distribution Coefficients for Coexisting Scourian Minerals

a) Clinopyroxene-orthopyroxene

	65-18	65-33	64-12	67-109	67-30	Mean (5)
La	2.83	1.93	5.93	2.62	5.91	3.84
Ce	3.90	5.93	5.18	2.71	8.88	5.32
Sm	18.2	12.2	19.8	5.51	31.8	17.5
Eu	11.9	13.5	8.85	7.29	23.0	12.9
Tb	15.1	7.87	13.7	5.69	17.9	12.1
Yb	4.71	3.73	8.59	7.23	5.63	5.98
Lu	2.99	1.75	7.29	9.02	5.87	5.38

b) Clinopyroxene-plagioclase

	65-18	65-33	64-12	66-11	65-41	67-109	67-30	Mean (7)
La	0.72	0.80	0.83	0.86	0.78	0.63	1.21	0.83
Ce	3.05	3.13	1.68	2.36	2.56	2.08	3.57	2.63
Sm	19.9	9.43	15.0	5.41	16.0	10.5	22.2	14.1
Eu	1.69	1.63	2.05	1.73	1.91	2.22	1.65	1.84
Tb	38.3	10.6	12.0	4.93	7.40	7.74	30.4	15.9
Yb	71.1	32.3	36.5	24.9	17.3	24.5	138	49.2
Lu	47.1	58.8	44.3	41.3	44.9	48.1	164	64.1

c) Orthopyroxene-plagioclase

	65-18	65-33	64-12	67-109	65-165	67-30	Mean (6)
La	0.25	0.42	0.14	0.24	0.28	0.20	0.26
Ce	0.78	0.53	0.32	0.77	0.43	0.40	0.54
Sm	1.09	0.77	0.76	1.91	0.42	0.70	0.94
Eu	0.14	0.12	0.23	0.30	0.05	0.07	0.15
Tb	2.53	1.35	0.88	1.36	0.58	1.70	1.40
Yb	15.1	8.67	4.25	3.38	16.0	24.5	12.0
Lu	15.8	33.5	6.09	5.32	29.2	27.9	19.6

d) Clinopyroxene-garnet

	65-33	65-41	67-109	67-30	Mean (4)
La	4.76	5.00	10.8	16.7	7.14
Ce	5.88	3.70	3.85		5.56
Sm	3.03	2.78	2.56	2.78	2.78
Eu	1.79	1.30	1.16	1.00	1.25
Tb	0.48	0.35	0.50	1.03	0.50
Yb	0.10	0.10	0.20	0.38	0.12
Lu	0.20	0.23	0.31	0.38	0.26

e) Hornblende-clinopyroxene

	64-12	67-109	Mean (2)
La	2.14	2.84	2.49
Ce	3.24	2.67	2.96
Sm	1.51	1.84	1.68
Eu	2.23	1.94	2.09
Tb	2.14	1.37	1.76
Yb	2.19	0.58	1.39
Lu	1.08	0.35	0.72

APPENDIX 3

Literature Mean REE Mineral Data

a) Clinopyroxene (ppm)

Rock Type No. of Samples Reference*	Dacite (1) (1)	Lizard Peridotite (1) (3)	Basalt-Andesite (3) (2, 5)	Rhyolite (1) (5)
La		0.038		
Ce	19.2		5.86	96.6
Pr		0.079		
Nd	25.9	0.963	6.94	80.6
Sm	9.9	0.907	2.25	19.8
Eu	1.67	0.408	0.645	3.60
Gd		2.04		
Tb		0.438		
Dy	18.2		2.07	12.0
Ho		0.713		
Er	9.2	2.16	0.994	5.47
Tm		0.32		
Yb	8.6	1.72	0.809	4.31
Lu	1.34	0.297		0.707

b) Orthopyroxene (ppm)

Rock Type No. of Samples Reference*	Dacite (5) (1)	Basalt-Andesite (2) (5)	Lizard Peridotite (3) (3)
La			0.006
Ce	5.75	0.353	
Pr			0.0043
Nd	3.47	0.484	0.047
Sm	0.88	0.247	0.050
Eu	0.13		0.0273
Gd			0.143
Tb			0.042
Dy	1.54	0.877	
Ho			0.110
Er	1.45	0.926	0.37
Tm			0.072
Yb	2.18	1.38	0.52
Lu	0.43		

c) Plagioclase (ppm)

Rock Type No. of Samples Reference*	Dacite (5) (1)	Basalt-Andesite (4) (5)	Granite (1) (7)
La			22
Ce	11.6	2.05	38
Nd	3.23	1.28	
Sm	0.45	0.297	1.5
Eu	1.46	0.453	0.76
Gd		0.344	
Tb			0.07
Dy	0.255	0.262	
Er	0.117	0.166	
Yb	0.12	0.178	0.12
Lu	0.019	0.031	0.02

d) Hornblende (ppm)

Rock Type No. of Samples Reference*	Dacite (4) (1)	Basalt-Andesite (1) (5)	Lizard Peridotite (1) (3)	Lherzolite Xenolith (1) (6)
La			2.2	39
Ce	51.9	3.26	6.1	32
Pr			0.90	3.9
Nd	57.9	3.88	4.9	11
Sm	20.0	1.37	1.65	2.5
Eu	2.77	0.422	0.751	0.66
Gd		1.76	2.59	2.4
Tb			0.46	0.58
Dy	26.2	1.87		2.0
Ho			0.708	0.50
Er	19.3	0.806	2.0	1.2
Tm			0.33	0.2
Yb	15.6	0.724	1.9	0.9
Lu	1.93	0.117	0.34	0.10

e) Garnet (ppm)

Rock Type No. of Samples Reference*	Dacite (1) (5)	Eclogitic and Ultrabasic Inclusions (5) (4)
Ce	20.0	1.24
Nd	15.0	1.69
Sm	15.1	1.24
Eu	1.42	0.673
Gd	53.6	3.33
Dy	122	7.23
Er	77.9	5.26
Yb	70.3	5.35
Lu	10.1	

*References

(1) Nagasawa and Schnetzler, 1971.

(2) Onuma _et al_., 1968.

(3) Frey, 1970.

(4) Philpotts _et al_., 1972.

(5) Schnetzler and Philpotts, 1970.

(6) Varne and Graham, 1971.

(7) Buma _et al_., 1971.

APPENDIX 4

Mean Literature REE Distribution Coefficients

a) Clinopyroxene - orthopyroxene

Rock Type No. of Samples Reference*	Dacite (1) (1)	Basalt-Andesite (1) (2)	Lizard Peridotite (3) (3)	Ultrabasic and Eclogitic Inclusions (4) (4)
La			4.80	
Ce	4.39	64.7	6.85	27.1
Pr			16.2	
Nd	7.87		18.5	29.2
Sm	9.43	55.6	17.7	26.4
Eu	8.74	33.1	14.4	25.4
Gd			14.0	
Tb		21.3	10.3	
Dy	7.65			14.5
Ho			6.53	
Er	4.26		5.90	10.4
Tm			4.40	
Yb	2.77	9.36	3.30	5.7
Lu	2.35	8.54	3.20	

b) Clinopyroxene-plagioclase

Rock Type No. of Samples Reference*	Dacite (1) (1)	Basalt-Andesite (2) (5)
Ce		1.64
Nd	7.78	3.38
Sm	18.0	6.52
Eu	1.16	1.20
Dy	58.1	15.8
Er	57.5	18.0
Yb	66.7	
Lu	60.9	

c) Orthopyroxene-plagioclase

Rock Type No. of Samples Reference*	Dacite (4) (1)	Basalt-Andesite (1) (5)
Ce	0.57	0.19
Nd	1.23	0.41
Sm	2.20	0.94
Eu	0.098	0.11
Dy	7.26	5.31
Er	13.6	11.1
Yb	23.1	20.8
Lu	26.7	24.4

d) Clinopyroxene-garnet

Rock Type No. of Samples Reference*	Ultrabasic and Eclogitic Nodules (5) (5)
Ce	11.3
Nd	5.31
Sm	1.85
Eu	1.07
Gd	0.65
Dy	0.22
Er	0.11
Yb	0.07

e) Hornblende-clinopyroxene

Rock Type No. of Samples Reference*	Lherzolite (3) (5, 6, 7)
Ce	2.25
Nd	1.71
Sm	1.60
Eu	1.60
Gd	1.52
Er	1.28
Yb	1.16

* References.

(1) Nagasawa and Schnetzler, 1971.
(2) Onuma _et al._, 1968.
(3) Frey, 1970.
(4) Philpotts _et al._, 1972.
(5) Schnetzler and Philpotts, 1970.
(6) Varne and Graham, 1971.
(7) Frey and Green, 1974.