THE DISTRIBUTION OF THE RARE-EARTH ELEMENTS IN
SILURIAN PELITIC SCHISTS FROM NORTHWESTERN MAINE

by

LONG-TSU YEH

B. S., National Taiwan University, 1969

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Geochemistry

Department of Geology

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1973

Approved by:

Robert Cullers

Major Professor

TABLE OF CONTENTS

ILLUSTRATIONS

TABLES

INTRODUCTION

General

The rare-earth elements (REE) have attracted the interest of geochemists for many years, but because of difficulties in analysis they were not studied much until the early 1960's. Several analytical techniques have been recently developed for the REE that give very accurate and precise results. Neutron Activation Analysis (NAA) is one new approach. In this technique, geologic samples are simultaneously irradiated in a nuclear reactor with standards of known concentrations so that the radioactivity of samples and standards can be compared in order to calculate concentrations of different elements in the samples. Radioactive samples are counted on high-resolution (Ge-Li) gamma-ray detectors coupled with 1024 to 4096 multichannel analyzers so that the energies and quantities of gamma rays from different elements in the same sample can be sorted out. Therefore, instrumental neutron activation analysis (INAA) has become an important technique for studies of many trace elements.

Some elements cannot be determined instrumentally because of emission of gamma-rays from other elements that are the same or of similar energies to the element of interest. Thus it may become necessary to chemically concentrate an element to remove interferring gamma-ray peaks from other elements. Other techniques such as X-ray fluorescence spectrometry and stable isotope dilution have been used recently to extend our capability to analyze for these same elements.

Statement of the Problem

A study of REE distributions around regionally metamorphosed pelitic schists of fairly restricted composition over a wide metamorphic grade has not yet been attempted. Such a study of rocks of restricted composition should

give some idea as to how metamorphic grade will affect the REE distributions in these rocks. Thus, one purpose of this study is to determine the distribution of the REE over a range of metamorphic grades in pelitic metasedimentary rocks of rather restricted major element composition from the Oquossoc and Rangeley quadrangles from northwestern Maine in order to see if the metamorphic grade of these pelitic rocks affects the REE distributions. Samples were also selected from several sedimentary formations of equivalent metamorphic grade (the Rangeley and Perry Mountain Formations) to determine any difference in RE distributions in the pelitic portions between the two different metasedimentary formations. The samples selected for this study were donated from the collection of Dr. C. V. Guidotti, (Department of Geology and Geophysics, University of Wisconsin, Madison).

Accuracy and Precision of Neutron Activation Compared to Other Techniques.

Prior to about 1960, an investigator working on distributions of REE always faced two main problems: 1) lack of sensitivity of analytical techniques, 2) lack of methods of ion exchange for the separation of pure REE for standards. However, as early as 1935, Noddack used X-ray spectrographic techniques to determine the amounts of REE in a composite mixture of 12 parts chondrite to 1 part achondrite. Later Schmitt, et al., (1960) determined the RE abundances in two ordinary chondritic meteorites by radiochemical neutron activation analysis (RNAA). The relative REE patterns of the two chondrites agree to within about $\pm$ 30 per cent with those found by Noddack (1935). In the same year that Noddack published his results, Minami (1935) published X-ray spectrographic measurements of the amounts of REE in composites of shales. Haskin and Gehl (1962) using RNAA analyzed the same shale composites as Minami did and obtained the same relative REE pattern, but found that the absolute contents of the REE were much higher than that determined by Minami.

Large amounts of some rocks have been ground up and carefully homogenized by the U.S.G.S. to be used as standards for interlaboratory comparison. The results from different investigators from two of these rocks, G-1 (a granite) and W-1 (a diabase) are compared in Table 1. Note that values for different NAA techniques and isotope dilution techniques agree reasonably well for the elements compared, and that agreement of these two methods with optical spectrographic data is much poorer. Note in Table 2 that this is partially due to the inherently poorer sensitivity of the optical spectrographic method for the REE. Isotope dilution is more precise and presumably more accurate than NAA, but both techniques are much more precise than all other techniques. NAA has the advantage over isotope dilution of less chance for sample contamination. Thus, NAA is an excellent technique to analyze for the REE if the proper equipment is available.

Trace Element Distributions in Metamorphic Rocks

Regional Metamorphism.--Relatively little work has been done on trace element distribution in metamorphic rocks and almost no work has been done on REE distributions in metamorphic rocks.

A few trace elements fractionate over a range of metamorphic grades in both contact and regional metamorphism, but most trace elements do not fractionate. For example, Shaw worked on sixty-three rocks representing unmetamorphosed shales through all grades of metamorphism to sillimanite schists and gneisses. His analyses showed that the concentration of most elements remained constant during regional metamorphism; only Ni and Cu showed a slight decrease, and Li and Pb showed an appreciable increase from low metamorphic grade through medium to high metamorphic grade. His work has general significance because it showed that a formation of fairly uniform composition retains the primary pattern of minor and trace elements even after

TABLE 1

Minor elements in G-1 and W-1 (ppm)

(Number of determinations in parentheses)

Element	G-1	W-1	Method	Reference
Ce	160		OS	Tennant and Fellows (1967)
	143.5(2)	20.0(2)	XRF	Aleksiev and Boyadjieva (1966)
	156	24	NAA	Tomura, et al., (1968)
	173(2)	23.6(2)	ID	Schnetzler, et al., (1967b)
Eu	1		OS	Tennant and Fellows (1967)
	1.0	0.9	XRF	Aleksiev and Boyadjieva (1966)
	1.04	1.04	NAA	Tomura, et al., (1968)
	1.24 $\pm$ 0.01(2)	1.12 $\pm$ 0.005(3)	ID	Schnetzler, et al., (1967b)
Gd	<10		OS	Tennant and Fellows (1967)
	10.2	4.5	XRF	Aleksiev and Boyadjieva (1966)
	4.8	3.4	NAA	Tomura, et al., (1968)
	4.58 $\pm$ 0.01(2)	4.01 $\pm$ 0.04(4)	ID	Schnetzler, et al., (1967b)
Nd	43		OS	Tennant and Fellows (1967)
	74(2)	13.3	XRF	Aleksiev and Boyadjieva (1966)
	44	21	NAA	Tomura, et al., (1968)
	66.4	15.1(3)	ID	Schnetzler, et al., (1967b)
Sm	<10		OS	Tennant and Fellows (1967)
	5	3.8	XRF	Aleksiev and Boyadjieva (1966)
	7.52	3.78	NAA	Tomura, et al., (1968)
	8.9(3)	3.76(2)	ID	Schnetzler, et al., (1967b)

OS = Optical Spectrography
XRF = X-Ray Fluorescence
NAA = Neutron Activation
ID = Isotope Dilution

TABLE 2

Sensitivity (p.p.m)

Analyst	Method	Y	La	Ce	Yb
Berman, S. (1957)	OS	50	50	200	1
Gordon, G.E., et al., (1968)	NAA	--	2	4	1.9

extensive metamorphism.   Thus, the pattern of minor and trace elements may be a useful guide to the character of the original rock.

Sighinolfi (1971), dealing with fractionating effects and geochemical trends related to high-grade metamorphism, found that the part of the deep crust granulite facies is significantly depleted in Li, Rb and possibly K and enriched in Zr, Sr, and Ba in comparison to lower grade rocks of the upper crust. He proposed that possible mechanisms for the movement of elements in deep-seated rocks consist of dehydration reactions accompanied by a migrating hydrous phase and of partial melting of rocks beginning with the amphibolite facies. The relative importance of those mechanisms in the movement of elements is largely unknown.

Green, et al., (1972), compared REE distributions (relative to chondrites) in gneisses in the amphibolite to granulite facies to determine the effect of metamorphic grade on these distributions. No significant difference was found in the REE distributions between these two metamorphic grades.

Contact Metamorphism.--On the other hand Frey, (1969) determined REE contents of three contact metamorphic rocks (blue-green hornblende amphibolite, brown-green hornblende amphibolite, and pyroxene granulite associated with the Lizard intrusion). He showed that following the increasing metamorphic gradient little change in REE distribution occurred in the conversion of blue-green hornblende amphibolite to brown-green hornblende amphibolite. There was a significant absolute REE abundance increase. In going from the brown-green hornblende amphibolite to the pyroxene granulite there was a decrease in absolute REE content and a relative loss of the light REE. Utilizing the REE data, he proposed that a reasonable mechanism responsible for the difference between the REE distribution of the pyroxene granulite and brown-green hornblende amphibolite is due to decomposition of amphibole in the premetamorphic

pyroxene granulite rock (which contains a relatively high concentration of the REE) to orthopyroxene (which can hold less of the REE than amphibole). Therefore, dehydration reactions may release REE into the aqueous phase which would be relatively enriched in the light REE. This postulate was strengthened by comparing the reduced RE contents of pyroxene granulite with that of intrusive recrystallized peridotites. The exterior recrystallized peridotites have greatly increased in RE contents than the interior of the intrusion.

Makrygina, et al., (1969) examined the behavior of Co, Ni, Cr, and V in some metamorphic rocks of the Patom Uplands. They showed that some trace elements fractionate in some types of rocks, but not in others. For example, the contents of Co, Ni, and V in silicate rocks (metapelites and calcareous siltstones) increased from the green-schist facies to the amphibolite facies during progressive metamorphism. However, these same elements did not fractionate in carbonate rocks (marls and marbles) over the same metamorphic grade.

Trace Element Distributions in Sedimentary Rocks

Diagenesis.--Potter, et al., (1963) compared trace element (V, B, Cr, Cu) concentrations between ancient and modern argillaceous sediments of the same environment (marine or fresh-water) in order to establish the validity of trace elements as environmental discriminators. They found that no major differences in trace element concentrations occur between ancient and modern argillaceous sediments of the same environment. This implied that trace element concentrations in ancient shales were not seriously modified by post-depositional diagenetic processes.

Similarly Condie, (1967) worked on twenty-three samples of slightly metamorphosed Early Precambrian graywackes to understand the geochemistry of some major and trace elements in these samples. The original chemical composition of the graywackes was not greatly affected by diagenesis and metamor-

phism, but was strongly influenced by the source areas. For example, the content of Sr in the Sheba graywackes was relatively depleted as compared to K, Ba, Ca, and Rb. This fact was interpreted in terms of abundance of Sr-depleted igneous rocks in the source areas. Similarly, a large concentration of Ni in the Sheba graywackes was interpreted as indicating a significant, although not major, ultramafic component in the source area of these rocks.

Girin, et al., (1970) investigated calcareous concretions from the Middle Jurassic miogeosynclinal deposits of the Greater Caucasus in order to analyze the mechanism of the diagenetic redistribution of REE. Here the products of diagenesis were concentrated in the calcareous concretions.

Their investigation showed that all concretions were characterized by an excess of mobile REE as compared with the surrounding clays. This implied that the REE fractionation occurred during diagenesis. They also pointed out that this fractionation was caused by the pH of the pore solution. In other words, there was a gradual change in the correlation between the lanthanides (from La to Dy and Yb) and alkalinity. With decrease in alkalinity, the role of the light lanthanides gradually decreased and the content of the intermediate lanthanides (Nd to Dy) and yttrium increased during the formation of concretions.

REE in the Sedimentary Cycle.--The REE distributions in the sedimentary cycle (including weathering of parent crystalline rocks and sedimentation of basins) have been determined in 31 composite samples representing more than 30,000 samples from the Russian Platform, (Ronov, A.B. et al., 1967). They showed that weathered mantles formed on the melanocratic rocks (enriched in the heavy REE) show greater range in the composition of the REE (accumulation of the light lanthanides and removal of the heavy ones) than the weathered mantles developed on the leucocratic rocks (containing higher concentrations

of the light REE).

These data showed that the mineralogical composition of the rocks and the chemical properties of the REE influenced the intensity of fractionation of the REE during weathering. Irrespective of the composition of the crystalline rocks, the content and ratios of REE in their weathering products was determined by the change from the zone of accumulation to the zone of leaching and were concentrated in the zone of accumulation so that the total REE content in the former zone was lowered and the total REE content in the latter zone was increased. Calculating the average contents of the REE in sedimentary rocks of all types, they found that the highest concentrations of the REE occurred in clays.

Balashov and Girin (1969, 1970) also found that the REE content in clays was high. They used acid leaching to separate the REE occurring in carbonates and apatite from the REE firmly bound in the clay mineral structures of shale. The REE extracted by acids were called mobile REE, and those remaining in the sample were called the residual REE. They found that clays contained a considerable reserve (20 to 95% of total REE in the rock) of REE and that the mobile rare earths increased from kaolinite to hydromica to montmorillonite.

GEOLOGY

General Information

The location of the Oquossoc and Rangeley quadrangles are shown in Figure 1 and the location of samples is shown in Figures 2 and 3. The rocks in these areas are primarily strongly folded and faulted Siluro-Devonian metashales, metasandstones, metaconglomerates, and metagraywackes (Moench, 1966, 1970). Samples are mainly from the Perry Mountain Formation (Silurian)

and the Rangeley Formations (Silurian). Moench (1970) described these formations in detail but the features most relevant to this study are summarized below.

The Rangeley formation is characterized by rapid deposition which is indicated by abundant features that are commonly attributed to turbidity currents. Graded bedding is ubiquitous in the Rangeley Formation. In addition, individual sandy or conglomeratic beds show no evidence of having been winnowed or reworked by bottom currents before deposition of the next overlying shale beds. Relict sedimentary textures in rocks of low metamorphic grade indicate that the sandy and conglomeratic sediments were composed of poorly sorted fragments of quartz, feldspar, and rocks set in a matrix of clay-rich detritus. The lower 4000 ft. (1200m) of the Rangeley Formation consists of coarse clasts of Paleozoic rocks of massively graded beds that are up to 30 ft. (9m) thick. This feature strongly implies that the lower part of Rangeley Formation was probably deposited rapidly.

In contrast, rocks of the Perry Mountain Formation were deposited more slowly and were more permeable than those of Rangeley Formation. Metasandstones of the Perry Mountain Formation are compositially and texturally more mature. Their even, cyclic beds suggests that individual sand beds were extensive and were permeable parallel to bedding. The cross lamination suggests that relatively slow traction currents were important. The Perry Mountain Formation was probably deposited as a continuous sheet, about 2000 ft. (600m) thick, over the Rangeley.

Prograde dynamothermal metamorphism is shown by isograds that mark the first occurrence of key minerals in the pelitic portions of the sequence. The metamorphic grade of the samples ranges from greenschist facies to amphibolite facies. The greenschist and amphibolite facies of the pelitic rocks are divided into eight zones (C. V. Guidotti, 1967); lower, middle and upper garnet

Figure 1. The locations of the portions of the Rangeley and
Oquossoc Quadrangles from which the samples in this study were obtained.

THIS BOOK CONTAINS NUMEROUS PAGES WITH DIAGRAMS THAT ARE CROOKED COMPARED TO THE REST OF THE INFORMATION ON THE PAGE.

THIS IS AS RECEIVED FROM CUSTOMER.

QUEBEC

NEW HAMPSHIRE   MAINE

N

Oquossoc   Rangeley

45°00'

VERMONT

71°00'   70°15'

44°00'
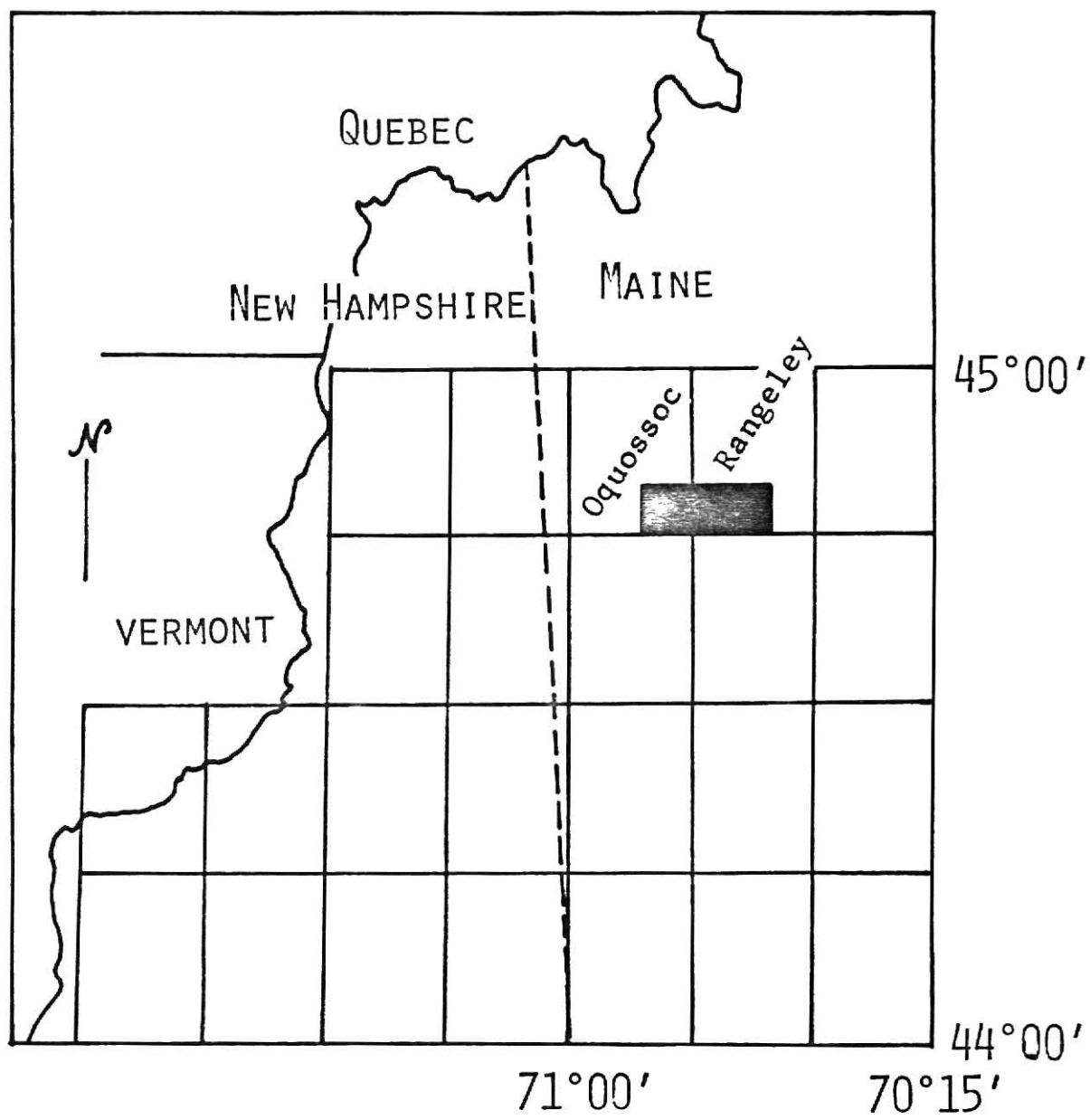
Figure 2. Sample Location Map.
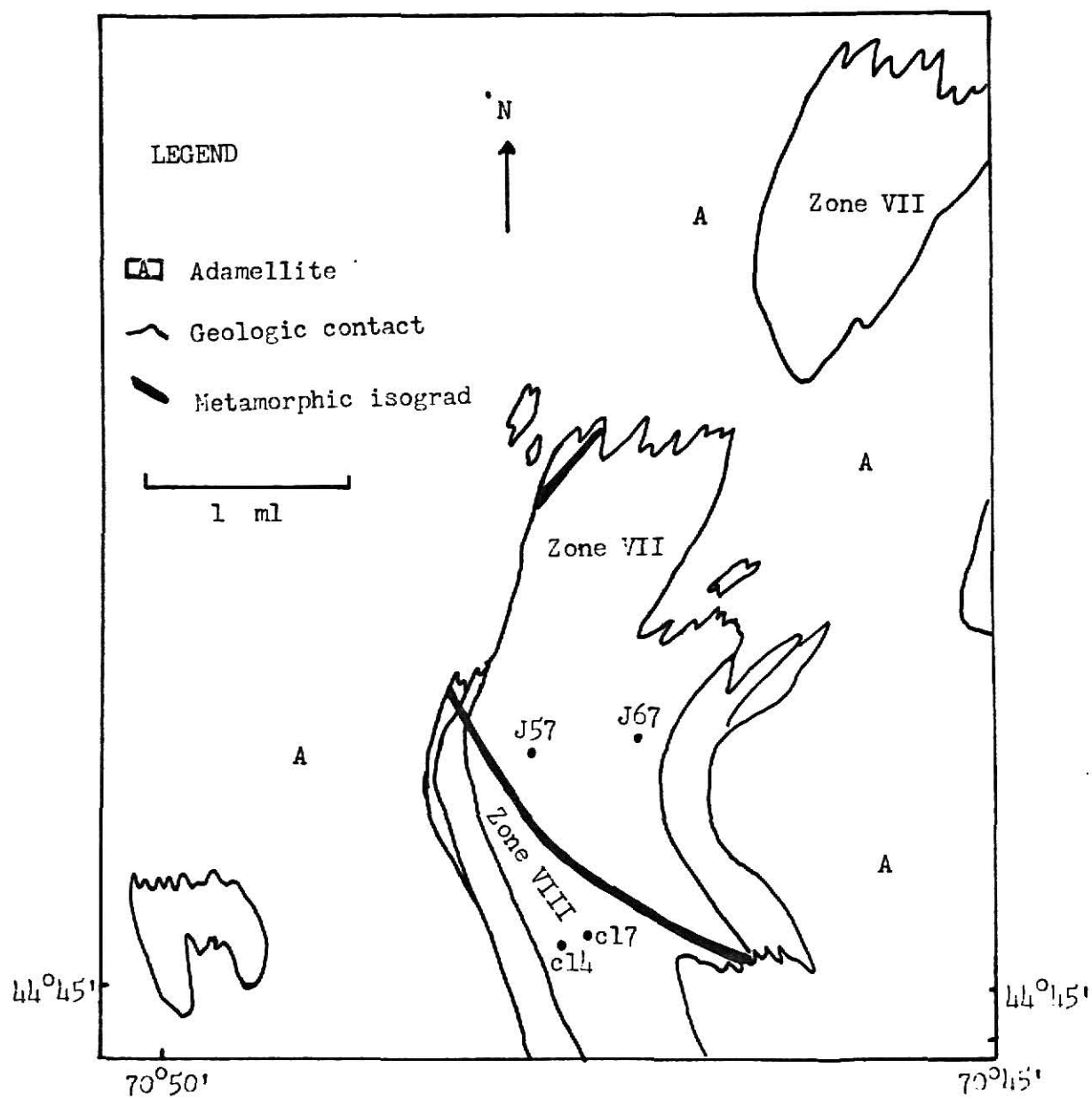
Figure 3. Sample Location Map.
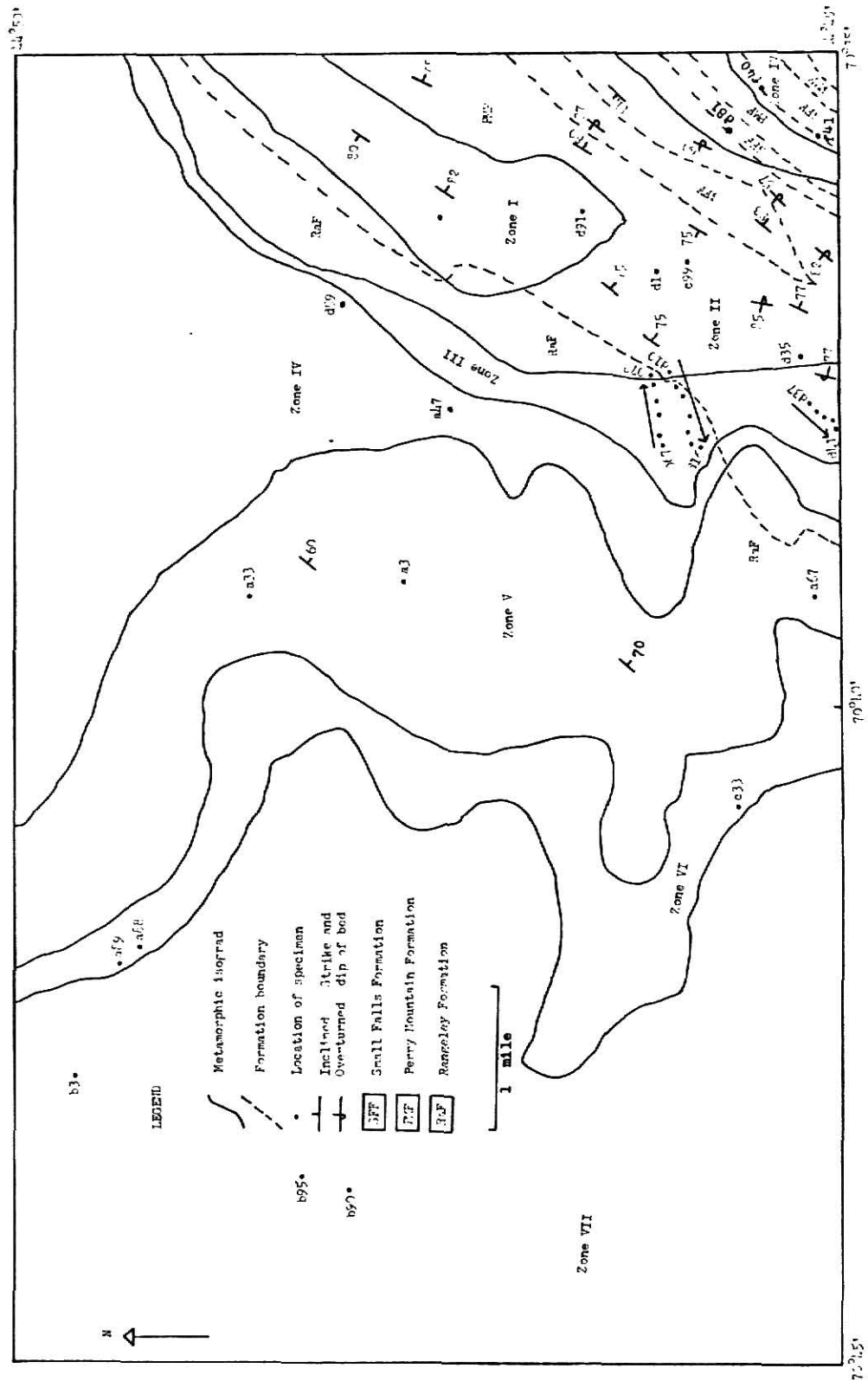
zone (Zone I, II, III); lower and upper staurolite zone (Zone IV, V) transi-
tion zone (Zone VI); lower and upper sillimanite zone (Zone VII, VIII).

Hand Specimen Description

Zone I - III rocks are greenschists and consist of a fine-grained matrix
composed of quartz, plagioclase, (An = 17) and porphyroblasts of idioblastic
garnet (1mm-2mm) and xenoblastic laths of biotite (3mm-6mm). The samples are
"fresh" and show only incipient weathering to a rust-colored surface stain.
The megascopic characters of Zone IV-VIII schists are similar to those of the
lower zones with the following exceptions. Porphyroblasts (3-6mm) of
xenoblastic staurolite are in Zone IV and persist to Zone VII. The quantity
of modal chlorite decreases from Zone IV and is absent in Zone VI. Modal
biotite seems to increase slightly from Zone III to VII. Also the size of
the micas gradually increase toward the higher grades of metamorphism.

Petrographic Description

Details of the petrography and the continuous and discontinuous reactions
that take place from Zone I to VIII are described in several publications by
Guidotti (1968, 1970). The basic metamorphic changes are outlined below.

In Zone I, medium to coarse-grained porphyroblasts of biotite laths
(3-6mm) and idioblastic crystals of garnet (1-2mm) are embedded in a fine
grained matrix (<0.03mm) of quartz, muscovite and plagioclase to give an over-
all lepidoblastic texture. Several grains of biotite and garnet are rimmed
with anomalously blue chlorite. Some of the grains of biotite and garnet have
poikiloblastic texture. The most prevalent accessory minerals are pyrite and
ilmenite. Other accessory minerals are apatite, zircon, and tourmaline. It
is very difficult to distinguish the untwinned plagioclase and quartz because
of very fine-grained size.

Zone II and Zone III schists are similar to Zone I except for a gradual increase in modal garnet (replacing chlorite) and biotite, and a gradual decrease in modal chlorite. Xenoblastic grains of staurolite with poikiloblastic texture first occur in Zone IV. Modal biotite rises drastically and garnet increases slightly at the expense of chlorite. These same trends continue from Zone IV to Zone V. In Zone VI, chlorite almost completely disappears. A trace of sillimanite is present and staurolite becomes slightly more abundant. In Zone VII, no chlorite is present. In Zone VIII, staurolite is absent, modal muscovite drops drastically, and sillimanite is much more abundant.

Point Counting and Modal Analysis

The thin-sections cut from each sample were point-counted according to the straight counting method described by Chayes (1956). A rectangle, 1 inch x 3/4 inch, was inked on each slide and approximately fifteen hundred points were counted. The counts were taken at 1mm intervals in each row with 0.3mm between the rows. One corner of the rectangle was selected as the starting point of the first traverse with each alternate traverse being taken in the reverse direction. The unique point under the microscope cross-hairs were recorded for each interval of the traverse. The total number of counts for each mineral in the slide was ascertained and recalculated to percent of the total. The results are summarized in Tables 3 and 4.

EXPERIMENTAL METHODS

Sample Preparation and Irradiation

Preliminary Preparation.--The sample pieces were washed with tap water and brush, rinsed with demineralized water, and dried with acetone. They were allowed to dry completely.

TABLE 3

Mineralogic Composition from Point Counts (Tabulated as Percents)

Sample No. Metamorphic Zone	Quartz and Plagioclase	Muscovite	Biotite	Chlorite	Staurolite	Garnet	Sillimanite	Others, (i.e. Apatite, Pyrite)
Ra-d73 I	50	25	7	17	---	trace	---	trace
*Ra-d73 I	48	30	9	12	---	trace	---	trace
Ra-d91 I	60	25	3	10	---	1	---	trace
*Ra-d91 I	52	28	5	13	---	1	---	trace
Ra-c99 II	45	25	9	20	---	trace	---	trace
Ra-d1 II	45	25	8	19	---	1.5	---	trace
*Ra-d1 II	44	27	12	13	---	1	---	3
Ra-d13 III	50	32	10	4	---	3	---	trace
Ra-d41 III	50	25	15	7	---	2	---	trace
*Ra-d41 III	48	28	17	4	---	2	---	trace
Ra-d59 IV	50	30	13	3	1	2	---	trace
Ra-a47 IV	50	30	15	2	1	1	---	trace
Ra-a3 V	45	25	15	6	5	1	---	3
Ra-a67 V	40	30	23	---	6	trace	---	trace
Ra-a33 V	50	25	20	1.5	2	1	---	trace
Ra-c33 VI	40	25	27	---	3.5	3	1.5	trace
Ra-a88 VI	45	25	22	---	5	1	trace	2
Ra-a89 VI	53	20	22	---	3	---	trace	2
Ra-b90 VII	35	25	25	---	10	0.5	0.5	4
*Ra-b90 VII	32	23	23	---	9	3	0.7	9.3
Ra-b3 VII	40	10	25	---	1	0.5	1.5	22
Ra-b95 VII	40	30	22	---	3	1	2.5	1.5
O-J-67 VII	35	20	30	---	12	1	1	trace
O-J-57 VII	44	28	20	---	---	trace	7	trace
*O-J-57 VII	40	26	22	---	---	1	10	trace
O-C-14 VIII	30	5	50	---	---	2	12	trace
O-C-17 VIII	40	30	27	---	---	0.5	2	trace
*O-C-17 VIII	35	29	29	---	---	3	3	trace

The point counts of * samples are done by writer. The others are done by Dr. Guidotti, C. V.

TABLE 4

Average Mineralogic Composition in Metamorphic Zone from Point Counts

Metamorphic Zone	Quartz and Plagioclase	Muscovite	Biotite	Chlorite	Staurolite	Garnet	Sillimanite	Other
I	55	25	5	13.5	---	trace	---	trace
II	45	25	8.5	19.5	---	trace	---	trace
III	50	28.5	12.5	5.5	---	2.5	---	trace
IV	50	30	14	2.5	1	1.5	---	trace
V	45	26.7	19.3	2.5	4.3	trace	---	trace
VI	46	23.3	23.3	---	3.8	1.3	trace	1.5
VII	38.8	22.6	24.4	---	5.2	trace	2.5	6
VIII	35	17.5	38.5	---	---	1.3	7	trace

Grinding Procedure.--The samples were crushed in a hardened-steel mortar and passed through a 100-mesh polyethylene sieve.

Irradiation.--Approximately 0.3g aliquots of each of the powdered samples and liquid irradiation standard were weighed ($\pm$0.0002g) into clean 2-dram polyethylene vials and heat sealed with a soldering iron.

A weighed Fe wire (about 50 mg weighed to $\pm$0.0002g) was wrapped around that part of each vial that contained the sample or standard. These wires were counted about 14 days after the irradiation, and the specific activities of the iron were used to correct for flux differences between the sample and standard.

The samples and the standards were sealed in separate polyethlene vials and were irradiated for 1.75 hours in the core of the General Atomic TRIGA Mark II Reactor at a flux of about 9 x 10^{12}- 10^{13} neutrons cm^{-2} sec^{-1}.

Preparation of Standard Solution and Carriers for the Separation Steps.-- Stock solutions of chlorides of each of the REE were made from the REE oxides (purity greater than 99.99 per cent Research Chemicals, Phoenix, Arizona) to contain approximately 10 mg of the REE ions per ml. Exact concentrations were determined by titrations with EDTA. From these standard solutions for each REE, aliquots were pipetted into a polyethlene bottle to produce a carrier solution and standard solution with the concentrations of each of the REE ions as given in Table 5.

Chemical Separation of the REE from the Rock Sample

The group separation of the REE from an irradiated rock sample are described in detail by Denechaud, E. B., et al., (1970). Some details of this procedure are outlined below. Carrier and tracer solutions were prepared for each rock sample prior to their irradiation.

TABLE 5

Concentrations of REE Standard Monitor and Carrier Solutions

Element	Standard Monitor	Carrier
	ug/ml	ug/ml
Y	27.9	558.0
La	24.08	842.8
Ce	75.3	878.5
Nd	27.98	559.6
Sm	6.54	541.6
Eu	2.24	559.6
Gd	5.68	562.0
Tb	1.098	549.2
Dy	9.008	559.6
Ho	1.120	690.5
Er	3.39	707.0
Yb	2.192	949.9
Lu	0.561	972.3

Exactly 2.00 ml of the REE carrier solution and 1.00ml Y^{88} tracer are pipetted into a clear zirconium crucible. Then about 50mg NaCl is dissolved in this solution and evaporated carefully to dryness overnight on a hotplate under very low heat or under a heating lamp. The same quantities of carrier and Y^{88} tracer used for each sample are then pipetted into a 50ml beaker to receive the irradiation standard.

Each irradiated sample is carefully poured into a zirconium crucible and fused with about 12g sodium peroxide with the rare-earth carriers and tracers. These samples are quite radioactive (gamma ray doses of 0.5-5 rem at contact) so appropriate shielding must be provided. Each fused sample is allowed to cool nearly to room temperature.

The cooled sample is then digested with about 50ml of demineralized water in a 400ml beaker. Once the rather vigorous reaction between the fused rock sample and water has subsided, concentrated HCl is added slowly with constant stirring to the beaker until all traces of precipitate have dissolved. Then about 25g of solid NH_4Cl and concentrated aqueous ammonia are added to the solution to obtain a pH of 9 in order to precipitate the REE, Fe, and Al hydroxides from the solution. The precipitate is centrifuged and the supernate is discarded into radioactive waste. Because the highest amount of radioactivity has been removed, the hydroxide precipitate is removed to a different hood that has minimal shielding. In this hood the hydroxide precipitate is dissolved in minimal concentrated HCl and is boiled for ten minutes on a hotplate. A 1.5 percent gelatin solution is then added to the precipitate to aid in precipitating silica. The silica is washed a minimum of 4 times in 8 M HCl.

The supernate is added to a 250ml separatory funnel. The Fe is extracted from this solution by adding ether to the solution in the sepratory funnel.

The ether and water separate into two layers and the lower aqueous phase is drained into a 400ml beaker. The aqueous phase must be boiled gently on a hotplate in order to remove all traces of ether. The REE are then precipitated as the hydroxides by the slow addition of 16 M NaOH (to pH of 9) to the solution.

The hydroxides are dissolved in a minimum of 2 M HCl. In order to minimize selective loss of the lightest and heaviest REE the resulting solution should have as small a volume as possible. The procedure is critical and every caution should be taken. The solution is heated nearly to boiling in a water bath, and then about 1.5ml of saturated oxalic acid solution are added with intensive stirring in order to precipitate the REE oxalates. The oxalate pre-cipitate and solution must then be allowed to cool to room temperature.

Once the solution has cooled, the REE oxalates are filtered under suction through a chimney filtration apparatus with an inside diameter of 1.5 cm onto a circle of Whatman No. 50 paper. The sample is mounted for radioassay by being centered exactly on a counting card. The irradiation standard is treated differently than the rock samples. The liquid standard is opened and rinsed with distilled water into the 50ml beaker containing its carrier and Y^{88} tracer. The solution is warmed nearly to boiling on a hot plate and 1.3ml of saturated oxalic acid are stirred in. The REE oxalates are filtered and mounted for radioassay in the same manner as are the samples. One-hundred percent yields of all REE are obtained in this procedure for the treatment of the standard.

Counting

Samples and standard solution are irradiated with neutrons and the gamma-rays emitted are observed with Ge(Li) detectors and associated electronics. Observed gamma-rays have been assigned to specific radionuclides on the bases of energy, relative intensity, and half-life.

Each sample is observed at several different times after irradiation to optimize determinations for species of several half lives. Spectra are taken at about 1 day, 3 day, 10 day, and 40 day intervals after the irradiation. Data from the 1024-or 4096 channel analyzer memory are read out on punched paper tape. The amount of a given element in a sample is computed from the ratio of the peak areas in the sample to the areas of corresponding peaks in the standard for that element. Corrections were applied for decay between sample and standard for different counting times. Photopeaks and counting times selected for the analyses are listed in Table 6.

Determination of Chemical Yields

Complete recovery of the carrier that is added to the rock samples before their dissolution is not achieved, and losses for the individual REE are not uniform and cannot be avoided. Thus, it remains necessary to include carrier for every REE for chemical processing, and to determine the percentage recovered for each. Following completion of count set IV, each sample and standard is counted about 50 min on the Ge(Li) detector to obtain about 15000 counts above background for the 1.836 Mev peak of Y^{88}. The Y^{88} acts chemically like Dy in this procedure so it can be used for Dy yields. Relative chemical yields for the remainder of the REE relative to Dy are determined by reirradiation of a portion of the recovered carriers of the samples and standard following completion of count set IV. A brief summary of the procedure follows.

The mounted sample of REE oxalate is cut open and about one-eighth of the precipitate is removed with a spatula and spread evenly onto a 3/4 cm diameter circle of Whatman No. 50 filter paper. Then two drops of a two percent solution of polystyrene in ethyl acetate are placed on the precipitate, and the solvent is evaporated at room temperature. When the ethyl acetate has evaporated from

TABLE 6

Summary of Information Pertaining to Radioassay

Count Set	Days After End of Irradiation	Duration of Count, Set (Seconds)	Nuclide	Half-Life	Energies of r-ray used, Mev
I	1	1800	^{153}Sm	47.0 h	0.1032*
			^{152}Eu	9.3 h	0.1218, 0.3444
II	3	3600	^{140}La	40.2 h	0.3288*, 0.4872*
			^{153}Sm	47.0 h	0.0697, 0.1032*
			^{166}Ho	26.9 h	0.0806
			^{177}Lu	6.74 d	0.2084
III	10	18000	^{140}La	40.2 h	0.3288, 0.4872
			^{160}Tb	72.1 d	0.2985*
			^{175}Yb	4.21 d	0.2826*, 0.3961*
			^{177}Lu	6.74 d	0.2084
IV	40	18000	^{141}Ce	33 d	0.1454
			^{152}Eu	12.7 y	0.1218*, 0.3444*
			^{153}Gd	242 d	0.0974
			^{160}Tb	72.1 d	0.2985
			^{169}Yb	32 d	0.1772*

*Peaks used in chemical yield determination on irradiated carrier, 8 days after irradiation of carrier.

the polystyrene and REE precipitate, a thin coating of lacquer is sprayed on to hold the precipitate firmly in place. The filter circle and precipitate are then heat-sealed between two sheets of polyethylene film. The identically prepared portions of the carriers from the samples and standard are then placed in a polyethylene vial and heat sealed. The vial with the samples are then irradiated for one hour at a neutron flux of about 1.62×10^{12} n/cm^{-2}/sec^{-1}.

The irradiated carriers are left to decay in the reactor pool for several days. On the eighth day after irradiation each is mounted on a card and counted for about 50 min. on the Ge(Li) detector at constant dead time. By comparing peak ratios for the REE in the samples to those of the standard, relative chemical yields are obtained for La, Sm, Eu, Tb, Yb, and Lu. (See Table 6 for peak energies used). The relative chemical yields for Ce, Gd, Dy, Ho, and Er are obtained by interpolation on a graph of percentage recovered versus atomic number based on measured values for La, Sm, Eu, Tb, Yb, and Lu. The relative yield for Dy is then converted to an absolute chemical yield for that element by multiplying it by the ratio of the Y^{88} tracer activity of the sample to that of the standard. An absolute chemical yield for each of the other REE is then obtained by multiplying the ratio of the relative chemical yield for the element to that for Dy by the absolute chemical yield for Dy.

Whole Rock Irradiation

The process of neutron irradiation followed by counting without any chemical separation is called whole rock irradiation or instrumental neutron activation analysis (INAA). Some samples (about 15 samples) collected from Rangeley and Perry Mountain Formations separately were analyzed with INAA by a method adopted from Gordon, et al., (1968) in order to compare La/Lu ratios and Cr between the two formations. The principal procedures for INAA were

exactly like that of NAA with the chemical separations.

After irradiations, the samples and monitors were transferred to clean polyethlene vials. The vials were counted on a Lucite sample holder mounted on the Ge(Li) detector face. These samples were counted on the sixth and fortieth day after irradiation. Relatively few gamma-ray peaks could be used with whole rock irradiations because of interferences with other radionuclides. Peak energies used for La and Lu are the same as those of the 3 day and 10 day count set of La and Lu (see Table 6). Peak energy used for Cr^{51} and its half-life are 320 Kev and 27.8 day respectively. Cr^{51} was counted on the fortieth day after irradiation. A second disadvantage of INAA compared to RNAA was the lower precision and accuracy obtained with INAA.

Calculation of Results

When net counts and uncertainties have been established, concentrations for each element are calculated for each peak as follows:

$$Cs = (As/Am) \cdot (Gm/Gs) \cdot (Fm/Fs) \cdot (Cm/Y)$$

where Cs – concentration of that element in the sample in ppm

Cm – concentration of that element in the standard monitor in ppm

As – peak area in counts per unit time for the sample

Am – peak area in counts per unit time for the standard monitor

Gs – weight of the irradiated sample in g

Gm – weight of the irradiated standard monitor in g

Fs – cpm/mg for the Fe wire surrounding the sample

Fm – cpm/mg for the Fe wire surrounding the standard monitor

Y – absolute chemical yield for the element

In a given count set a given element may have several peaks (e.g., La has four useful peaks) that should give the same sample/standard ratio for that element in the sample. Where several values for a single element in a given

sample have similar uncertainties, an arithmetic average is taken to obtain a single value for the element in the sample and the uncertainties are propagated as standard deviations. When several values for a given element have significantly different uncertainties, the value with the lower uncertainty may be used to represent the sample, if the values are significantly different between the different peaks.

Analytical Precision and Accuracy

Duplicate analyses of the U. S. Geological Survey standard rock BCR-1 (a basalt) were first obtained in order to provide an estimate of the accuracy and precision of the radiochemical NAA and instrumental NAA. The analytical precision and accuracy may be estimated from data given in Table 7. Our precision at the level of 0.1-150 ppm found for the individual REE in most of the samples was usually better than ± 3 percent for La, Ce, Sm, Eu, and Ho; better than ± 5 percent for Tb, Yb, and Lu, and about ± 15-30 percent for Gd.

The precision and the accuracy of the REE using the INAA is believed to be less than that of the RNAA. The results of one sample (Ra-d 41) using the two techniques can be compared in Table 8 and 9. The results for Lu agree within 9.7% and the La only within 38% between the instrumental and radio-chemical analysis. Thus, the absolute values for the INAA should not be taken too seriously, but the INAA serves to distinguish between the drastically different light RE concentrations of the Perry Mountain and Rangeley Formations.

RESULTS

Radiochemical Neutron Activation Analysis

The absolute concentrations (parts per million) for the REE in the samples are given in Table 8. In Figure 4a, the average REE abundances in

Table 7. Abundances of the REE (ppm) in standard rock BCR-1 compared to others.

Reference	La	Ce	Sm	Eu	Gd	Tb	Ho	Yb	Lu
This study, RNAA	26.40 ±0.79	54.9 ±2.4	7.25 ±0.11	2.05 ±0.09	8.91 ±3.4	1.21 ±0.14	1.54 ±0.08	3.33 ±0.3	0.540 ±0.034
Haskin, et al. (1970) RNAA	25.18 ±0.78	54.22 ±0.85	7.23 ±0.28	1.966 ±0.028	8.02 ±0.89	1.154 ±0.058	1.342 ±0.086	3.48 ±0.04	0.526 ±0.002
Gordon, et al., (1968) INAA	23 ±2	46 ±5	5.9 ±0.5	1.95 ±0.10	----	1.0 ±0.1	----	3.2 ±0.4	0.60 ±0.05

TABLE 8

Abundances of the REE (ppm) in the Pelitic Schists from N. W. Maine

Sample No.; Metamorphic Zone	La	Ce	Sm	Eu	Gd	Tb	Ho	Yb	Lu	$\sum$ RE
Ra-d73-66 I	9.23 ±0.25	24.29 ±0.36	3.32 ±0.19	0.930 ±0.028	5.09 ±0.96	1.156 ±0.043	1.492 ±0.037	4.619 ±0.087	0.80 ±0.038	78.4
Ra-d91-66 I	10.10 ±0.32	21.01 ±0.69	2.48 ±0.12	0.749 ±0.004	4.27 ±0.76	0.681 ±0.024	0.904 ±0.003	3.30 ±0.17	0.648 ±0.06	64.07
Ra-c99-66 II	3.68 ±0.18	8.13 ±0.81	1.106 ±0.005	0.4848 ±0.0080	3.41 ±0.35	0.807 ±0.067	0.888 ±0.042	3.46 ±0.13	0.652 ±0.064	35.64
Ra-d1-66 II	10.04 ±0.34	26.08 ±0.71	2.79 ±0.26	0.711 ±0.011	4.36 ±0.64	0.5019 ±0.009	0.708 ±0.012	2.03 ±0.12	0.4121 ±0.0071	67.76
Ra-d41-66 III	3.78 ±0.20	10.54 ±0.70	1.680 ±0.033	0.480 ±0.015	3.83 ±0.98	0.739 ±0.041	1.120 ±0.034	4.66 ±0.26	0.914 ±0.031	44.35
						Perry Mt. Formation Avg. = 58.04				
Ra-d13-66 III	35.03 ±0.97	75.92 ±0.72	6.393 ±0.033	1.789 ±0.033	5.39 ±0.81	0.774 ±0.011	1.052 ±0.017	2.388 ±0.050	0.4090 ±0.0070	175.7
Ra-d59-66 IV	53.7 ±2.4	127.9 ±6.1	11.61 ±0.25	2.224 ±0.054	10.2 ±1.1	1.602 ±0.054	1.793 ±0.054	4.65 ±0.27	0.835 ±0.032	297.1
Ra-a47-66 IV	24.55 ±0.64	49.0 ±2.0	4.980 ±0.059	1.270 ±0.029	6.1 ±1.3	0.740 ±0.038	0.971 ±0.011	2.50 ±0.14	0.459 ±0.016	125.2
Ra-a67-66 V	35.51 ±0.23	87.9 ±1.4	7.235 ±0.045	1.795 ±0.030	8.0 ±1.3	0.606 ±0.013	0.644 ±0.044	1.315 ±0.084	0.2445 ±0.0098	192.2
Ra-a33-66 V	51.3 ±1.5	112.0 ±3.0	9.47 ±0.14	1.859 ±0.036	10.4 ±1.9	1.290 ±0.045	1.600 ±0.044	3.48 ±0.20	0.739 ±0.023	262.1

TABLE 8 (CONT.)

Abundances of the REE (ppm) in the Pelitic Schists from N. W. Maine.

Sample No.; Metamorphic Zone	La	Ce	Sm	Eu	Gd	Tb	Ho	Yb	Lu	RE
Ra-c33-66 VI	58.6 ±2.8	147.3 ±7.7	12.43 ±0.25	2.272 ±0.053	13.3 ±2.4	1.378 ±0.048	1.840 ±0.058	3.99 ±0.24	0.823 ±0.020	330.6
Ra-a88-66 VI	50.09 ±0.50	124.8 ±1.5	10.78 ±0.19	1.936 ±0.014	13.1 ±1.9	1.491 ±0.055	1.754 ±0.45	3.90 ±0.19	0.629 ±0.043	285.9
Ra-b3-66 VII	43.6 ±1.5	106.8 ±5.7	8.99 ±0.14	1.990 ±0.041	11.1 ±2.0	1.310 ±0.053	1.670 ±0.053	3.900 ±0.23	0.768 ±0.025	247.6
Ra-b95-66 VII	64.47 ±0.94	133.7 ±1.2	12.44 ±0.28	2.460 ±0.0025	10.8 ±1.7	1.289 ±0.052	2.163 ±0.050	4.27 ±0.19	0.768 ±0.025	318.0
0-J-67 VII	31.7 ±0.38	66.33 ±0.53	6.081 ±0.010	1.202 ±0.025	5.7 ±1.1	0.8435 ±0.0034	0.986 ±0.024	2.454 ±0.028	0.4529 ±0.0091	158.22
0-J-57 VII	46.07 ±0.35	102.9 ±0.17	9.421 ±0.083	1.923 ±0.012	9.4 ±1.6	1.100 ±0.030	1.310 ±0.041	3.28 ±0.15	0.599 ±0.036	240.96
0-C-14 VIII	68.90 ±2.1	153.1 ±1.3	13.98 ±0.41	2.966 ±0.019	11.6 ±1.6	1.879 ±0.064	2.259 ±0.043	4.05 ±0.23	0.729 ±0.062	357.56
0-C-17 VIIII	49.1 ±1.2	122.1 ±1.6	10.50 ±0.29	1.890 ±0.025	9.4 ±1.5	1.224 ±0.018	1.610 ±0.064	4.178 ±0.029	0.878 ±0.026	275.3

Rangeley Formation Avg. = 251.26

TABLE 9

La/Lu Ratio (normalized to chondrites) & Cr, La, Lu contents (ppm)
in pelitic schists using INAA

Sample No., Formation	La	Lu	Cr	La/Lu
Ra-d41 PM	2.34±0.24	0.83±0.04	99.1±10	0.29
Ra-d10 PM	5.60±0.25	0.49±0.03	82.4±5.5	1.17
Ra-d37 PM	12.7 ±0.2	0.39±0.02	53.2±3.6	3.35
Ra-d35 PM	1.27±0.90	0.35±0.02	88.9±9.6	0.38
			Avg. = 80.9±7.2	1.40
Ra-d16 RF	56.03±0.73	0.29±0.03	70.5±4.9	19.96
Ra-72 RF	30.29±0.27	0.26±0.02	63.3±4.7	12.04
Ra-67 RF	50.66±0.51	0.28±0.02	84.1±9.1	18.70
Ra-d11 RF	75.65±0.27	0.25±0.02	81.2±8.8	31.27
Ra-71 RF	109.78±0.89	0.89±0.03	66.5±4.1	12.75
Ra-d12 RF	71.59±0.47	0.51±0.02	81.9±5.1	14.51
Ra-69 RF	135.4 ±0.4	0.41±0.02	90.1±5.70	34.13
Ra-d14 RF	92.52±0.35	0.99±0.04	84.4±5.3	9.66
			Avg. = 77.75+5.95	19.13

each metamorphic zone of the Rangeley Formation are compared with those in chondrites (Haskin, et al., 1968a). There is no significant correlation between metamorphic grade and the REE distributions. The light REE contents are higher than chondrites, and the REE concentrations are quite similar to an average of concentrations of the REE in typical crustal materials (Herrman, 1970). For example, the mean La/Lu ratio of the Rangeley Formation normalized to chondrites is 8.0 (Range = 5.53 to 15.0); the La/Lu ratio determined by Herrman for crustal materials is 7.0.

In Figure 4b, the REE abundances for each of the five samples in the Perry Mountain Formation are compared with those in chondrites (Haskin, et al., 1968a). Again there is no significant correlation between REE content and metamorphic grade. However, the light REE contents are still higher than that of chondrites. The mean La/Lu ratio of the Perry Mountain Formation normalized to chondrites is 1.3 (Range = 0.427 to 2.52). This value is more than a factor of six lower than the Rangeley Formation.

In Figure 5, the average REE contents normalized to chondrites in the Rangeley and Perry Mountain Formations are compared with composites of North American and European shales normalized to chondrites. The REE distributions in the Rangeley Formation are quite similar to that of North American and European shales. On the other hand, there is a significant depletion of light REE contents in Perry Mountain Formation compared with those in North American and European shales. There is no significant difference between heavy REE contents among the same samples when they are compared with one another.

All analyses except d13 show negative Eu anomalies. Eu is depleted by a factor of 0.75 ± 0.10 (mean $\pm$ standard deviation) relative to its interpolated value between Sm and Gd. This value is close to that obtained by Haskin, et al.,

Figure 4a. (Top) Comparison of the average REE content in each metamorphic zone of the Rangeley Formation relative to chondrites.

Figure 4b. (Bottom) Comparison of the REE content of each sample of the Perry Mountain Formation relative to chondrites.
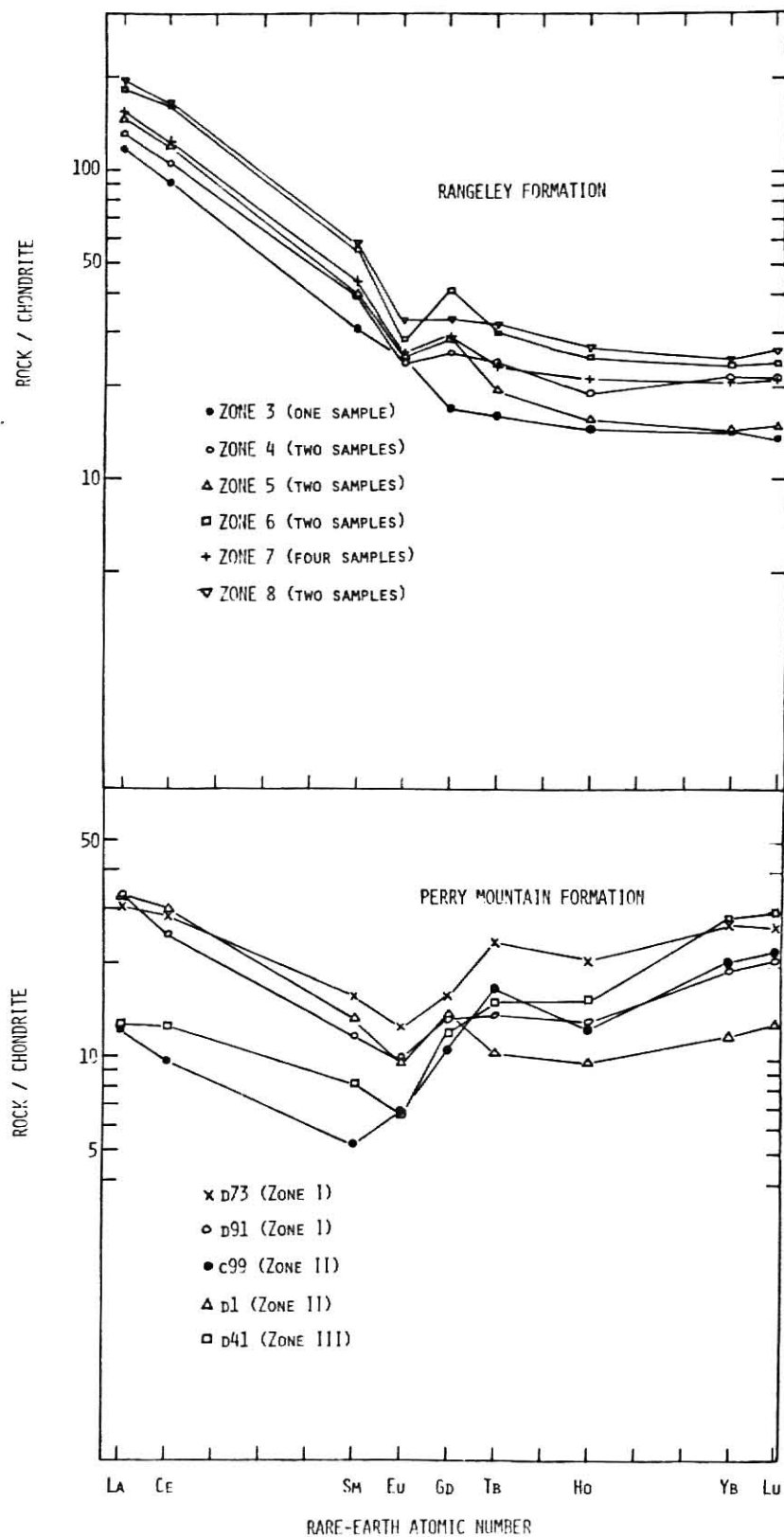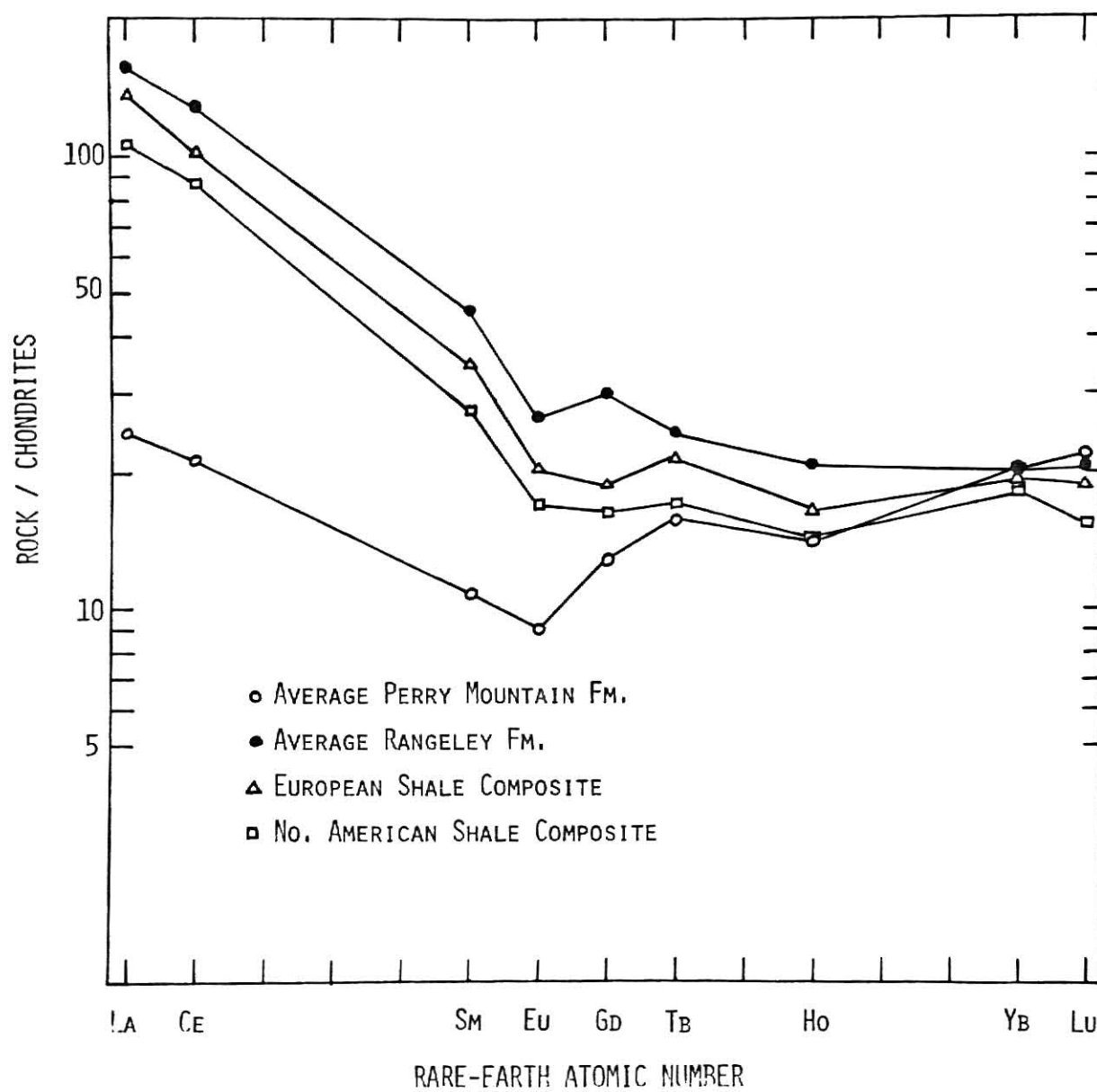
RANGELEY FORMATION

ROCK / CHONDRITE

• ZONE 3 (ONE SAMPLE)
○ ZONE 4 (TWO SAMPLES)
△ ZONE 5 (TWO SAMPLES)
□ ZONE 6 (TWO SAMPLES)
+ ZONE 7 (FOUR SAMPLES)
▽ ZONE 8 (TWO SAMPLES)

PERRY MOUNTAIN FORMATION

ROCK / CHONDRITE

× D73 (ZONE I)
○ D91 (ZONE I)
● C99 (ZONE II)
△ D1 (ZONE II)
□ D41 (ZONE III)

LA CE   SM EU GD TB   HO   YB LU

RARE-EARTH ATOMIC NUMBER

Figure 5. The REE abundances of the average of the metasediments in the Rangeley and Perry Mt. Formations normalized to chondrites are compared to the N. American and European shale composites normalized to chondrites.

(1968a) for a composite of North American shales (0.67), European shales (0.69), and metamorphic shales (0.77). There is no difference between the Rangeley (0.74 $\pm$ 0.10) and Perry Mountain Formations (0.79 $\pm$ 0.08) in the size of negative Eu anomaly.

Instrumental Neutron Activation Analysis

The La/Lu ratios and the absolute concentrations in parts per million for the Cr, La, and Lu in the samples using INAA are given in Table 9. Samples d81, f40, and f41 are likely in the Small Falls Formation so these results are not included in this table. The average La/Lu ratios for the samples analyzed by INAA is 19.13 (range = 9.66 to 31.27). The La/Lu ratio for the INAA is significantly higher than that for the RNAA. The absolute Cr contents (ppm) in both the Rangeley and Perry Mountain Formations are about the same. (Average Cr content in Perry Mountain Formation is 80.9 $\pm$ 7.2; average Cr content in Rangeley is 77.75 $\pm$ 5.95). The Cr content of these metasediments is much lower than the Fig Tree Shale which probably has a high percent of ultramafic rocks in the source area (Danchin, 1967). The Cr content of the Rangeley and Perry Mountain Formations are similar to those of all other shales and metashales (Turekian and Wedepohl, 1961).

INTERPRETATION OF RESULTS

There is no significant relationship between metamorphic grade and REE distributions in the Rangeley Formation (Figure 4a) or in the Perry Mountain Formation (Figure 4b). The significant depletion of light REE contents in the Perry Mountain Formation could be due to the kind of ultramafic source rocks from which the sediment came. In order to test this hypothesis, Cr contents in several samples (see Table 9) were determined by using INAA. This procedure

was used because ultramafic rocks often contain low light REE concentrations and extremely high concentrations of the elements Cr and Ni, and these characteristics have been used as evidence for high percentages of ultramafic rocks in source areas of some shales and graywackes (e.g., Condie, 1967; Danchin, 1967). The analyses showed that there is no significant difference between Cr contents in the Rangeley and Perry Mountain Formations (Table 9). Hence, it would seem unlikely that the initial composition of the source materials cause the large depletion of light REE contents in the Perry Mountain Formation.

Similarly it would seem unlikely that diagenesis could be another mechanism which causes this depletion of light REE contents. The conditions of diagenesis of these samples should be about the same because several samples (e.g., d-10 and d-11) that were collected only a few tens of feet apart show these wide differences in light REE content. If diagenesis were a reasonable mechanism, there should not be these wide differences in light REE contents between d-10 and d-11.

REE distributions in the Rangeley Formation do not show marked depletion or enrichment relative to the patterns of North American and European shale composites (Figure 5). However, the Perry Mountain Formation is very much depleted in the light REE compared to that of the composites of North American and European shales (Figure 5), but there is little difference between the concentration of Lu or Yb in the samples from the two formations. For example, samples d-13 and d-41, collected from the same metamorphic grade (Zone III), but from different formations (d-13 is from the Rangeley Formation, d-41 from the Perry Mountain Formation) have identical model analyses, but d-41 shows a significant depletion of the light REE.

In addition to the continuous and discontinuous reactions taking place in the pelitic metasediments undergoing metamorphism in this system, there is also a progressive loss of water at higher grades. This series of dehydration reactions in progressive metamorphism may cause the depletion of some elements such as the RE elements, and, in fact, has been found to cause depletion of Li, Rb, and K from the amphibolite to granulite facies of regional metamorphism (Sighinolfi, G. P., 1971). However, no change in REE patterns has been observed with increasing grade from amphibolite to granulite facies in a series of metamorphosed gneisses in Norway (Green, et al., 1972) and no significant change in the REE with changing metamorphic grade over the greenschist to amphibolite facies in pelitic metasediments have been found in this study. Therefore, it is unlikely that the REE are mobile during regional metamorphism from the greenschist to the granulite facies.

The other mechanisms which would cause the significant depletion of light REE contents in the Perry Mountain Formation are clay mineral contents, accessory, detrital mineral contents, and environments of deposition. Some Russian geochemists (Balashov, Y. A., et al., 1969) who studied the behavior of the REE in sedimentary rocks, have found that clays often have a large capacity for capturing REE, and different clays have a selective capacity for different REE. It was also found that there is a relative enrichment of the REE assemblages in the light lanthanides from montmorillonite to hydromica to kaolinite-rich clays. Therefore, it may be possible that the large depletion of light REE contents in Perry Mountain Formation could be due to high contents of montmorillonite formation.

The light REE distributions done by Balashov, et al., (1968) are not low enough to cause the very low light REE distributions of the Perry Mountain Formation. On the other hand, one kaolinite sample analyzed by Chaudhuri and

Cullers (unpublished data, 1973) does give a REE distribution very similar to the Perry Mountain Formation. Other kaolinite samples are more similar to other shales and clays thus analyzed.

It has been found that accessory minerals such as garnet, zircon, and apatite have played a significant role in controlling REE distributions in granitic rocks (Lyskhovich, V. V., 1962). Therefore, a small amount of accessory minerals depleted in the REE could cause some of the depletion of light REE in the Perry Mountain.

The environment of deposition and the intensity of weathering in the source area of the Rangeley Formation is quite different from that of the Perry Mountain Formation. This contrasting difference in environment of deposition or the intensity of weathering in the source area could be another important factor which could cause the depletion of light RE contents in the Perry Mountain Formation. The Rangeley Formation is characterized by rapid deposition (described in previous section) which would offer little chance for chemical interaction between sediments and sea water. On the other hand, the Perry Mountain Formation is characterized by slower sedimentation and reworking by bottom currents. Also the Perry Mountain Formation is characterized by intense chemical weathering in the source, while the Rangeley is not. It may be possible that the difference in intensity of weathering and/or lower sedimentation and reworking by bottom currents could have permitted greater chemical and biochemical interaction between bottom sediments and sea water and might result in the significant depletion of REE contents in Perry Mountain Formation.

Under normal conditions, the oxidation state for all members of REE is +3. Ce^{+3} could be oxidized to the +4 state and Eu^{+3} reduced to the +2 state under conditions which occur in nature (Haskin, L. A., et al., 1966). There-

fore, Ce and Eu may be separated from the rest of the coherent (trivalent) rare-earth group by natural processes and these abundances may appear anomalous on our normalized curves.

All the analyses except Ra-dl3 show negative Eu anomalies. On the other hand, Ce abundances are normal in all the analyses. These data suggest trivalent oxidation state for Ce and suggest that some Eu^{+3} may have been reduced in natural sedimentary environments. Also, it is found that grains of pyrite are scattered in both the Rangeley Formation and the Perry Mountain Formation. This fact implies that a reducing environment prevails because presumably pyrite is a stable mineral under reducing conditions. The conclusion is that negative Eu anomalies in pelitic schists are due to a reducing environment.

SUMMARY OF THE CONCLUSIONS

Based on all the data obtained during this investigation and on the interpretation of results presented in the preceding section, the following conclusions are in order:

1. No appreciable change in REE patterns is observed with increasing grade in pelitic metasediments from the greenschist facies to amphibolite facies of regional metamorphism.

2. Samples from the Perry Mountain Formation show large depletions in light REE contents compared with those of the Rangeley Formation. These significant differences in light REE contents between the Perry Mountain Formation and other sedimentary rocks are believed to be due to clay mineral contents as modified by climate and/or environment of deposition. Smaller variations of REE content within each formation are likely due to the variation in the original

accessory minerals present in the original rock.

3. Eu anomalies in all the analyses are likely due to partial reduction of Eu^{+3} to Eu^{+2} in the sedimentary environment.

ACKNOWLEDGMENTS

REFERENCES CITED

Allen, G. C., and Ragland, P. C., 1972, Chemical and mineralogical variations during prograde metamorphism of the Great Smoky Mountains, North Carolina and Tennessee: Geol. Soc. Am. Bull., v. 83, p. 1285-1298.

Balashov, Y. A., and Girin, Y. P., 1969, On the reserve of mobile rare earth elements in sedimentary rocks: Geochem. Int., v. 6, p. 649-659.

Berman, S., 1947, Determination of yttrium, lanthanum, cerium, neodymium, and ytterbium in test samples granite G-1 and diabase W-1 by a combined chemical-spectrochemical technique: Geochim. et Cosmoch. Acta. v. 12, p. 271-272.

Condie, K. C., 1967, Geochemistry of early Precambrian graywackes from Wyoming: Geochim. et Cosmochim. Acta., v. 31, p. 2135-2149.

Condie, K. C., Macke, J. E., and Reimer, T. O., 1971, Petrology and geochemistry of Early Precambrian graywackes from the Fig Tree Group, South Africa: Geol. Soc. Am. Bull., v. 81, p. 2759-2776.

Danchin, R. V., 1967, Chromium and nickel in the Fig Tree Shale from South Africa: Science, V. 158, p. 261-262.

Denechaud, E. B., Helmke, P. A., and Haskin, L. A., 1968, Analysis for the rare-earth elements by neutron activation and Ge(Li) spectrometry: J. Radioanal. Chem., v. 1, p. 337-348.

Frey, F. A., 1969, Rare earth abundances in a high-temperature periodtite intrusion: Geochim. et Cosmochim Acta., v. 33, p. 1429-1447.

Frey, F. A., Haskin, M. A., Poetz, J. A., and Haskin, L. A., 1966, Rare earth abundances in some basic rocks: Jour. Geophys. Res., v. 71, p. 6091-6105.

Girin, Y. P., Balashov, Y. A., and Bratishko, R. K., 1970, Redistribution of the rare earths during diagenesis of humid sediments: (Geochem. Int., No. 5, p. 616-631.

Gordon, G. E., Randle, K., Goles, G. G., Glrliss, J. B., Beeson, M. H., and Oxley, S. S., 1968, Instrumental activation analysis of standard rocks with high-resolution gamma-ray detectors: Geochim. et Cosmochim. Acta., v. 32, p. 369-396.

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

Green, T. H., Brunfelt, A. O., and Heier, K. S., 1972, Rare earth element distribution and K/Rb ratios in granulites, mangerites and anorthosites, Lofoten-Vesteraalen, Norway: Geochim. et Cosmochim. Acta., v. 36, p. 241-257.

Guidotti, C. V., 1968, Prograde muscovite pseudomorphs after staurolite in the Rangeley-Oquossoc areas, Maine: Am. Mineralogist, v. 53, p. 1368-1376.

Guidotti, C. V., 1970, The mineralogy and petrology of the transition from the lower to upper sillimanite zone in the Oquossoc Area, Maine: Jour. of Petrology, v. 11, p. 277-336.

Haskin, L. A., Wildeman, T. R., Frey, F. A., Collins, K. A., Keedy, C. R., and Haskin, M. A., 1966, Rare earths in sediments: Jour. Geophys. Res., v. 71, p. 6091-6105.

Haskin, L. A., Frey, F. A., Schmitt, R. A., and Smith, R. H., 1966, Meteoritic, solar, and terrestrial rare-earth distributions: Physics and Chemistry of the Earth, New York, Pergamon Press, New York, v. 7, p. 169-316.

Haskin, L. and Gehl, M. A., 1963, The rare earth contents of standard rocks G-1 and W-1 and their comparison with other rare-earth distribution patterns: Jour. Geophys. Res., v. 68, p. 2037-2043.

Haskin, L. A., Wildeman, T. R., and Haskin, M. A., 1968, An accurate procedure for the determination of the rare earths by neutron activation: Jour. Radioanal. Chem., v. 1, p. 337-348.

Krauskopf, K. B., 1962, Factors controlling the concentrations of thirteen rare metals in sea-water: Geochim. et Cosmochim. Acta., v. 9, p. 1-32.

Lyakhovich, V. V., 1962, Rare earth elements in the accessory minerals of granitoids: Geochemistry, v. 1, p. 39-56.

Melsom, S., 1970, Precision and accuracy of rare earth determinations in rock samples using instrumental neutron activation analysis and a Ge(Li) detector: Jour. Radioanal. Chem., v. 4, p. 355-363.

Fleischer, Michael, 1965, U. S. Geological Survey standards - I. Additional data on rocks G-1 and W-1: Geochim. et Cosmochim. Acta., v. 33, p. 65-79.

Moench, R. H., 1970, Premetamorphic down-to-basin faulting, folding, and tectonic dewatering, Rangeley area, Western Maine: Geol. Soc. Am. Bull., v. 81, p. 1463-1496.

Phillpotts, J. A., and Schnetzler, C. C., 1968, Europium anomalies and the genesis of basalt: Chem. Geol., v. 3, p. 5-13.

Philpotts, J. A., Schnetzler, C. C., and Thomas, H. H., 1967, Rare earth and barium abundances in the Bununu Howardite: Earth Planet Sci. Lett., v. 2, p. 19-22.

Potter, P. E., Shimp, N. F., and Witters, J., 1963, Trace elements in marine and fresh-water argillaceous sediments: Geochim. et Cosmochim. Acta., v. 27, p. 669-694.

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

Schimitt, R. A., Smith, R. H., Lasch, J. E., Mosen, A. W., Olehy, D. A., and Vasilevskis, J., 1963, Abundances of the fourteen rare earth elements, schdium, and yttrium in meteoritic and terrestrial matter: Geochim. et Cosmochim. Acta., v. 27, p. 577-622.

Shaw, D. M., 1954, Trace elements in pelitic rocks. Part I: Variation during Metamorphism. Part II: Geochemical Relations: Geol. Soc. Amer. Bull., v. 65, p. 1151-1182.

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

Smales, W., 1960, Methods in Geochemistry, p. 297-357.

Smith, J., 1967, Petrography of Brite Ignimbrite, Trans Pecos, Texas: Kansas State University, M. S. Thesis, 88 p.

Towell, D. G., Winchester, J. W., and Spirn, R. V., 1968, Rare earth distributions in some rocks and associated minerals of the batholith of Southern California: Jour. Geophys. Res., v. 70, p. 3485-3496.

Winkler, H. G. F., 1967, Petrogenesis of metamorphic rocks: New York, Springer-Verlag, 237 p.

THE DISTRIBUTION OF THE RARE-EARTH ELEMENTS IN
SILURIAN PELITIC SCHISTS FROM NORTHWESTERN MAINE

by

LONG-TSU YEH

B. S., National Taiwan University, 1969

———————————————

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Geochemistry

Department of Geology

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1973

ABSTRACT

REE contents in thirty-three samples of a series of metamorphosed
pelitic schists in the greenschist and amphibolite facies from N. W. Maine
have been determined by neutron activation analysis. No appreciable change
in rare-earth element (REE) patterns is observed with increasing grade from
the greenschist facies to amphibolite facies. Samples from the Perry Moun-
tain Formation show large depletions in light REE contents compared with those
of Rangeley Formation. These significant differences in light REE contents
between the Perry Mountain Formation and other sedimentary rocks are believed
to be due to differences in clay mineral contents as modified by climate and/or
environment of deposition. Smaller variations of REE content within each
formation are likely due to the variation in the original accessory minerals
in the original rock. Eu anomalies in all the analyses are likely due to
partial reduction of Eu^{+3} to Eu^{+2} in the sedimentary environment.