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THE DETERMINATION AND INTERPRETATION OF RARE EARTH ABUNDANCES IN HYBRID GRANITOID ROCKS OF THE SOUTHERN SNAKE RANGE, NEVADA

By

Doug Cain

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Signed: ______________________
Student

Golden, Colorado
Date: 3-12, 1974

Approved: Thomas Wildeman
Thesis Advisor

____
Head of Department

Golden, Colorado
Date: 3-12, 1974

ABSTRACT

Rare earth element (REE) abundances in whole rocks and major minerals from a small stock in eastern Nevada, along with adjoining sedimentary rocks have been determined by neutron activation analysis. The stock varies smoothly in composition from granodiorite (CaO = 4.5 percent) in contact with limestone to quartz monzonite (CaO = 0.5 percent) in contact with quartzite. Regular trends in chemistry and mineralogy accompany the composition change which is believed to result from host rock assimilation.

An average REE distribution for the intrusive can be roughly equated to the parent magma REE distribution. Fractionation of the REE in the whole rocks with respect to this average is the opposite of that expected for differentiation, and can be attributed to uptake of the REE in the accessory minerals which contain 80-98 percent of the REE except Eu. Europium is concentrated in the feldspars except in the high CaO rocks. The plagioclases contain most of the REE that are associated with the major minerals.

The REE data is consistent with transport of the light REE to the high CaO rocks with subsequent incorporation in accessory minerals, while the heavy REE were probably concentrated in a residual aqueous phase with uptake in the late crystallizing low CaO rocks.

TABLE OF CONTENTS

Table of Contents Con't Page

LIST OF TABLES AND FIGURES

Tables

Figures

LIST OF TABLES AND FIGURES

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INTRODUCTION

The rare earth elements (REE) have been shown to be useful in the interpretation of geologic processes (Haskin and others, 1966; Zielinski and Frey, 1970; Balashov and others, 1970). Their usefulness stems from the facts that the REE are present in trace amounts in most rocks and that they behave as a coherent group in geochemical systems. This group behavior is attributed to two facts; first, the REE are all normally found in the +3 oxidation state; and second, there is an almost linear trend of ionic radii with atomic number. Lanthanum has the largest radius and Lu the smallest. Only two of the REE can be in an oxidation state other than +3 in natural systems. Cerium can be oxidized to the +4 state, and Eu can be reduced to the +2 state. These changes act as a natural indicator of oxidizing strength. Because of the generally smooth trends found in the group, anomalies in Ce or Eu are easily seen.

A few terms that will be used throughout this work are defined below. The REE as used here are La (atomic number 57) through Lu (atomic number 71). Assimilation is the process of interaction between a magma and its host rocks. A magma that assimilates foreign material undergoes a chemical change, or contamination, and such contaminated magma will crystallize as a hybrid rock. Granitoid is a term applied to igneous rocks with the texture of a granite, without concern for composition.

Haskin and others (1966) noted that "Information on RE patterns and concentrations for rocks of intermediate composition is meager." Most of the data that are available are from volcanic rocks, or from single nonrelated samples. Most of the analyses on mineral separates are on feldspars, especially plagioclase. Only two studies of related groups of intermediate to acidic plutonic rocks and their mineral fractions have been reported in the literature. Towell and others (1965) present RE data on four rocks and some separated minerals from the Batholith of Southern California. Buma and others (1971) have examined the REE in a suite of New England granites. This study will try to help fill this informational gap. Besides providing information on RE distributions in intermediate to acidic plutonic rocks, this study presents the first RE data on a suite of assimilated rocks. The rare earth data are used as a geochemical tool in an attempt to help understand the process of assimilation.

The study area has been the site of investigations by Donald E. Lee and others from the U.S. Geological Survey since 1961. The materials described herein were selected for study because the area is well exposed and easily accessible, and field relations are well defined; results of previous field and laboratory studies on the area provide a large fund of background information; and splits of highly purified mineral phases were available.

GEOLOGICAL AND GEOCHEMICAL BACKGROUND

The study area is in the southern Snake Range of east central Nevada, which is in the eastern part of the Basin and Range province (fig. 1).

The granitoid rocks outcrop north and east of the Mount Wheeler Mine, as seen in fig. 1. The areas of interest to this study are the Snake Creek-Williams Canyon area, the largest of the three intrusive bodies, and the Pole Canyon-Can Young Canyon area north of it. In this study, the two areas will be referred to simply as the Snake Creek area and the Pole Canyon area, respectively. Eight rocks, along with separated mineral fractions from six of the rocks, have been studied.

This section is taken from U. S. Geological Survey Professional Paper 668: "Hybrid Granitoid Rocks of the Southern Snake Range, Nevada" (Lee and Van Loenen, 1971), with exceptions as noted.

Geologic Setting

The granitoid rocks, of middle Jurassic age (160 million years), intruded a sequence of mostly quartzite and carbonate rocks. The sedimentary rocks in contact with the intrusives are the Precambrian Shingle Creek Quartzite and Osceola Argillite, and the Cambrian Prospect Mountain Quartzite, Pioche Shale, and Pole Canyon Limestone.

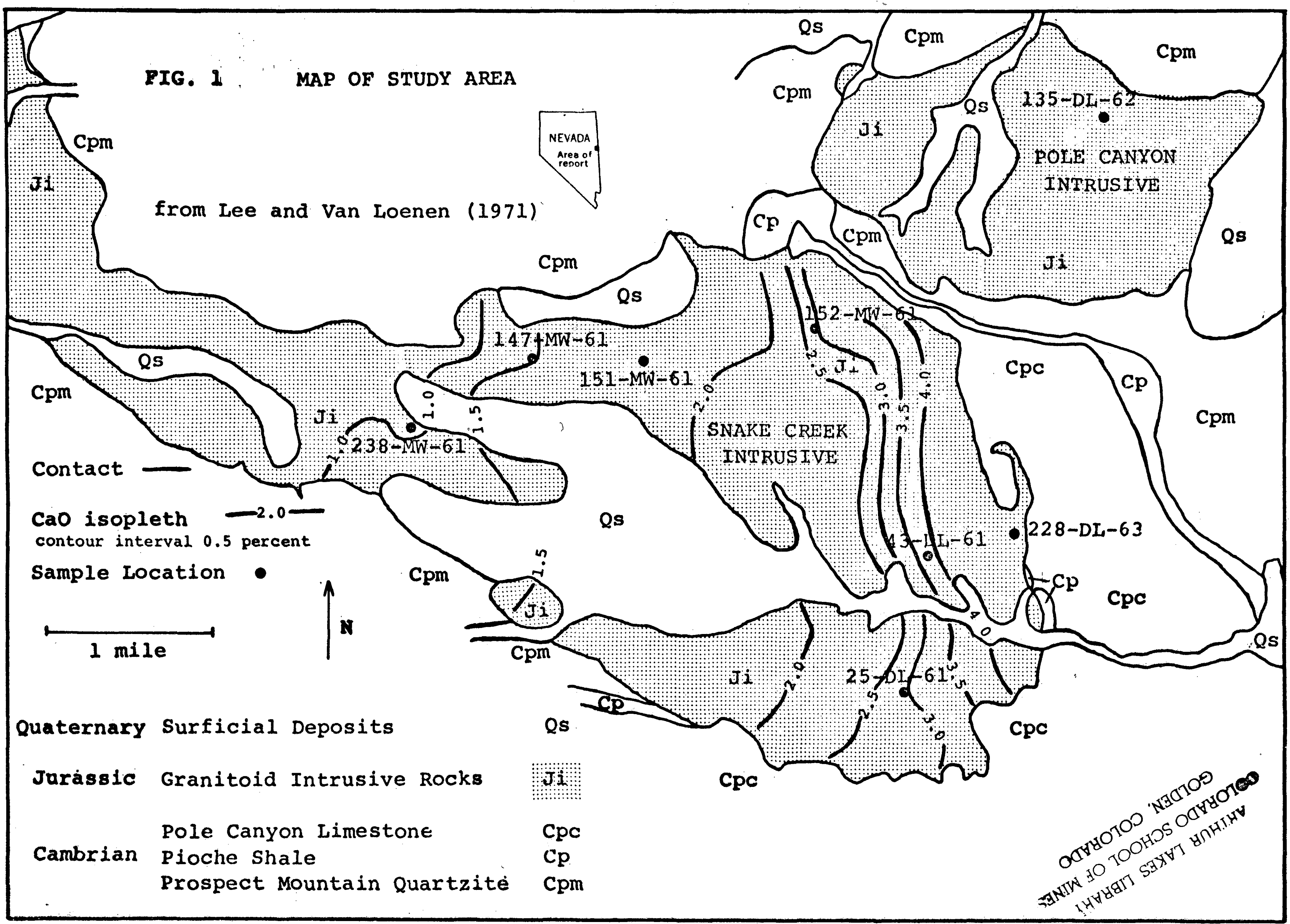


FIG. 1 MAP OF STUDY AREA

from Lee and Van Loenen (1971)

The Snake Creek and Pole Canyon intrusives are discussed separately below.

The Snake Creek intrusive is dome-like and probably has not been unroofed anywhere to a depth of more than 1000 ft (Drewes, 1958). The intrusive is roughly concordant with the overlying rocks, but there is a notable discordance in the south (Drewes, 1958). The intrusive contacts the Prospect Mountain Quartzite in the west and the Pole Canyon Limestone in the east. The Pioche Shale lies between the quartzite and limestone, and many partly assimilated xenoliths of this rock are seen in the eastern part of the outcrop. Stoping appears to have taken place in parts of the outcrop, but there is little evidence of contact metasomatism in the host rocks.

The Pole Canyon intrusive is also roughly domal in form and is in contact with Prospect Mountain Quartzite on all sides. The Pole Canyon intrusive consists of two main phases that are roughly equal in outcrop area; these are a "host" intrusive and a late aplitic and pegmatic material. Xenoliths are not seen in this outcrop.

Sedimentary Rocks

Lee and Van Loenen (1971) present major and minor element analyses for a total of 34 sedimentary rock samples of Prospect Mountain Quartzite, Osceola Argillite, Pioche Shale, Wheeler Limestone, and Pole Canyon Limestone.

The Osceola Argillite is the oldest rock in the area exposed in contact with the granitoid rocks to an appreciable extent. It is about 750 ft thick and shows the greatest effect of contact action of any of the sedimentary rocks. The Prospect Mountain Quartzite is about 3500 ft thick in the study area and is fairly pure quartz rock with SiO_2 generally greater than 90 percent. The Pioche Shale is probably 300 to 450 ft thick in the study area. The upper fourth is fine grained calcareous quartzite, with interbeds and lenses of limestone, whereas the lower three fourths is micaceous to silty shale with a limestone unit in the lower part. The limestone, known locally as the Wheeler Limestone, ranges from 5 to 25 ft in thickness. The Wheeler Limestone contains from 4 to 14 percent Mg and from 3 to 35 percent SiO_2. The Pole Canyon Limestone is a massive, fairly pure carbonate rock, about 2000 ft thick.

Chemistry and Mineralogy of the Granitoid Rocks

The Snake Creek outcrop alone has 87 samples analyzed for major and minor elements and mineralogic modes, and these analyses are presented by Lee and Van Loenen (1971). On the basis of these analyses, CaO isopleths have been constructed on the map of the intrusive (fig. 1) by Lee and Van Loenen. A large, but smooth and continuous, variation of CaO is noted, from less than 1 percent in the west to greater than 4 percent in the east. These large variations over such a small horizontal distance (3 miles) are attributed to assimilation of the host rocks.

Lee and Van Loenen (1971) normally correlate trends in major and minor elements to CaO rather than to SiO_2, and that convention will generally be used in this study. For ease of comparison, however, the major oxides from the Snake Creek intrusive are plotted versus SiO_2 in fig. 2. Daly's average andesite, dacite, and rhyolite, from Barth (1962, p. 164), are plotted for comparison. The two sets of lines nearly coincide: assimilation has produced a series of rocks with major oxides essentially the same as a series of differentiated rocks.

A look at some trace element data, though, indicates that something besides differentiation has occurred. Lee and Van Loenen (1971) noted that La increases as CaO increases in these rocks, which is opposite of the trend observed in differentiated rocks (Haskin and Haskin, 1968; Towell and others, 1965). Also, Ba normally has the same relation as K to CaO (Taylor, 1969), that is, as CaO increases, Ba decreases; in these rocks, however, Ba increases as CaO increases.

Figures 3 and 4 summarize the mineralogy of the Snake Creek rocks. The trend for the major minerals are rather striking, but are not unexpected, considering the chemistry of the rocks. The large amount of biotite in the most mafic

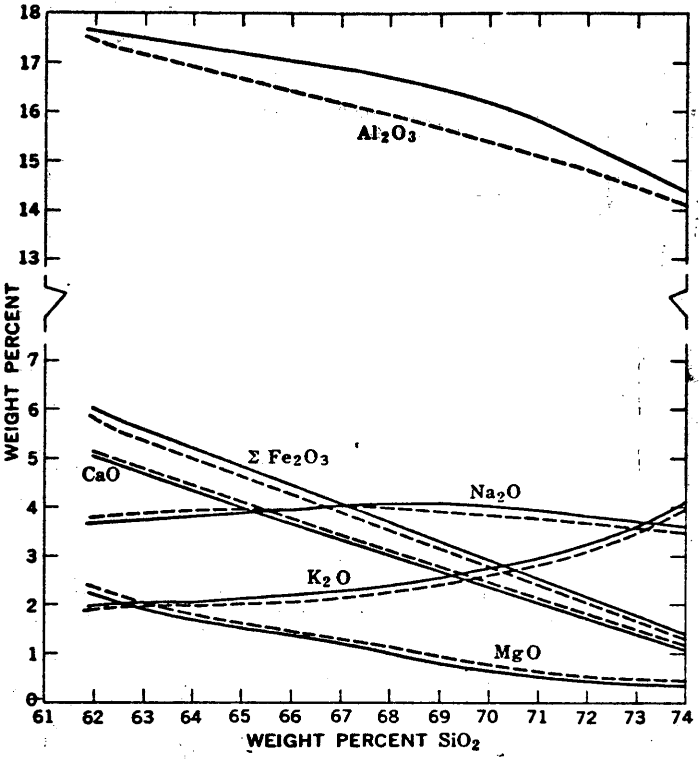


FIG. 2: Variation diagram comparing Daly's average andesite-dacite-rhyolite (solid lines; Barth, 1962, p. 164) with granitoid rocks of the Snake Creek area, from Lee and Van Loenen (1971).

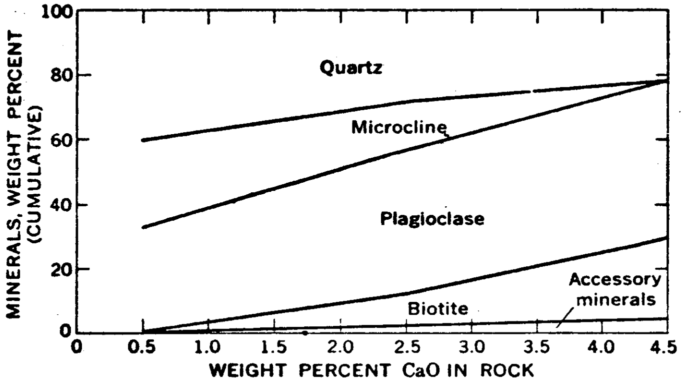


FIG. 3: General relations between Cao content and mineralogy, for rocks of the Snake Creek area, from Lee and Van Loenen (1971).

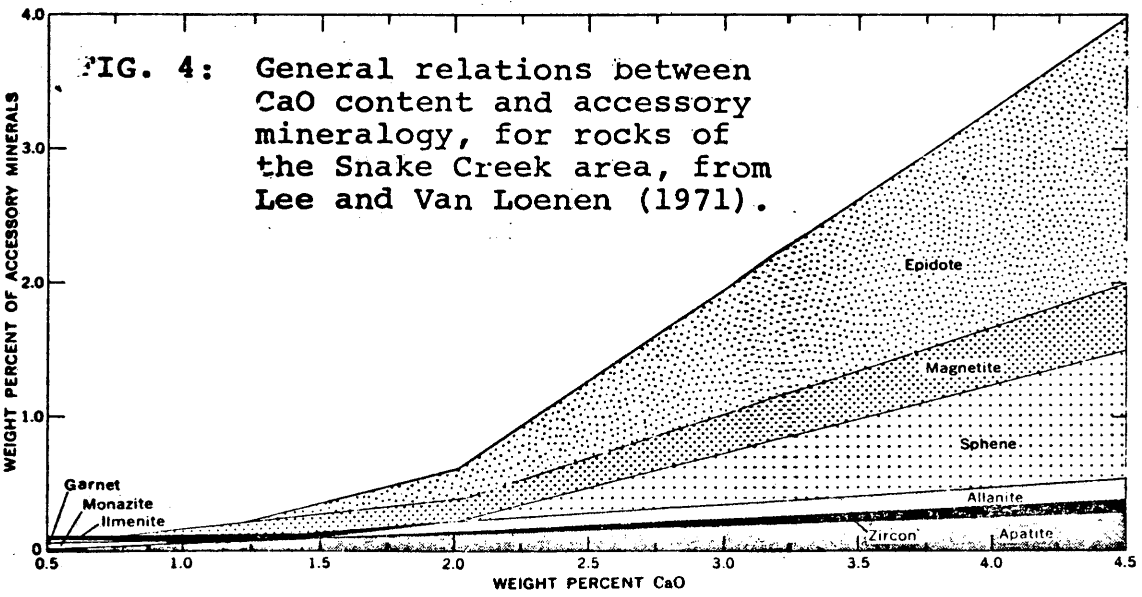


FIG. 4: General relations between CaO content and accessory mineralogy, for rocks of the Snake Creek area, from Lee and Van Loenen (1971).

rocks should be noted. Large amounts of biotite have been noted in other areas of hybrid rocks (Turner and Verhoogen, 1960, p. 156). Two distinct suites of accessory minerals are present. The low CaO rocks have small amounts of garnet, monazite, and ilmenite. The accessories in the high CaO rocks are different, though, consisting of epidote, sphene, magnetite, apatite, allanite, and zircon. One fact noted in the literature (Wyatt, 1954; Nockolds, 1933) is the abundance of zircon and apatite in hybrid rocks. These minerals often have an acicular habit in hybrid rocks, which is the case in the Snake Creek rocks.

Nine rocks have been analyzed (Lee and Van Loenen, 1971) from the Pole Canyon area for major and minor elements and mineralogic mode. These analyses show CaO ranging from .87 to 1.8 percent. These variations are attributed to variations in the Osceola Argillite, which is believed to have been assimilated. The stratigraphic position of the Osceola Argillite is near the position of the Pole Canyon intrusive and this fact lends credence to this hypothesis. The nine analyses are for rocks of the host intrusive phase and no data is presented for the aplitic rocks of this area.

The major mineralogy of these rocks does not follow linear trends as in the Snake Creek area. The major difference in the mineralogy of the two areas is the presence of 4 to 12 percent muscovite in the Pole Canyon rocks. This difference clearly sets these rocks apart from the Snake Creek rocks and implies a different genesis.

Summary of Chemistry and Mineralogy

The Snake Creek intrusive varies from granodiorite (CaO = 4.5 percent) in contact with limestone to quartz monzonite (CaO = 0.5 percent) in contact with quartzite. The CaO content changes smoothly over a distance of about 3 miles and is accompanied by changes in major and minor element chemistry and major and accessory mineralogy. These changes are attributed to host-rock assimilation. The Pole Canyon intrusive is set off from the Snake Creek intrusive by its chemistry and mineralogy. Muscovite is an essential mineral of the Pole Canyon rocks. This distinctive rock type is believed to have been caused by assimilation of the Osceola Argillite.

The evidence cited by Lee and Van Loenen (1971) in support of the hypothesis of assimilation includes the following:

1. Presence of acicular zircon.
2. Abundance of acicular apatite.
3. Abundance of biotite in the mafic rocks.
4. High content of H_2O and F.
5. Concentration of light REE in the high CaO rocks.
6. Differences in accessory mineral suites and abundances in the high CaO and low CaO rocks.

7. Because of the accessory minerals, high CaO rocks are richer in the light REE, Zr, P, Ti, Ba, and Sr than the low CaO rocks.

SAMPLING AND ANALYTICAL TECHNIQUES

Sample Locations

The locations of samples of intrusive rocks are shown in fig. 1. All samples were obtained from Lee, who collected them as grab samples. The seven samples for REE analysis from the Snake Creek intrusive were chosen to cover the full range of CaO content, and also to provide the most supporting data from Lee and coworkers. One representative sample from the Pole Canyon intrusive was analyzed. Locations of sedimentary rocks analyzed are not shown, since composite samples were prepared as discussed in the next section.

Kinds of Samples Analyzed

Table 1 lists the sample numbers and kinds of samples analyzed from each sample location. Some of the plagioclases have a rather large impurity of quartz. Plagioclase analyses are presented as if all the rare earth present in the mixtures were in the plagioclases. This should be a good approximation (Buma and others, 1971). Composite sedimentary rock samples are shown in Table 1. These composites were prepared by mixing equal weights of the samples shown in the table.

A total of 8 whole rocks, 6 plagioclases, 6 biotites, 4 potassium feldspars, 1 muscovite, and 5 sedimentary rock composites have been analyzed for the REE. In addition, Rb

TABLE 1

SAMPLES ANALYZED

Granitoid Rocks

Sample Number	% CaO in Rock	Whole Rock	Plagio- clase	Biotite	Potassium Feldspar
238-MW-61	.78	X			
147-MW-61	1.5	X	X	X	X
151-MW-61	1.8	X	X	X	X
25-DL-61	3.1	X	X	X	X
152-MW-61	3.2	X	X	X	
43-DL-61	3.9	X	X	X	
228-DL-63	4.5	X			
135-DL-62	.98 (Pole Canyon)	X	X	X (and Muscovite)	X

Sedimentary Rock Composites

Sedimentary Rock	Composite of Sample Numbers
Osceola Argillite	Ar1, Ar2, Ar3, Ar4, Ar5, Ar6
Pioche Shale	S1, S2, S3, S4, S6, S7, S8, S9
Prospect Mountain Quartzite	Q2, Q3, Q4
Pole Canyon Limestone	P1, P2, P3, P5, P6, P7, P9
Wheeler Limestone	WLS1, WLS2, WLS3, WLS4, WLS5

All sample numbers are from Lee and Van Loenen (1971).

and Sr were analyzed for us by Willis Doering of the U.S. Geological Survey on 5 whole rocks, 5 plagioclases, and 1 potassium feldspar (Doering, 1968). REE data is also available for 5 allanites (Lee and Bastron, 1967), 5 apatites (Lee and others, 1973), 2 sphenes (Lee and others, 1969), and 2 monazites (Lee and Bastron, 1967) from these rocks.

Neutron Activation Analysis

The neutron activation analysis method used here is essentially that described by Jarvis (1972). The major difference is that on the samples of whole rocks, REE were radioassayed also on the day of irradiation. This extra count allows two more REE, Dy and Er, to be determined. In all, then, a maximum of 12 REE were analyzed on the whole rocks and a maximum of 10 REE on the mineral separates.

Analytical uncertainty of the analyses is believed to be ±10 percent for the REE except for Ce, Dy, and Er. This is based on duplicate analyses where uncertainty is expressed as percent deviation from the mean. Cerium was within 17 percent, and samples were not reanalyzed for Dy and Er. Three duplicate analyses with standard deviations and percent deviations are listed in Appendix B. Large percent deviations are noted for the biotite and plagioclase, especially for the light REE. It is believed that these deviations are the result of sample inhomogeneity. In samples with low total RE content such as these, contamination by a small amount of high RE content accessory minerals could cause deviations of this sort. Calculations on 152-MW-61 biotite indicate that the presence of one part per 10,000 in the amount of allanite in the sample would increase the concentrations of the light REE by as much as 10 to 25 percent.

An analysis of USGS standard rock G-2 is also included in Appendix B. The rock was analyzed for nine REE. It is compared to REE analyses presented by Flanagan (1973). We follow his convention of indicating whether a value is recommended, an average, or a magnitude. The percent deviations for G-2 are within 10 percent for Nd, Sm, and Lu, and within 17 percent for La, Ce, Eu, Gd, Yb, and Tb. Many of the samples analyzed, especially the biotites and feldspars have REE contents much lower than G-2 or any of the duplicate samples that were analyzed. It is expected that the analytical uncertainty will increase somewhat at these lower values.

Many of the feldspars and biotites have quantities of some of the REE that are below the detection limit for the method used. Since rock and mineral samples analyzed by this method usually have enough REE to be detectable, data on the detection limits is lacking in the literature. The following is the method used in this study for determining the detection limits.

Counting statistics dictate that an analyzable peak should be 3 times the square root of the background above background. Background counts were determined on all analyzable peaks of a standard, and these values gave minimum counts per minute for an analyzable peak. This data was put through the normal computer analysis and generated detection limits for each peak on each count in ppm. Detection limits were determined on a standard because standards are prepared to resemble the samples in REE content. Besides depending on the background, the detection limit in ppm depends on sample weight. Appendix B contains calculated detection limit data for a .1 gm and a .5 gm sample in ppm, and absolute detection limit in nanograms. For comparison, the smallest amount of a given element detected is included. The detection limit was exceeded for La and Ho. Both of these occurrences were on the same sample: 43-DL-61 biotite. On closer examination of this sample, it was found to have a very low background count. The low background allowed a reduction in detection limit by roughly a factor of 2-5. When looking at the detection limits, then, it should be noted that these apply in the strictest sense only to samples with background the same as the standard.

Analytical Interferences

Several extraneous peaks and some direct interferences were found in the gamma-ray spectra of most of the samples. Extraneous peaks, peak broadening, inconsistency between counts, baseline alteration, and results which were anomalous with the overall REE distribution were cause for close examination and possible rejection of data.

Neodynium, Eu, and Tb peaks were affected by interferences in many of the samples, especially the potassium feldspars and biotites, which were very low in most of the REE. Examination of energies, mechanisms of production, relative intensities and half lives from Lederer and others (1967) indicate that all three of these interferences were caused by Ba^{131}. Europium and Tb both have other analyzable gamma peaks, so values were usually determined for these elements even though the interfered peak was thrown out. In many cases, though, the Nd .0911 MeV peak is the only countable Nd peak, so no analysis was possible.

Peaks of three other nuclides have been detected in the spectra, although these peaks don't directly interfere with any REE peaks. Two of the other nuclides are also Ba isotopes, Ba^{133m} and Ba^{135m}, while the third is Sc^{46}.

Barium should not survive the chemical separation along with the REE. On this basis, attributing interferences to Ba is questionable. The data for Ba^{131} as a contaminant are very strong, however, with seven peaks in the spectra corresponding to peaks of this isotope. The Ba interference was also strongest in the potassium feldspars and biotites, which would be expected to have more Ba, since Ba has a strong association with K.

RESULTS

The results of the rare earth analyses are compiled in Appendix A. This appendix also includes values for the North American Shale Composite (NASC), and the Snake Creek Intrusive Average (SCIA). The NASC, a composite of 40 North American shales, represents an average REE distribution for the earth's crust (Haskin and others, 1968). The SCIA is discussed in a later section.

Method of Data Presentation

Each of the determined REE distributions were ratioed with a standard distribution, element by element. The NASC, SCIA, and some of the whole rocks were used as standard distributions in this study. The ratioing accomplishes two purposes. It eliminates the effect of concentration differences due to differences in relative abundances of odd and even atomic number elements, and it allows a comparison to be made with a "normal" or standard distribution.

Many of the figures in this section use this ratio method. The plots presented here are drawn by the Calcomp Plotter of the CSM Computing Center using a program developed by the author. The ratios are plotted on a logorithmic scale, since this allows greatly different REE concentrations to be plotted on the same plot, and also factors of depletion or enrichment are more accurately shown. Atomic number is the abscissa, and the ratios are connected with straight lines.

Rare Earth Balance for the Snake Creek Intrusive

To obtain a REE balance for the intrusive, two pieces of information are necessary. The first is an average RE distribution for the whole intrusive, and the second is a good estimate of what role the REE in the assimilated sedimentary rocks played in the production of this distribution.

Figure 5 shows the RE distributions for the 5 sedimentary rock composites. The sedimentary rocks are ratioed against the NASC, and the Osceola Argillite, Pioche Shale, and Pole Canyon Limestone all have the shale pattern, with only relative enrichment or depletion of all the REE. Both the Wheeler Limestone and the Prospect Mountain Quartzite show heavy REE enrichment. As far as assimilation is concerned, this enrichment is not significant for the Wheeler Limestone, since it represents only a small volume of rock. The Prospect Mountain Quartzite is much more important, since it is potentially a greater contributor of material for assimilation and could have a greater effect on the RE distribution of the intrusive. The heavy REE enrichment in the quartzite may be caused by zircons. Many authors have noted the predominance of the heavy REE (HREE) over the light REE (LREE) in zircons (Lyakhovach, 1962; Nagasawa, 1970; Buma and others, 1971).

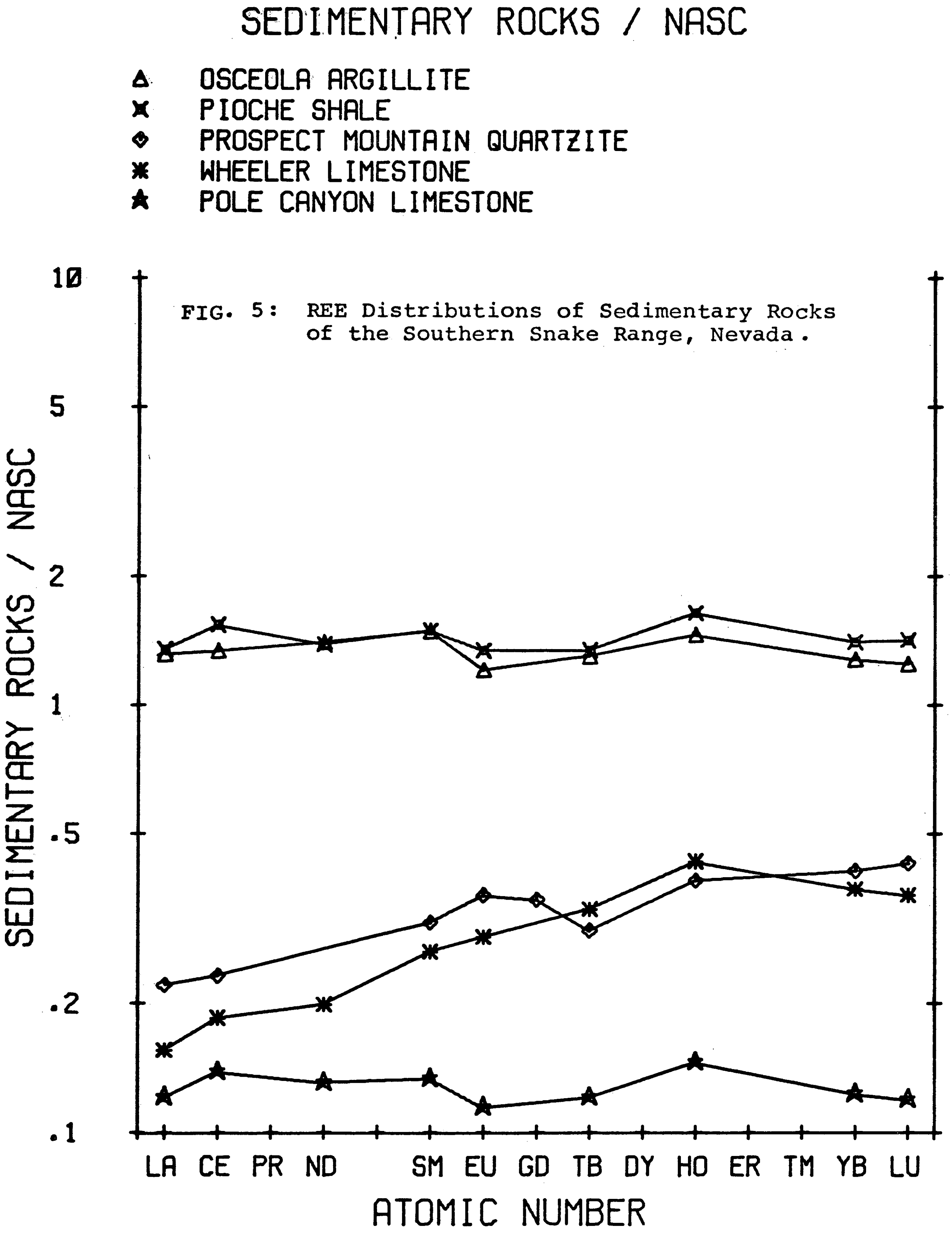


FIG. 5: REE Distributions of Sedimentary Rocks of the Southern Snake Range, Nevada.

Lee and Van Loenen (1971) found about 500 ppm Zr in the quartzite, the highest Zr content in any of the sedimentary rocks.

An average for the Snake Creek intrusive was generated in the following way. Each whole rock sample was used to represent the CaO region of the intrusive in which it falls, as shown in Table 2. Regions were constructed by drawing lines roughly parallel to the CaO isopleths of Lee and Van Loenen (1971). Each sample was weighted according to the percent of total outcrop surface it represented. The RE distribution this process produced is called the Snake Creek Intrusive Average (SCIA), and is tabulated in Appendix A. This average is based only on data from rocks exposed at the surface, and as such may or may not represent the RE distribution of the whole intrusive.

TABLE 2

Generation of SCIA

Sample Number	CaO of Sample (%)	CaO Region Represented (%)	% of Total Area
238-MW-61	.78	.5-1.1	21
147-MW-61	1.5	1.1-1.6	13
151-MW-61	1.8	1.6-2.5	43
25-DL-61	3.1	2.5-3.5 South	6.7
152-MW-61	3.2	2.5-3.5 North	5.0
43-DL-61	3.9	3.5-4.1	6.2
228-DL-63	4.5	4.1-4.5	5.9

Lee and Van Loenen (1971) state that the contact effects of the Snake Creek intrusive are slight, and because of this we can look at the intrusive as a separate system. That is, the intrusive may have assimilated country rocks, but is appears that little material crossed the contacts that are presently observed in the field. Because of this lack of contact metasomatism, then, limits can be set on the amount of limestone and quartzite assimilated, and indirectly on the amount of shale. This will allow an estimate of how the REE from the assimilated rocks might have affected the SCIA. Since the Prospect Mountain Quartzite and Pole Canyon Limestone (which are expected to be the greatest contributors of material for assimilation) both have abundances of most of the REE that are lower than the SCIA (Appendix A), it is expected that assimilation of these rocks will not significantly alter the RE distribution of the SCIA. A quantitative demonstration of this expectation follows.

The calculation involves determining how much limestone would be necessary to raise the CaO content of the whole intrusive from the lowest value observed up to the average amount observed. The quartzite calculation is similar. The average CaO and SiO_2 content of the intrusive were determined in the same way as the REE in the SCIA. Given that the average CaO content of Pole Canyon Limestone is 52.56 percent (Lee and Van Loenen, 1971), the smallest amount of CaO found in the intrusive is .5 percent, and the average CaO content of the intrusive is 2.1 percent, the following equation defines the mix required to generate the average CaO content of the intrusive:

$$.5256X + (1 - X).005 = .021$$

where X = amount of Pole Canyon Limestone necessary to give the resulting CaO content. Solving for X, it is found that only about 3 percent Pole Canyon Limestone is necessary to raise the CaO content to 2.1 percent.

A similar calculation can be made for the Prospect Mountain Quartzite, with 62 and 73 percent the lowest and average values respectively, in the intrusive, and the average value of SiO_2 in the quartzite 92 percent. A much larger quantity, almost 40 precent quartzite, would be necessary to account for the SiO_2 content of the intrusive. These are surely rough calculations, and indicate probable maximum amounts of assimilated material. It should be noted that only one of the above cases would occur, unless fairly extensive mixing of assimilated quartzite and limestone occurred, which appears doubtful from the field relations and chemistry of the Snake Creek intrusive rocks.

The limit set on the Pioche Shale is 5 percent for quartzite assimilation and about 1 percent for assimilation of limestone, based on the stratigraphic thickness of the beds involved.

From the chemical data presented by Lee and Van Loenen (1971), it appears that assimilation of quartzite and limestone both occurred, and so an intermediate case should be examined, with a sum of all three sedimentary rocks being considered. The following estimate was taken as reasonable: 2 percent Pole Canyon Limestone, 20 percent Prospect Mountain Quartzite, and 3 percent Pioche Shale.

Figure 6 shows how the REE in the sedimentray rocks for the three cases discussed will affect the REE in the SCIA. The figure is a plot of the SCIA leaving out the REE contribution from the sedimentary rocks. It is readily apparent that the assimilation of Pole Canyon Limestone has almost no effect on the SCIA, either in an absolute or relative sense. Assimilation of 40 precent quartzite and 5 percent shale has the effect of lowering the RE distribution somewhat, and depleting the heavy REE with respect to the light REE. The intermediate case shows a lowering of the RE distribution with a slight depletion of the heavy REE.

In working with the REE, we are more interested in the relative REE distribution than the absolute REE distribution. That is, it is usually more important to examine changes in the RE pattern (i.e., fractionation of REE, size of Eu anomaly) than to note that the whole RE pattern is shifted up or down with no change in shape. Figure 6 shows that even though the RE pattern of the SCIA may be shifted down by subtracting out

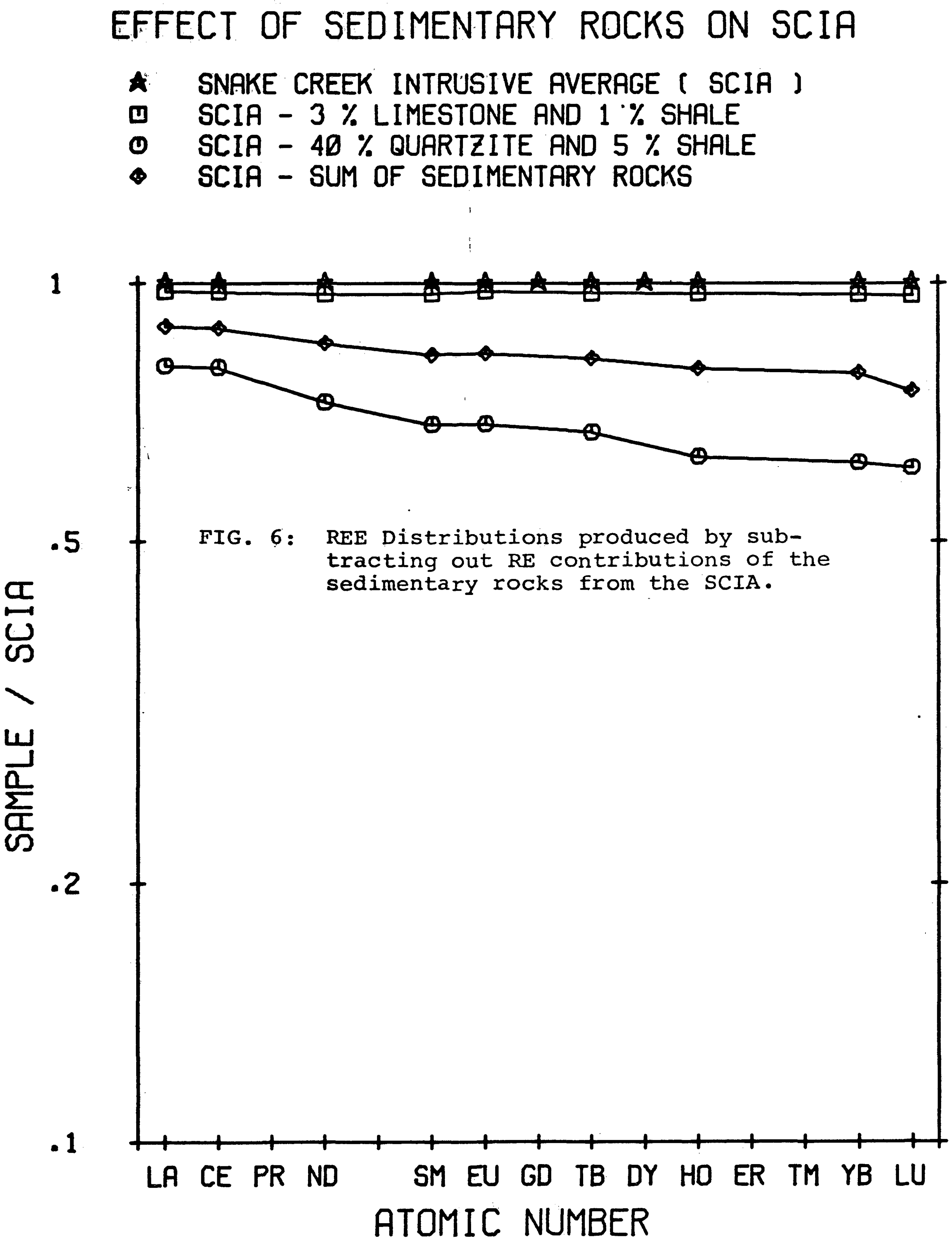


FIG. 6: REE Distributions produced by subtracting out RE contributions of the sedimentary rocks from the SCIA.

the contribution of assimilated sedimentary rocks, the shape of the pattern changes little. Only a slight depletion of the heavy REE is noted for the two cases that involve assimilation of quartzite, due to the slightly enriched heavy REE in this rock as discussed earlier. Very little absolute or relative change is seen for assimilation of limestone and shale only. These results are the consequence of 4 facts:

1. Both the Prospect Mountain Quartzite and Pole Canyon Limestone, which are probably the greatest contributors of material for assimilation, have REE abundances less than the SCIA.
2. The Pole Canyon Limestone has abundances of all the REE that are about one-sixth of those in the SCIA.
3. The Prospect Mountain Quartzite has abundances of the light REE less than a third of those found in the SCIA, and heavy REE abundances about two-thirds of those found in the SCIA.
4. The estimated amounts of sedimentary rocks assimilated, coupled with REE abundances in these rocks, net small changes in the SCIA, most of which result from dilution.

Because of these small change in the SCIA caused by assimilation of sedimentary rocks, the Snake Creek intrusive can be regarded as a <u>closed system</u> with respect to <u>relative</u> REE distributions.

Since the Snake Creek intrusive can be looked at as a closed system with respect to relative REE distributions, the SCIA can be roughly equated with the RE distribution that would have been expected in the parent magma! It is logical, then to look for a rock with this same RE distribution. Figures 7 and 8 are plots of the whole rocks versus the SCIA. Two extreme RE patterns are seen, with variations between them. The high CaO rocks have light REE enrichment along with Eu enrichment, while the low CaO rocks (.78 and 1.5 percent CaO) have Eu depletion and heavy REE enrichment. No single sample shows itself to be like the SCIA, however. The dividing line between the two patterns seems to be between 147-MW-61 whole rock (CaO = 1.5 percent) and 151-MW-61 whole rock (CaO = 1.8 percent). Both of these rocks have light REE approximately equal to the heavy REE, but 147 has a Eu depletion while 151 has Eu enrichment. It appeared that a mixture of these two rocks might be very similar to the SCIA, which is presumed to have the REE distribution of the parent magma. A plot of these two rocks, and the average of the two is shown in fig. 9. The agreement with the SCIA is striking and leads the author to believe that these two rocks are only slightly changed from the parent magma, at least for the REE. This data also suggest that this range of CaO content (1.5-1.8%) represents the furthest westward influence of limestone assimilation in these rocks. Lee and Van Loenen (1971) show

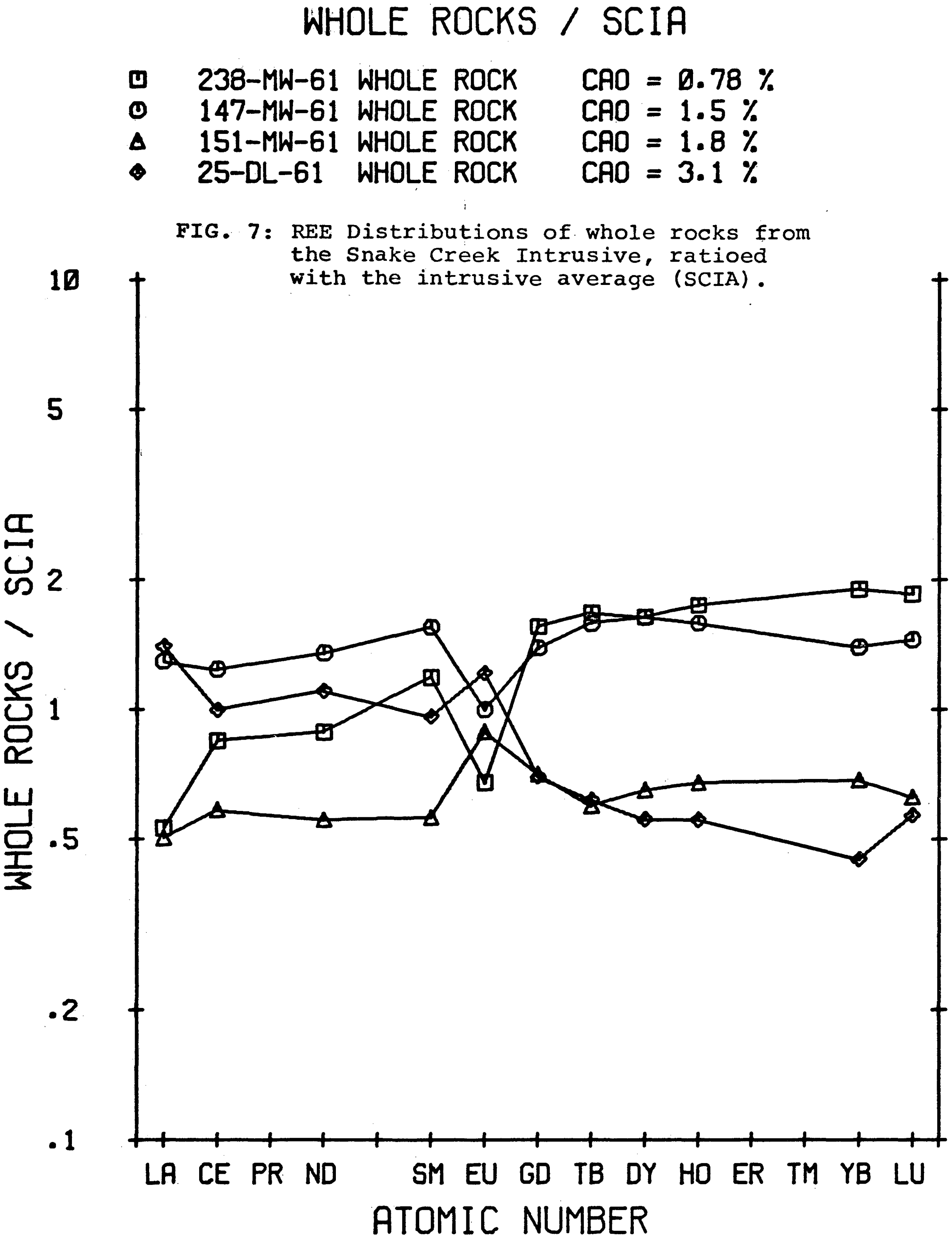


FIG. 7: REE Distributions of whole rocks from the Snake Creek Intrusive, ratioed with the intrusive average (SCIA).

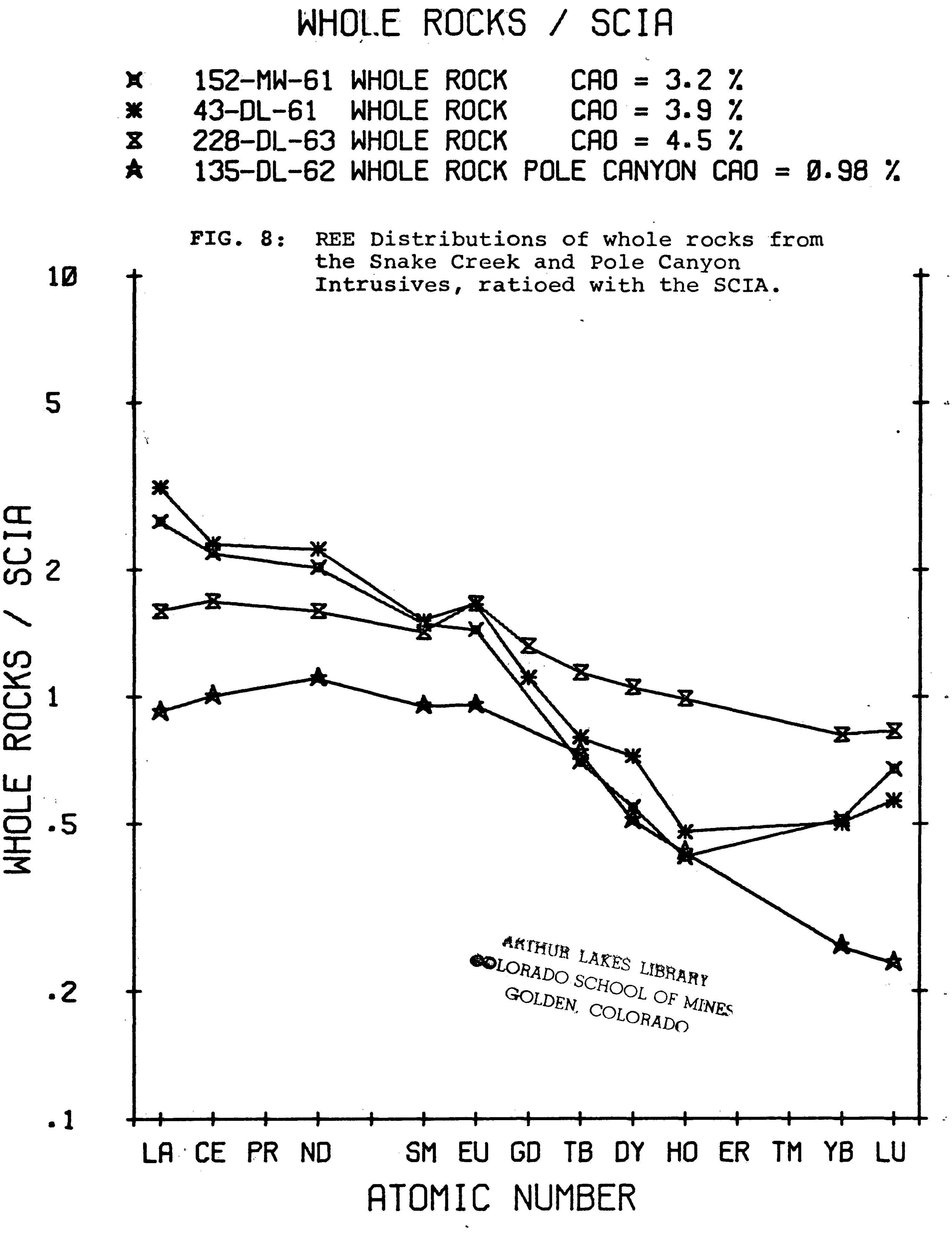


FIG. 8: REE Distributions of whole rocks from the Snake Creek and Pole Canyon Intrusives, ratioed with the SCIA.

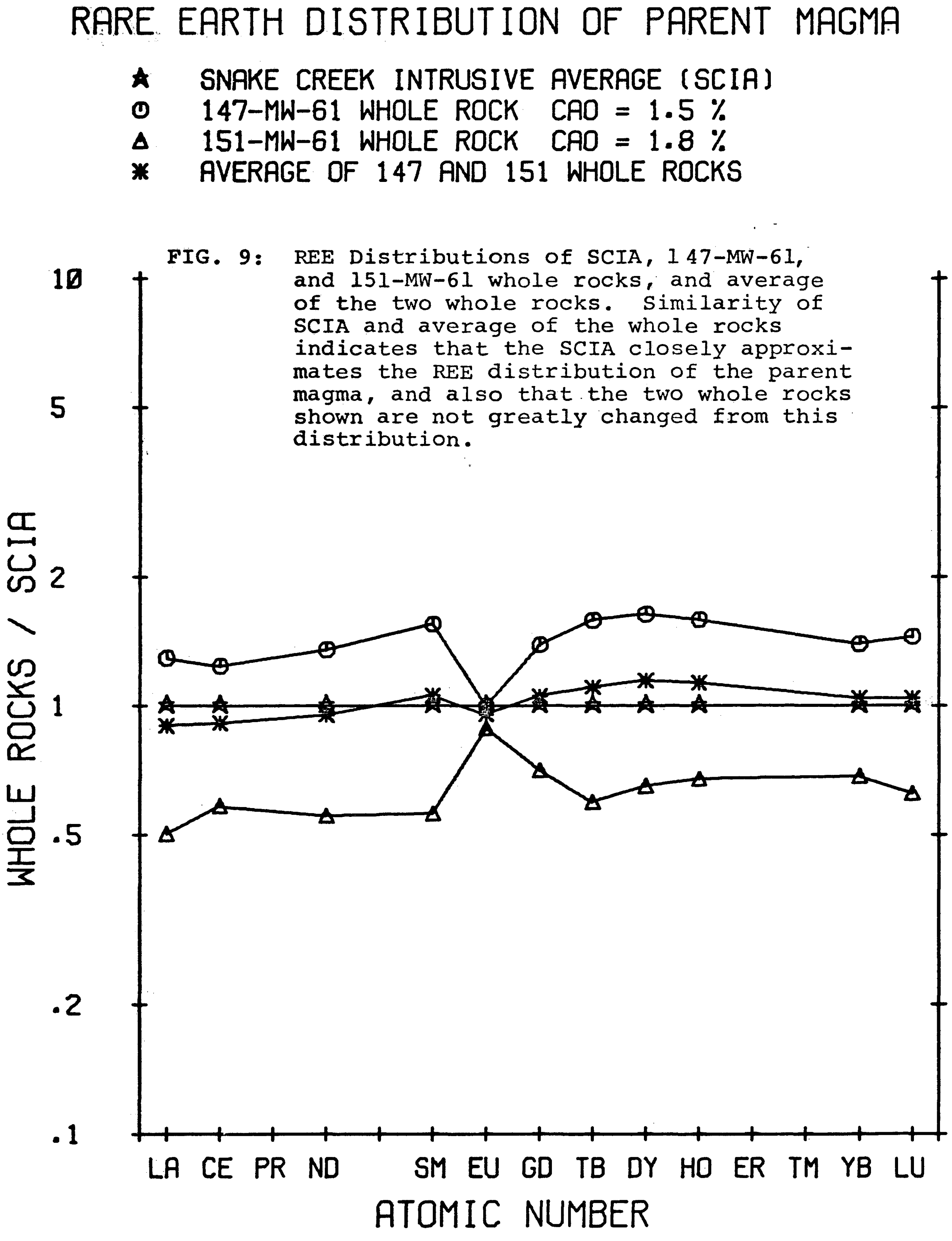


FIG. 9: REE Distributions of SCIA, 147-MW-61, and 151-MW-61 whole rocks, and average of the two whole rocks. Similarity of SCIA and average of the whole rocks indicates that the SCIA closely approximates the REE distribution of the parent magma, and also that the two whole rocks shown are not greatly changed from this distribution.

that other parameters show marked changes in roughly the same range of CaO. This data will be more closely examined in a later section.

Extending the parent magma idea to the major oxides is the next logical step, but the model breaks down here due to the fact that the system cannot be looked at as closed with respect to the major oxides, especially CaO and SiO_2.

REE in Granitoid Whole Rocks

The distribution and CaO dependence of the REE in the granitoid whole rocks is now discussed in more detail.

One feature of the REE distribution noted earlier is the increased fractionation of the REE as the CaO content of the rocks increases. A quantitative index of REE fractionation is the ratio La/Yb, which is plotted for the whole rocks in fig. 19. The La/Yb ratio increases with increasing CaO content, the opposite of the trend found by Towell and others (1965) for rocks of about the same range of CaO, from the batholith of southern California, which Larsen (1948) believed were the result of magmatic differentiation. Haskin and others (1968) present REE data on 3 rock composites: <60 percent SiO_2, 60-70 percent SiO_2, and <70 percent SiO_2, while Taylor (1969) presents data for the series andesite-dacite-rhyolite. The La/Yb ratios for these samples are fairly constant and range from 6-13. This is about the same range seen in the low CaO rocks of the Snake Creek intrusive, but the high CaO rocks show La/Yb ratios about ten times this large. High La/Yb ratios in granitic rocks are not unknown however, and Buma and others (1971) report values of La/Yb >100 for two New England granites. They also show trends of La/Yb increasing with CaO, MgO, and Al_2O_3 in 8 granites. The high La/Yb ratios in the two granites are believed to be the result of HREE concentrating minerals, involving either a partial melting process, or complexation and removal in a fluid phase.

As noted by Lee and Bastron (1967) and Lee and Van Loenen (1971), the distribution of the REE in the mafic rocks of the Snake Creek intrusive is similar to that found in carbonatites. The Snake Creek rocks show increasing RE fractionation coupled with increasing total RE content as CaO increases, and an extrapolation of this trend leads into the carbonatite field of Loubet and others (1972) on a plot of La/Yb versus total RE content. Processes that might have caused the large changes in RE fractionation over such a small horizontal distance are discussed in a later section.

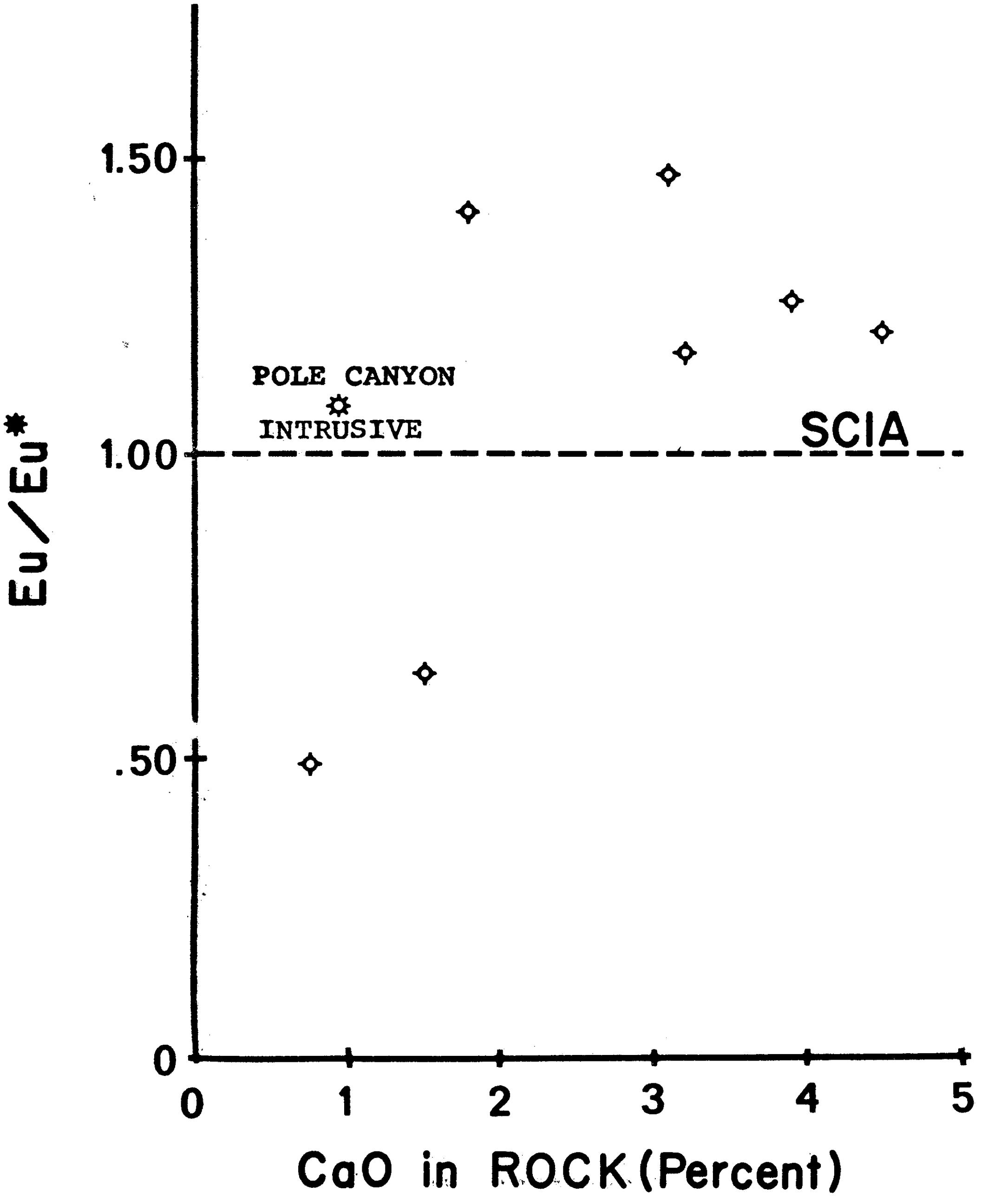
The highest CaO rock, 228-DL-63, with CaO = 4.5% doesn't fit the Snake Creek La/Yb trend, as shown in fig. 19. This rock also has lower total RE content than would be expected. These deviations are attributed in part to a contact effect due to assimilation of relatively large amounts of Pole Canyon Limestone with a low La/Yb of 10 and low total RE content of about 20 ppm. Early crystallization of this rock, might also have been a contributing factor, effectively removing this rock from the processes that contributed to the genesis of the other rocks of the Snake Creek intrusive.

The La/Yb ratios for the 1.5 and 1.8 percent CaO rocks, earlier attributed to be very similar to the parent magma in RE content, plot very near the La/Yb of the SCIA, giving further support to this hypothesis.

The other striking feature of fig. 7 and 8 is the anomalous behavior of Eu with respect to the other REE. The Eu anomaly can be quantified by defining Eu* as the Eu expected by interpolation between the nearest REE on either side of Eu in a plot of the REE versus a given standard. The ratio Eu/Eu*, where Eu is the actual value of europium on the plot, is a measure of the Eu anomaly. Figure 10 is a plot of Eu/Eu* for the granitoid rocks with the SCIA used as the standard (as in fig. 7 and 8). As noted earlier, only two rocks show Eu depletion ($Eu/Eu^* < 1$) with respect to the SCIA, while all the others show Eu enrichment. Towell and others (1965) noted a well defined trend of Eu/Eu* in relation to the differentiation index $1/3\ SiO_2 + K_2O - CaO - MgO - FeO$. No such direct trend is noted in a plot of Eu/Eu* versus CaO for the Snake Creek rocks. Instead, the rocks are divided into two groups, indicating two or more dominant processes were probably involved in the formation of these rocks. As

FIG. 10

Eu ANOMALIES IN THE WHOLE ROCKS WITH RESPECT TO THE SCIA



pointed out earlier, the dividing line for the two processes appears to be near 1.5 to 1.8 percent CaO. Were the trend smoother it would be reasonable to expect that plagioclase crystallization in the earlier crystallizing high CaO rocks (Lee and Van Loenen, 1971, p. 32-33) might account for removal of Eu from the liquid phase, leaving the low CaO rocks depleted in Eu. Without a smoother trend, it is concluded that plagioclase crystallization was not the sole factor in producing the Eu/Eu* trends found in the Snake Creek rocks, and other processes will be considered in a later section.

The one whole rock from the Pole Canyon area has a distinctive RE distribution (fig. 8). The LREE are all about the same as the SCIA, while the heavy REE (HREE) show increasing depletion with atomic number. The similarity of the LREE to the SCIA suggests that this rock crystallized from the same parent magma as the Snake Creek rocks.

As pointed out by Lee and Van Loenen (1971), the Pole Canyon intrusive is made up of two phases, a host intrusive and a late pegmatitic and aplitic phase. Haskin and Frey (1966), show that aplites from the Susamyr batholith have RE distributions dominated by the HREE, and assert that the aplites crystallized from hot aqueous solutions containing alkalai metal ions, fluoride, and carbonate which complex the HREE preferentially to the LREE. Mineyev (1963) has demonstrated that these complexes may be broken by precicipitation of the alkalai metals, with subsequent precipitation of the REE. The only important accessory mineral found in the aplites and pegmatites by Lee and Van Loenen (1971) was garnet. Garnet is usually a HREE concentrator in granites (Lyakhovich, 1962), and may contain the HREE in the aplites and pegmatites that are missing from the Pole Canyon host intrusive. These HREE may have concentrated in an aqueous phase as complexes during crystallization of the Pole Canyon intrusive to be precipitated later with garnets in the aplites and pegmatites. Since a RE analysis is not available for an aplite from the Pole Canyon area, it is only speculation to infer a genetic relationship between the host intrusive and the late aplitic and pegmatitic material. The available RE data does point in this direction however. Lee and Van Loenen (1971) state that "The main intrusive along with some associated aplite, crystallized during Middle Jurassic time, about 160 m.y. ago."

In any case, the distinctiveness of the Pole Canyon host intrusive rocks extends also to various RE parameters as shown.

REE in Mineral Separates

The REE are useful not only in looking at their concentrations in a rock, but also in determining their distribution among the constituent minerals of a rock (Schnetzler and Philpotts, 1968 and 1970; Buma and others, 1971).

Schnetzler and Philpotts (1968 and 1970) have shown that it is useful to plot phenocryst-groundmass·partition coefficients for the REE in volcanic rocks. These partition coefficients are simply the ratio of the individual REE in the phenocryst to that determined in the groundmass. These ratios are useful primarily in determining relative affinities of the REE for a liquid or solid phase. The problems that exist in using these coefficients, and factors that may limit their accuracy are discussed by Schnetzler and Philpotts (1968) and consist mostly of equilibrium, zoning, and kinetics arguments. In plutonic rocks the analagous parameter to the partition coefficient is the mineral-whole rock ratio. The use of this ratio is further complicated by the lack of easily definable crystallization sequences in these rocks. Although mineral-whole rock ratios may not net data on liquid-solid partitioning, Buma and others (1971) have found mineral-whole rock REE ratios to be useful in interpreting the origin and differentiation of 5 New England granites. It is on this basis that mineral-whole rock ratios are used in this work.

Feldspars

The plagioclases and potassium feldspars are discussed together in this section because of similarities in their RE distributions. Six plagioclases and four potassium feldspars were analyzed for the REE (Table 1).

In contrast to the whole rocks, the plagioclases show similar RE distributions when plotted with the SCIA as a standard. The plagioclases all show LREE > HREE with a large positive Eu anomaly. The La/Yb ratios of the plagioclases fall within a narrow range (La/Yb = 18 to 34) while the whole rocks show ratios ranging from 10 to 86 (fig. 19).

What would cause the plagioclases to show such similar RE distributions all across the outcrop while the whole rocks show large changes? It is of interest to note that the mineral-whole rock ratios for the REE in the Snake Creek plagioclases fall near the lower end of the range of partition coefficients reported in the literature for rocks ranging in composition from basalt to dacite (Schnetzler and Philpotts, 1968 and 1970; Dudas and others, 1971; Nagasawa and Schnetzler, 1971). Plagioclases from 2 granites (Towell and others, 1965; Buma and others, 1971) also show mineral-whole rock ratios greater than the Snake Creek plagioclases. This data suggests that the plagioclases crystallized from a liquid phase with lower RE content than what is observed in the whole rocks. The La/Yb data indicates that the liquid from which the plagioclases crystallized had roughly constant La/Yb, much different from the whole rocks.

Examination of the mineral-whole rock ratios for the plagioclases (fig. 11), also gives indications of what might have caused the low plagioclase RE contents and small range

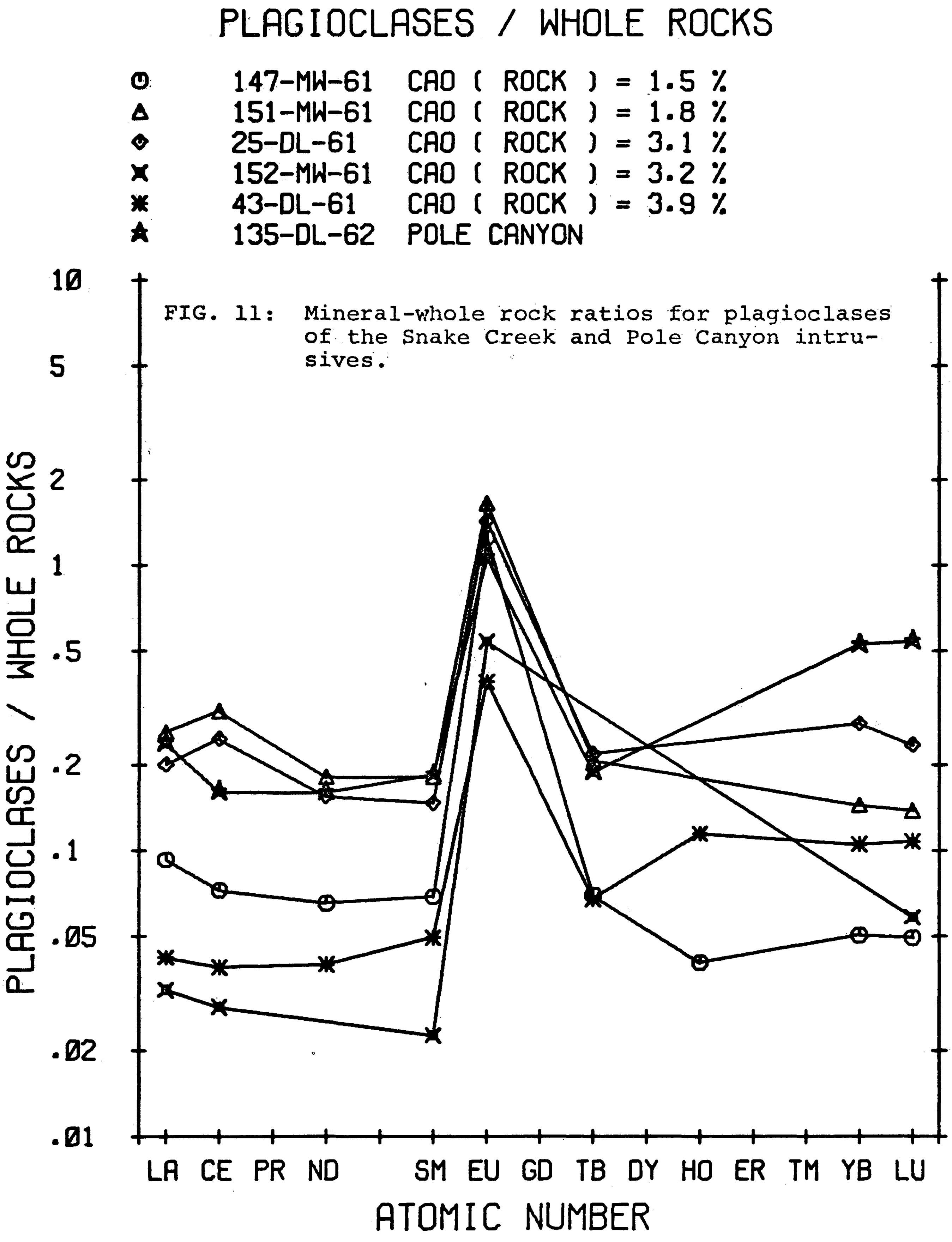


FIG. 11: Mineral-whole rock ratios for plagioclases of the Snake Creek and Pole Canyon intrusives.

of fractionation. The fractionation trends for the mineral-whole rock ratios of fig. 11 are summarized in Table 3. Since the plagioclases all show the same trends when ratioed with the same standard, the trends in Table 3 are due primarily to the RE distribution in the whole rocks.

TABLE 3

Fractionation Trends in Plagioclases

Sample Number	% CaO in rock	Fractionation Trend
147-MW-61	1.5	LREE > HREE
151-MW-61	1.8	LREE ≃ HREE
25-DL-61	3.1	LREE ≲ HREE
152-MW-61	3.2	LREE < HREE
43-DL-61	3.9	LREE < HREE
135-DL-62	.98 (Pole Canyon)	LREE < HREE

Few plagioclase REE partition coefficients with LREE < HREE are reported in the literature (Schnetzler and Philpotts, 1968 and 1970; Dudas and others, 1971; Nagasawa and Schnetzler, 1971), yet the plagioclases from the high CaO rocks of the Snake Creek intrusive and from the Pole Canyon intrusive all show this trend. It is believed that crystallization of accessory minerals prior to plagioclase crystallization could alter the RE distribution in the liquid phase to cause the fractionation trends seen. Accessory mineral crystallization could also account for the relatively low mineral-whole rock ratios. It is important to note in Table 3 that the trend changes at about CaO = 1.8 percent. Lee and Van Loenen (1971) note that at about this range of CaO content a change in accessory mineral suites is seen (fig. 4). The relation of accessory mineral crystallization to RE contents in the whole rocks and major minerals is discussed extensively in a later section.

The plagioclases then, are very similar in RE distribution, and examination of the plagioclases with respect to the whole rocks suggests that extensive accessory mineral crystallization caused changes in RE content and RE distribution in the magma prior to plagioclase crystallization.

The potassium feldspars (fig. 12) from the Snake Creek and Pole Canyon rocks are very low in RE content, containing concentrations of the REE, except Eu, that are lower than the plagioclases by factors of 2-10. The concentrations were so low that no HREE were detected for 3 of the 4 samples analyzed. The fourth sample, from rock 25-DL-61, deviates widely from the other distributions. Lee (1972) noted that this rock had much greater quantities of accessory minerals than would be expected from its CaO content, and also contained a distinctive apatite. Lee and Bastron (1967) point out that this rock was taken near a large xenolith and

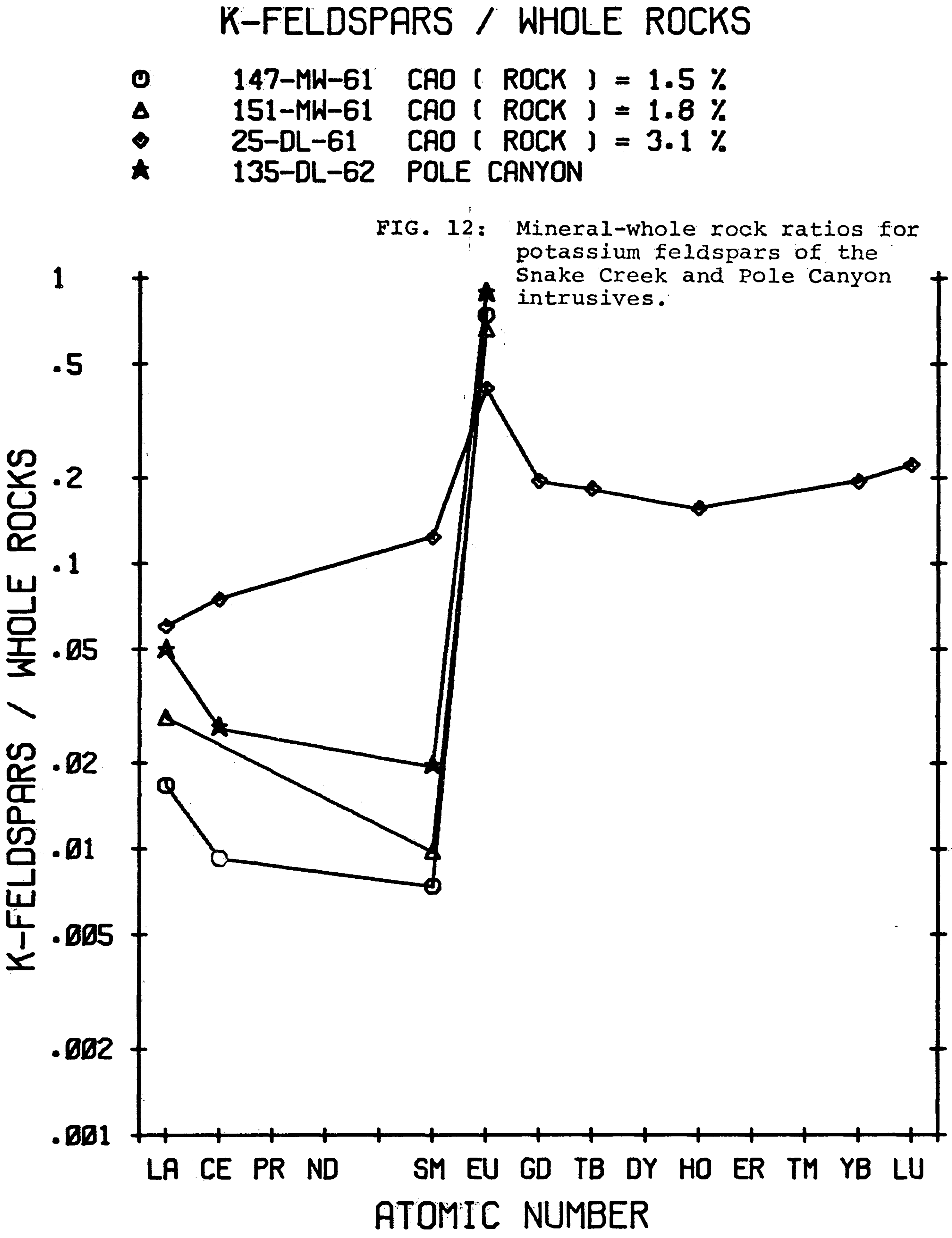


FIG. 12: Mineral-whole rock ratios for potassium feldspars of the Snake Creek and Pole Canyon intrusives.

suggest that RE fractionation and also RE content respond to whole rock composition over small distances. Whether the potassium feldspar from this rock is contaminated (possibly due to the large accessory mineral content) or represents an actual deviation due to proximity to a xenolith is impossible to say.

Since HREE data is available for only one potassium feldspar, no discussion of RE fractionation is possible.

Eu Anomaly

Anomalous behavior of Eu is evident in figs. 11 and 12. This behavior has been explained by reduction of Eu^{+3} to Eu^{+2} which is similar in size to Sr^{+2}, a common constituent of feldspars (Towell and others, 1965). Nagasawa (1971) has shown that Sr and Eu have similar partition coefficients between coexisting potassium feldspar and plagioclase and because of this similarity it may be reasoned that most of the Eu was in the +2 state during crystallization, causing anomalous behavior with respect to the other REE. On the other hand, Schnetzler and Philpotts (1970) show that Eu anomaly increases with increasing alkalai content of the feldspar, and argue that crystal chemical control of Eu in the feldspars is a dominant factor over such things as temperature, pressure, and redox conditions.

Sr data is available on only one set of coexisting potassium feldspar and plagioclase, from sample 25-DL-61, earlier discussed as possibly being contaminated with accessory minerals. An accessory mineral contamination is not as serious for this calculation as for a calculation of Eu/Eu*, since the accessory minerals show sizeable Eu depletions with respect to the other REE. Calculation of Eu and Sr partition coefficients between these two feldspars gives the same answer: 0.24. According to Nagasawa (1971) this indicates that most of the Eu was in the +2 state, and behaved in a manner very similar to Sr^{+2}. Because of the suspected contamination though, this data should be used with caution.

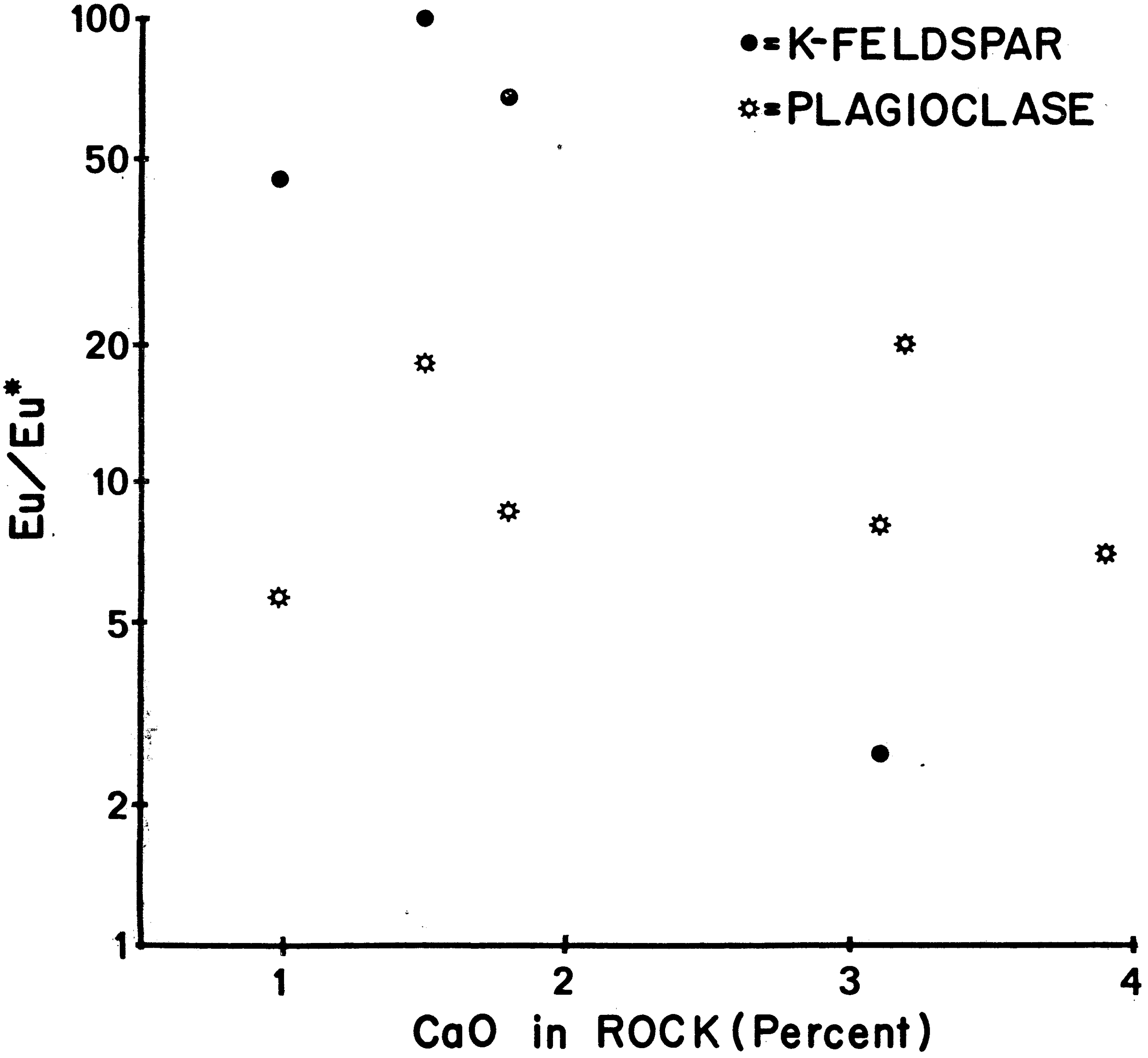
The Eu anomalies (Eu/Eu*) are plotted for the 10 feldspars analyzed in this study in fig. 13. The Eu anomalies are calculated using the respective whole rocks as the standard distributions as in fig. 11 and 12, and are plotted versus CaO rather than An content of the feldspar, since An content is only available for the plagioclases.

As seen in fig. 13, the Eu anomalies in the feldspars do not respond to whole rock chemistry in a direct way.

Plotting the Eu/Eu* of the plagioclases versus An as done by Schnetzler and Philpotts (1970) and expanded by Dudas and others (1971) shows that the 2 plagioclases with the largest Eu/Eu* fit their trend, but the other 4 are too low. Over the small range of An content (18-28 percent) of the plagioclases studied in this work, crystal chemical control of Eu must not have been a dominant process.

FIG. 13

Eu ANOMALIES IN FELDSPARS WITH RESPECT TO THEIR WHOLE ROCKS



The only trend noted in the Eu anomaly is the greatly higher Eu anomaly in the potassium feldspars as compared to coexisting plagioclase, in three cases by almost an order of magnitude. The potassium feldspar from 25-DL-61 shows a very low Eu/Eu*, which could be caused by accessory mineral contamination, or other factors as discussed earlier. It appears that the greatly increased Eu/Eu* in the potassium feldspars is caused more by decreases in concentrations of RE adjacent to Eu than by increases in Eu itself relative to the plagioclases. This observation is consistent with the analytical data on the feldspars (Appendix A) which shows that Eu concentrations differ between the feldspars by factors of 1.2 to 2.6 while Sm concentrations differ by 9.3 to 18 (excluding the feldspars from 25-DL-61). Mason (1966, p. 88) states that "as a general rule, little or no atomic substitution takes place when the difference in charge on the ions is greater than one, even when size is appropriate." REE (except Eu) trying to substitute into K^+ sites may have a difficult time, while substituting for Ca^{+2} may be much easier, accounting for the differences in the REE except Eu. If Eu is in the +2 state it should be able to substitute in K or Ca sites.

Biotites

Lee and Van Loenen (1970) have studied the biotites from the Snake Creek and Pole Canyon intrusives. Their results indicate different magmatic affinities for the Snake Creek and Pole Canyon rocks. In the Snake Creek area, the trends in whole rock chemistry are reflected in compositional trends of the biotite.

Most of the biotites analyzed for REE show CaO contents less than .1 percent, (Lee and Van Loenen, 1970) attesting to their relative freedom from Ca-bearing accessory minerals. Since most of the accessory minerals found in these hybrid rocks are associated with the biotite, it is essential that the biotites are highly purified. Even with careful purification processes, including ultrasonic cleaning (Lee and Van Loenen, 1970) the one biotite sample chosen for a duplicate analysis (152-MW-61) showed possible contamination by RE accessory minerals. As little as one part per 10,000 of allanite contamination in this biotite could cause the LREE to appear 10-25 percent higher than they actually are. The contamination problem is magnified by the fact that even if the values determined are taken as upper limits of REE content, the biotites show lower concentrations than the potassium feldspars, which are much lower than the plagioclases in REE. The concentration of REE determined in the biotites are generally less than 1 ppm (excluding 152-MW-61 biotite), while REE concentrations in allanite may be as high as 50,000 ppm, and in monazite 100,000 ppm. Because of this contamination problem, the biotite data has been interpreted with caution.

The mineral-whole rock ratios for the biotites are plotted in fig. 14. The ratios show the characteristic pattern (Schnetzler and Philpotts, 1970; Buma and others, 1971) favoring the HREE. These biotites show roughly the same ratios as the partition coefficients of the biotite reported by Schnetzler and Philpotts (1970) from a dacite, but are much lower than ratios reported by Buma and others (1971) for a biotite from a granite. These low mineral-whole rock ratios may be due to accessory mineral crystallization prior to biotite crystallization as discussed for the plagioclases, or because these mineral separates are relatively clean with respect to accessory minerals.

The La/Yb ratios of the biotites vary widely, however (fig. 19) and follow no trend. This fact suggests that these biotites may still be contaminated by minute quantities of accessory minerals, which alter the La/Yb ratio and the absolute RE content seen in the biotites.

The behavior of Eu in the biotites is also erratic, with apparent Eu depletions on some samples, while others show normal Eu.

Since the RE data on the biotites is erratic and contamination is suspected, no conclusions about the genesis of the granitoid rocks can be drawn.

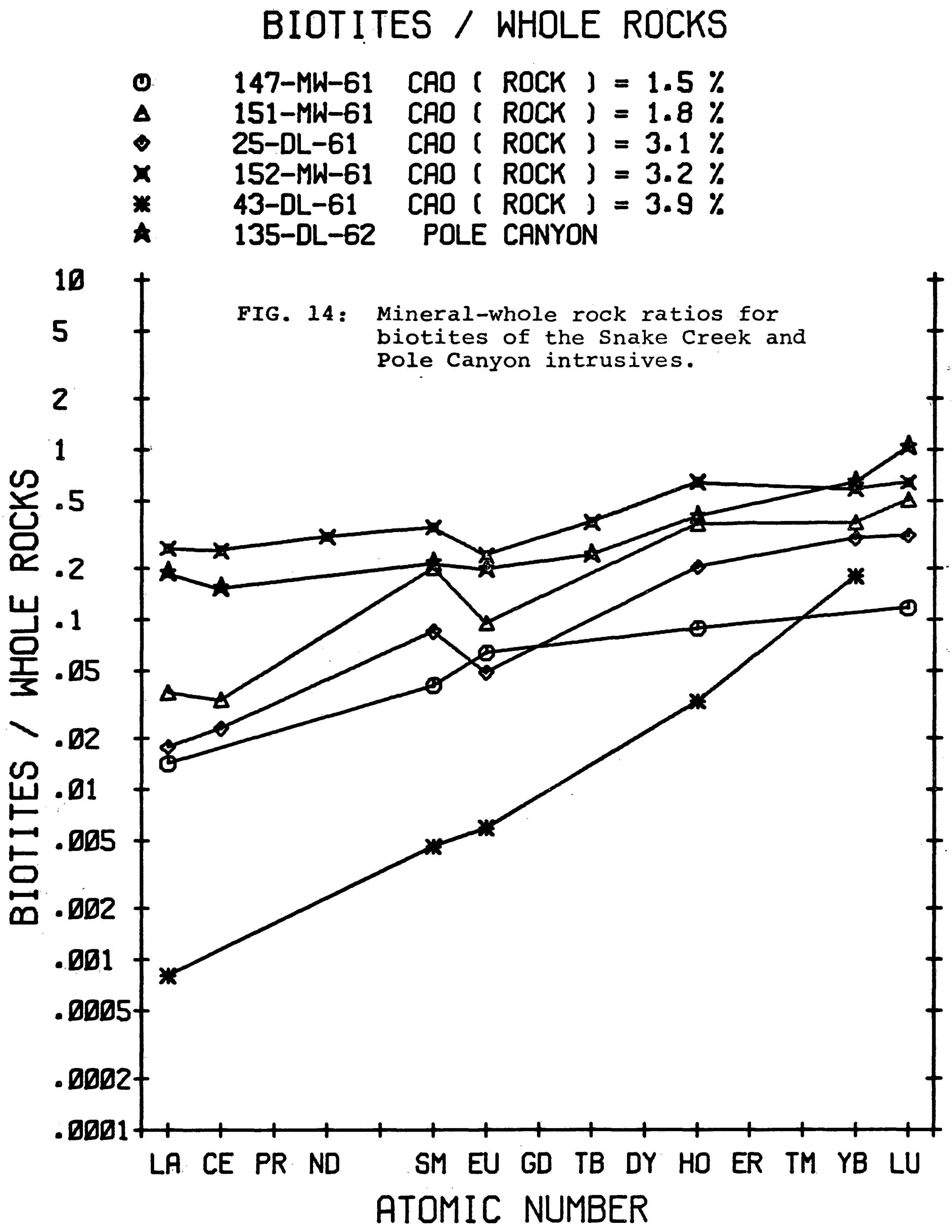


FIG. 14: Mineral-whole rock ratios for biotites of the Snake Creek and Pole Canyon intrusives.

Coexisting Biotite and Muscovite

As discussed earlier, the rocks of the Pole Canyon intrusive are distinctive in hand specimen largely because of the presence of large crystals of muscovite. Lee and Van Loenen (1970) describe the relation of biotite and muscovite in these reocks:

> "Typically, phenocrysts of muscovite as large as 2 cm across contain small biotite euhedra that are easily visible with a hand lens. It is not uncommon for as many as 20 biotite crystals to be included within a single large grain of muscovite. Petrographically the muscovite and biotite, both of which are very fresh looking, are seen to be associated and often intergrown. They appear to have formed in equilibrium. The muscovite contains no dark inclusions, nor does it present any other evidence that it is secondary after biotite."

REE were analyzed on 135-DL-62 Biotite and Muscovite from the Pole Canyon intrusive and the mineral-whole rock ratios are plotted in fig. 15. Before discussing these ratios though, a few words about the biotite contamination problems discussed earlier are in order. Two factors indicate that the RE distributions presented here are characteristic of the biotite and muscovite, and not caused by accessory minerals.

1. Fewer accessory minerals are present in the Pole Canyon intrusive, and as noted above the muscovite contained no fine grained inclusions.

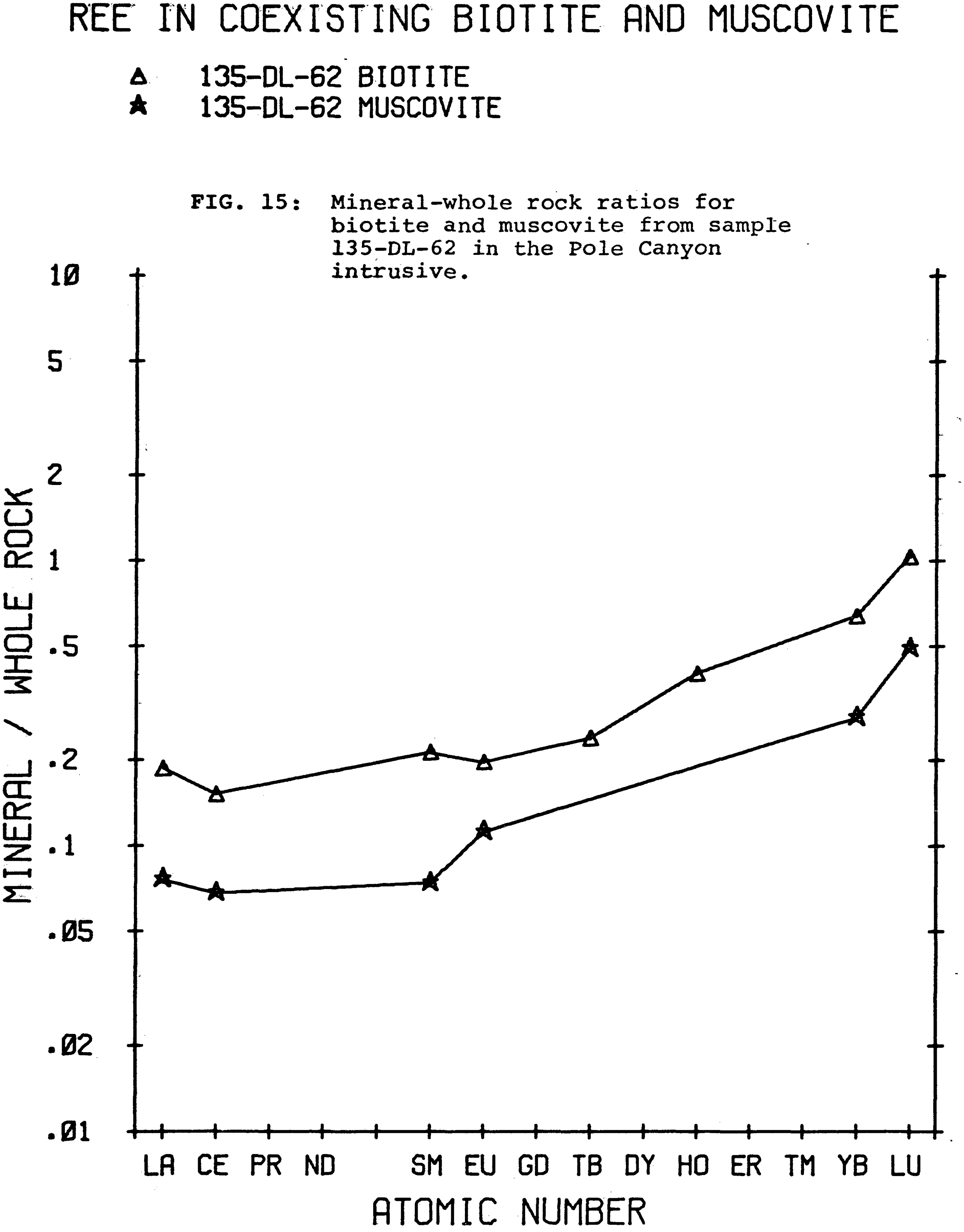


FIG. 15: Mineral-whole rock ratios for biotite and muscovite from sample 135-DL-62 in the Pole Canyon intrusive.

2. The striking parallelism of the RE distributions indicates that the REE are responding to a distinctive type of crystal structure, not accessory mineral contamination. This parallelism would be highly fortuitous were it the result of accessory mineral contamination, especially considering the different specific gravities for the two minerals (biotite - 3.03 to 3.07 (Lee and Van Loenen, 1970); and muscovite - 2.87 (Lee, 1972)).

Both REE distributions show the HREE favored over the light REE, and as noted above the distributions are remarkably parallel. This parallelism is interpreted as being a response to the similar sheet structure and available sites in these two minerals. The muscovite RE contents (except Eu) are about one half to one third of those found in the biotite. The muscovite shows a larger content of Eu than would be expected. This difference in Eu and other REE between the two micas may be interpreted in the same manner as between the feldspars discussed earlier. The trivalent REE would find it more difficult substituting for monovalent potassium in muscovite, than for divalent Fe or Mg or trivalent Fe in biotite, while divalent Eu could substitute with relative ease for monovalent K or divalent Fe or Mg or trivalent Fe.

Accessory Minerals

The accessory mineralogy of the Snake Creek rocks is summarized in fig. 4. Lee and coworkers have made further studies of the following accessory minerals in these rocks: epidote, (Lee and others, 1971); sphene, (Lee and others, 1969); allanite and monazite, (Lee and Bastron, 1962 and 1967); zircon (Lee and others, 1968), and apatite (Lee and others, 1973). The data in this section is taken from these papers, and only a brief look at the RE data in these papers is contained here.

Figure 16 shows the mineral-whole rock ratios for a characteristic sample of each group of accessory minerals on which extensive RE data is available. Limited RE data is also available on the epidotes and zircons. The allanites and monazites show similar distributions, both with the LREE greatly predominant over the HREE. The apatites and sphenes also both show similar RE patterns, with depleted LREE and a maxima in the range Sm-Ho. Although complete RE data is not available on the zircons and garnets from these rocks, it is expected that their RE distributions would be dominated by the HREE (Nagasawa, 1970; Lyakhovich, 1962; Schnetzler and Philpotts, 1970; Buma and others, 1971). It should be noted that all of the mineral-whole rock ratios for the accessory minerals are greater than one, in contrast to the major minerals where all the mineral-whole rock ratios (except for Eu on some of the plagioclases) are less than one. This indicates that the accessory minerals are RE concentrators, while the major minerals are not.

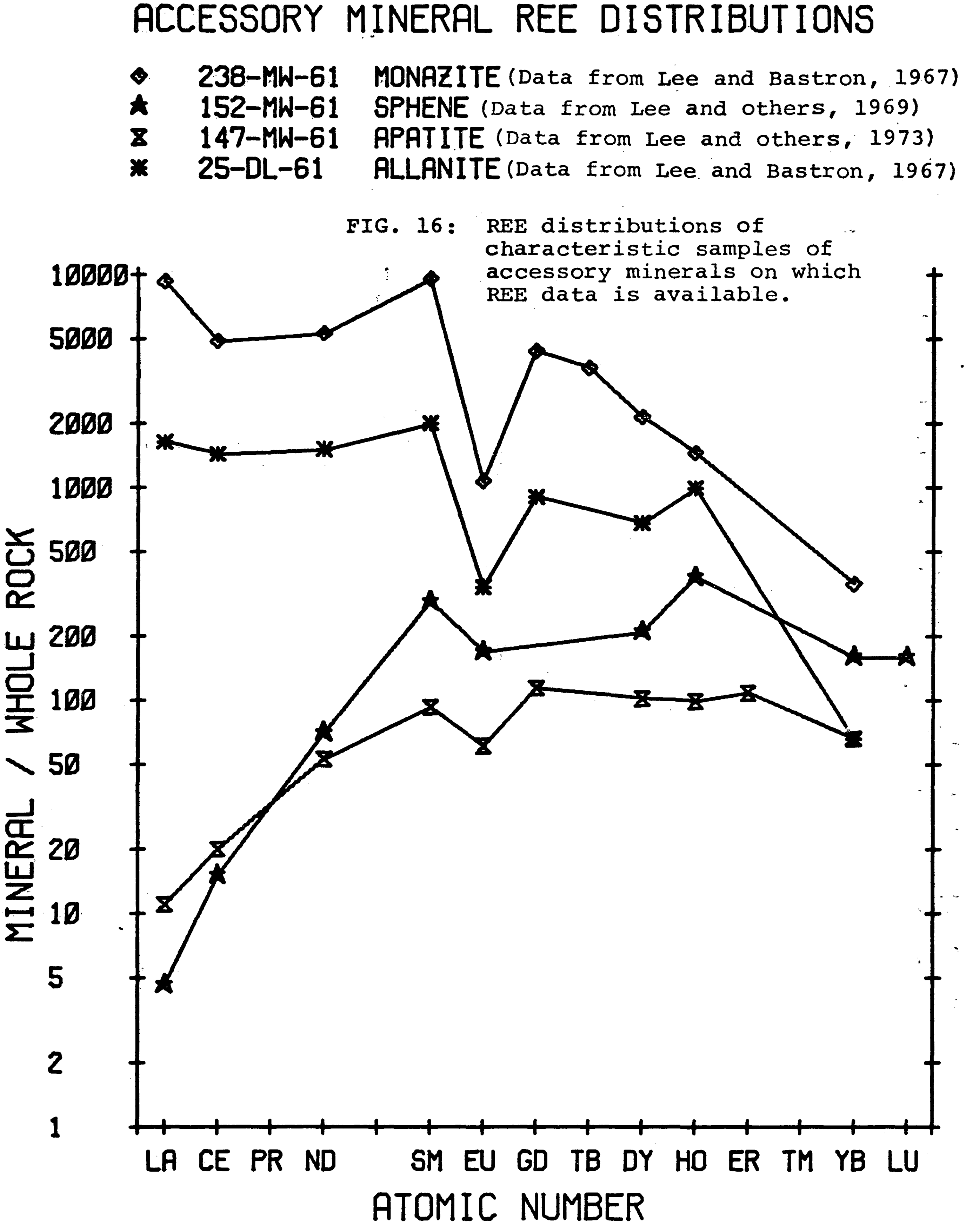


FIG. 16: REE distributions of characteristic samples of accessory minerals on which REE data is available.

The accessory minerals from the 8 rocks analyzed show regular trends of La/Yb increasing with whole rock CaO content (fig. 19). The allanite and monazite ratios, though, are by far the highest, ranging from 100 to more than 1000, while the apatites and sphenes are in the range 1-10. Zircon and garnet La/Yb ratios are expected to be less than 1. These trends are in accord with a similar trend for the whole rocks, and this type of trend is discussed in most of the papers mentioned above.

All the accessory minerals show Eu depletions. Since plagioclase fractionation data for this work and petrograhpic evidence from Lee and Van Loenen (1971) indicate that the accessory minerals in these rocks probably crystallized before the plagioclase, these Eu depletions are interpreted as being caused by divalent Eu. This conclusion is consistent with that reached by Nagasawa (1970) based on data from zircons and apatites from dacites and granites.

The role of accessory minerals in the production of the RE distributions found in these rocks is discussed in the next two sections.

REE Balance for the Whole Rocks

This section will answer the question of where the REE are contained in these rocks, and try to explain the distributions. Wide variation exists: some samples reported in the literature contain most of the REE in the major minerals, while others have most of the REE in the accessory minerals. Buma and others (1971) show most of the REE in the major minerals of one granite (Peabody), while most of the REE are in the accessory minerals of two other granites (Quincy and Narragansett Pier). Gavrilova and Turanskaya (1958) concluded that about 60 percent of the elements La-Sm in a monazite granite are associated with the monazite. Towell and others (1965) found that most of the REE in the San Marcos gabbro were contained in the major minerals, while in the Rubidoux Mt. leucogranite more than half of the REE were associated with the accessory minerals. Balashov and others (1970) show that the rock forming minerals of a gabbro-diorite intrusion contain 70 to 98 percent of the REE. Haskin and others (1966) conclude that on the basis of data available at that time, "The amount of REE incorporated in or inseparably associated with the rock forming minerals is a significant fraction of, and may include the bulk of, the REE in the rock."

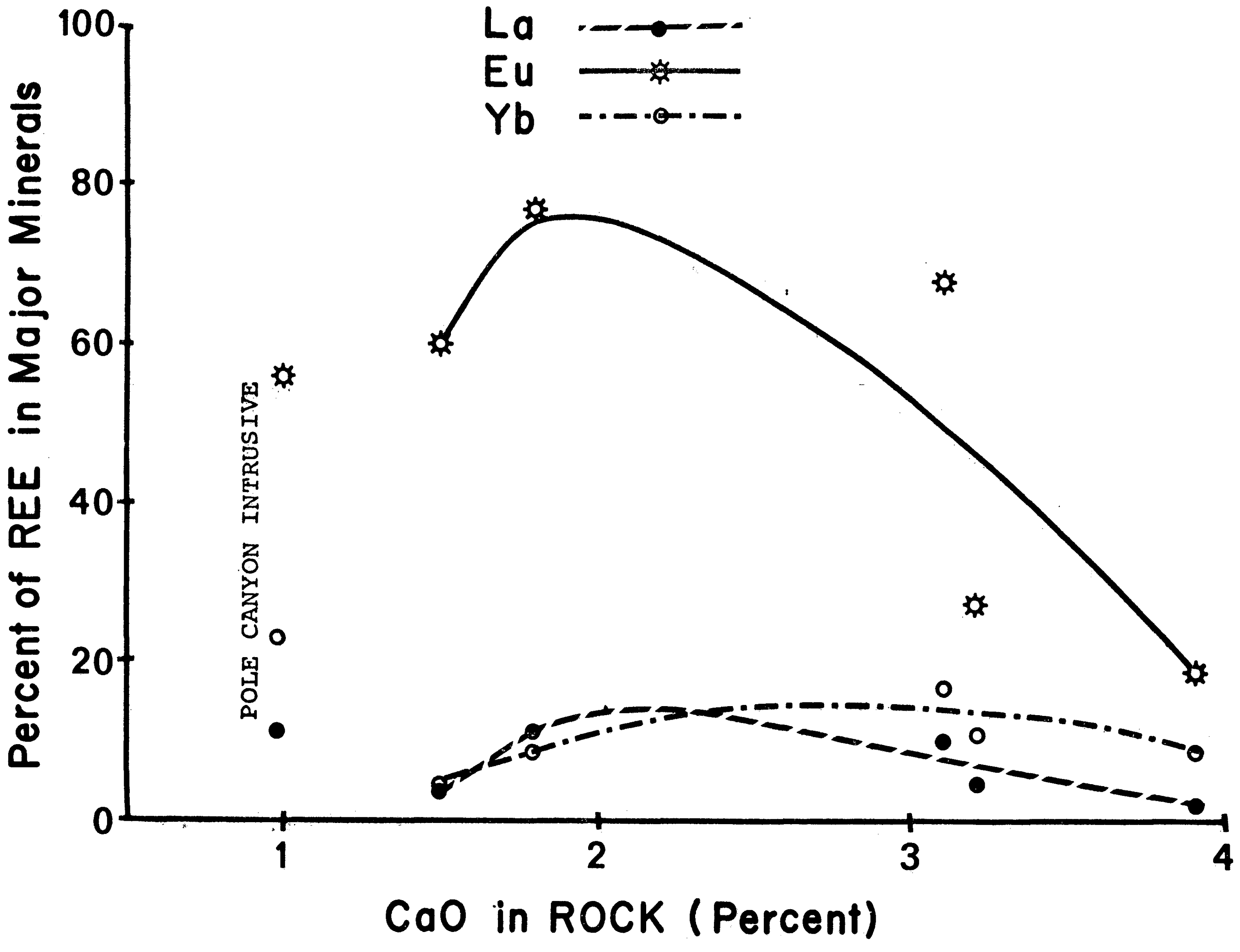
The data used in this section are primarily from the whole rocks and major minerals analyzed during this study, coupled with modal abundances for the major minerals from Lee and Van Loenen (1971). Although REE data are available on many of the accessory minerals, the only available modal abundance data on these minerals are from weights recovered during mineral separation work, and are probably not as accurate as the major mineral modal abundance data, which were determined on calibrated x-ray diffraction patterns. Also, since the accessory minerals are REE concentrators, even small uncertainties in their modal abundances could result in large uncertanties in the absolute amounts of REE with respect to amounts in the whole rock.

Distribution of REE Between Major and Accessory Minerals

Figure 17 shows the weight percent of La, Eu, and Yb in the major minerals for the Snake Creek and Pole Canyon intrusives. The remainder of the REE is presumed to be in the accessory minerals. The La and Yb content are low in the major minerals, generally less than 20 percent. This is probably due to concentration of La in allanite in the high CaO rocks, and in monazite in the low CaO rocks, while Yb is taken up by zircon and garnet in the high and low CaO rocks, respectively. The percent Yb in the major minerals becomes increasingly greater than the percent La as the CaO content in the rocks increases. The rise of Yb is caused by an increase in modal abundance of biotite which contains the HREE preferentially to the LREE. The content of Eu in the major minerals is much higher than La or Yb, due to enrichment of Eu in the feldspars and depletion in the accessory minerals. All three REE show smaller percentages in both the low and high CaO rocks, with

FIG. 17

DISTRIBUTION OF REE BETWEEN MAJOR AND ACCESSORY MINERALS



a broad maximum in the intermediate range. Lanthanum and Eu both show greatest percent in the major minerals in the CaO range 1.5-2.0 percent. The two whole rocks from this range of CaO also show the smallest changes from the SCIA (parent magma) REE distribution (fig. 9). The combination of these two observations indicates that assimilation of either limestone or quartzite contributed to concentration of the REE in accessory minerals. Since Eu shows the largest variation in percent in the major minerals of the three REE shown, and because even in the high CaO rocks, where plagioclase makes up about half the rock only about 20 percent of the Eu is contained in the major minerals, Eu seems to be an especially good indicator of REE uptake by accessory minerals.

The Pole Canyon intrusive shows more La and Yb in the major minerals than the Snake Creek intrusive, probably due to less accessory minerals in this rock. The major mineral Eu content is in general agreement with this trend.

In summary, the REE except Eu are contained between 80 to 98 percent in the accessory minerals. Eu varies widely, but is higher than the other REE in the major minerals due to enrichment in the feldspars. La and Eu show the highest percent in the major minerals least differentiated from the parent magma, indicating that assimilation encouraged uptake of the REE in accessory minerals.

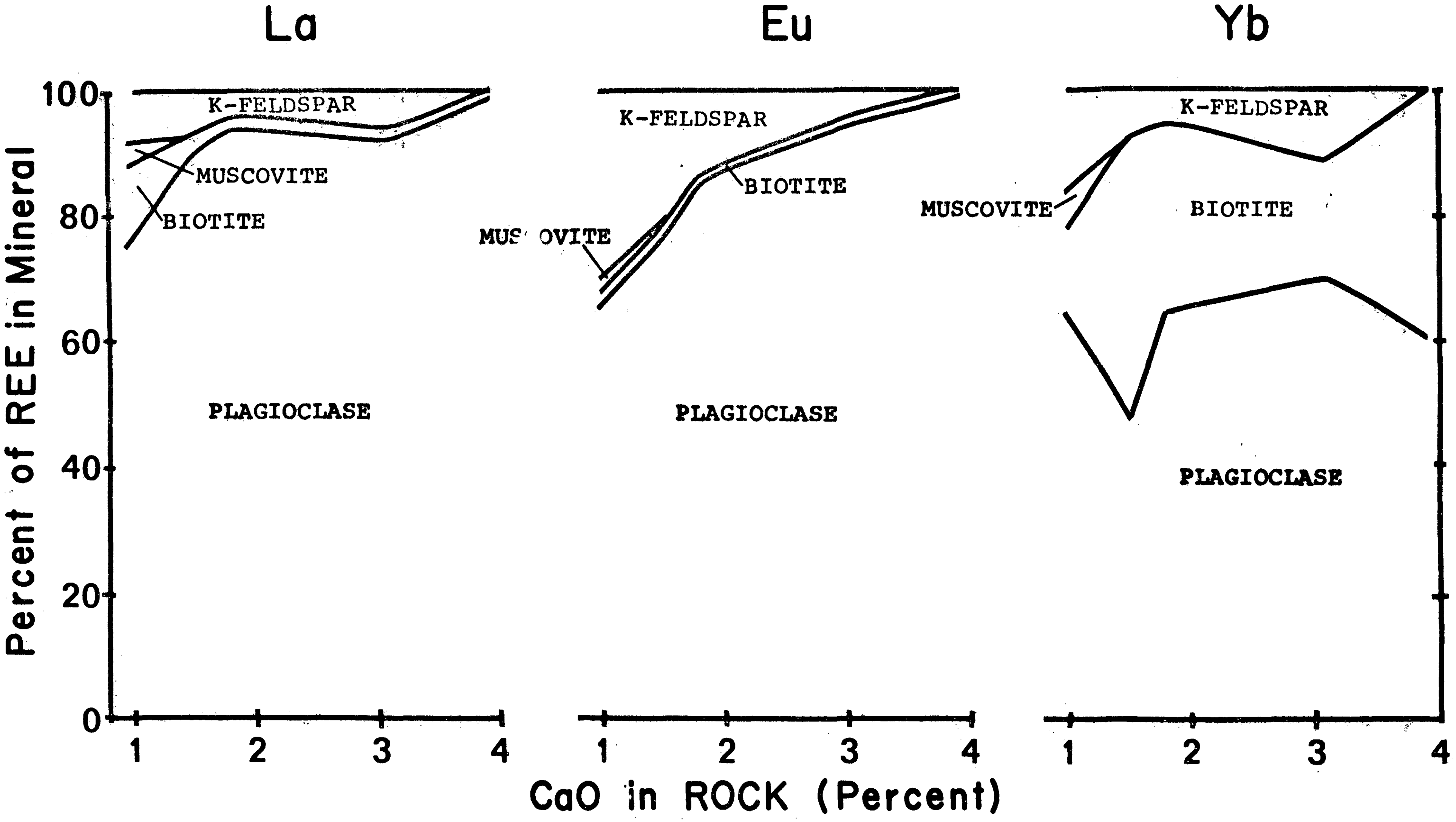
Distribution of REE Among Major Minerals

Figure 18 shows how La, Eu, and Yb are distributed among the major minerals of the rocks. The REE content in the major minerals has been normalized to 100 percent for easier comparison. The bulk of the major mineral REE are contained in the plagioclase, and the percentage increases with CaO content for both La and Eu. In the 3.9 percent CaO rock greater than 95 percent of the major mineral La and Eu are contained in the plagioclase. Very little K-feldspar is present in this high CaO rock. Biotite and muscovite account for very minor amounts of La and Eu except in the Pole Canyon intrusive. Biotite contains from 20 to 40 percent of the Yb in the Snake Creek major minerals. No trend of Yb in biotite is noted with CaO, which may be related to contamination problems with the biotites. K-feldspar contains more Eu than would be expected from the amount of La and Yb in this mineral, indicating again that K-feldspar competes more strongly with plagioclase for Eu than for the other REE.

Earlier data indicated that the REE content in the major minerals did not vary in a direct way with CaO. Thus, the change in percentage of REE in each major mineral with CaO appears to be a result of changes in the modal abundance (fig. 3) of the major minerals.

REE DISTRIBUTION AMONG THE MAJOR MINERALS

FIG. 18: REE in the major minerals have been normalized to 100 percent and plotted to show how the REE in the major minerals are distributed among plagioclase, biotite, K-feldspar, and muscovite. Data on sample 152-MW-61 has been excluded because of contaminated biotite.



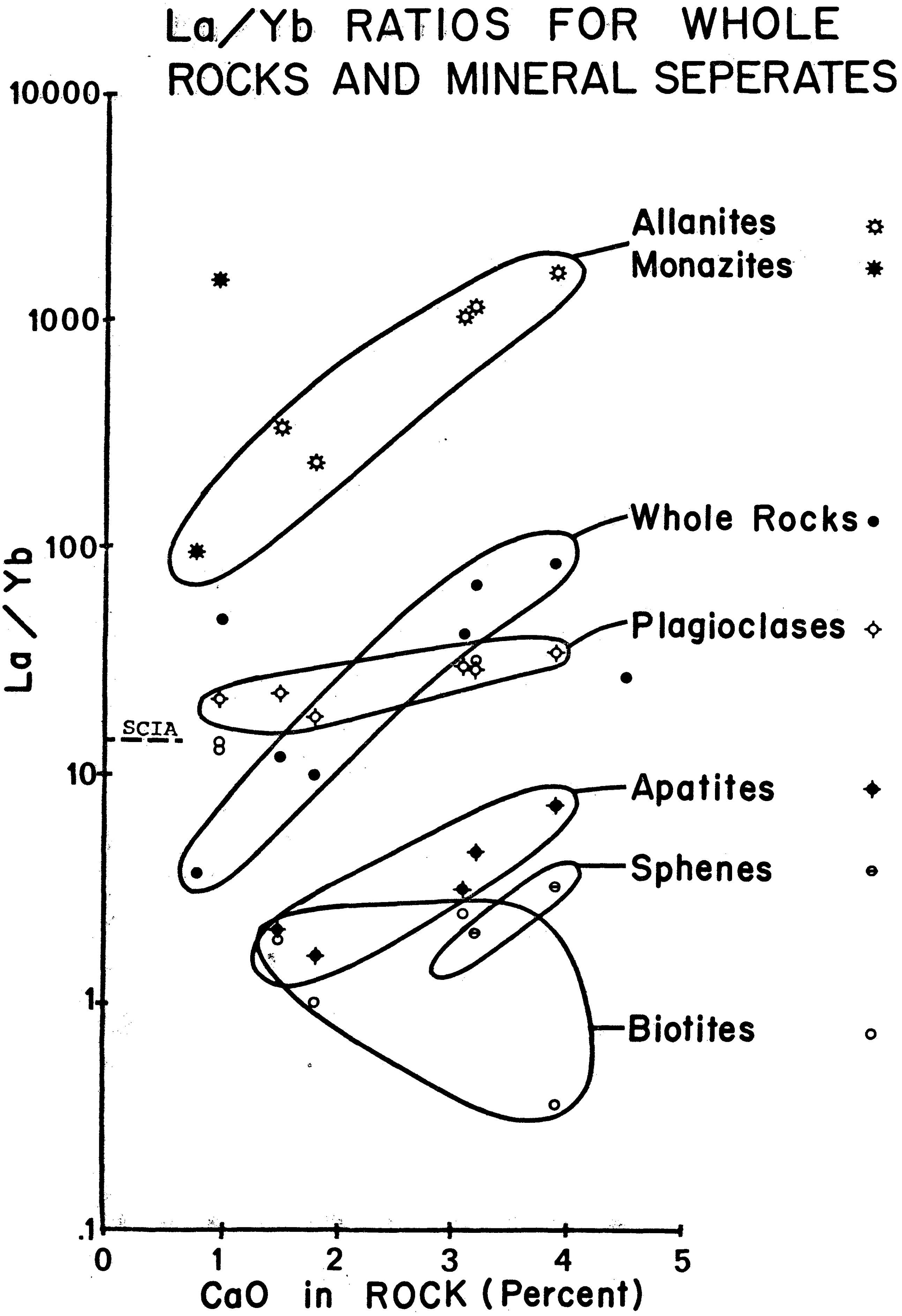
Trends in La/Yb

The La/Yb ratios for the whole rocks and mineral separates are plotted versus CaO content in the rock in fig. 19. The ratios are plotted on a 5 cycle log scale so that all the minerals may be compared to each other.

The parallelism of the whole rock and all the accessory mineral trends is striking. Rare earth fractionation in the whole rocks is accounted for by fractionation of the REE in the accessory minerals. The major minerals, however, do not share this parallelism. The plagioclases show a well defined trend with CaO, but the trend is not that of the whole rocks. It was suggested earlier that the plagioclase trend was due to crystallization of accessory minerals prior to plagioclase crystallization. This would require accessory minerals with La/Yb less than the whole rocks on the low CaO end of the intrusive, and accessories with La/Yb greater than the whole rocks on the high CaO end. The low La/Yb accessories on the low CaO end would be apatite and garnet. REE data on the garnets from these rocks are not available but data from Lyakhovich (1962) indicates La/Yb ratios of about .1 for garnets. The high La/Yb accessory on the high CaO end would be allanite. These La/Yb ratios in the accessory minerals lend credence to the explanation of the plagioclase La/Yb trend.

The whole rocks and mineral separates from the Pole Canyon intrusive (135-DL-62, CaO = 0.98 percent) do not generally fit

FIG. 19


La/Yb RATIOS FOR WHOLE ROCKS AND MINERAL SEPERATES
10000
1000
100
10
1
.1
La / Yb
SCIA
0
1
2
3
4
5
CaO in ROCK (Percent)
Allanites ✡
Monazites ✱
Whole Rocks ●
Plagioclases ✧
Apatites ✦
Sphenes ⊖
Biotites ○

the trends for the Snake Creek rocks or minerals. Their La/Yb ratios are generally higher than would be expected for their CaO content. While the whole rock ratio is probably high due to removal of HREE in an aqueous phase, as discussed earlier, the high La/Yb ratios in the major minerals are probably due to crystallization of smaller amounts of LREE concentrating accessory minerals, allowing the LREE to be incorporated in the major minerals.

Summary of REE Balance for the Whole Rocks

To summarize this section plots of REE distributions of all the minerals from 2 whole rocks are plotted in figs. 20 and 21. The REE concentrations in the minerals are all adjusted according to their modal abundances, so that the ordinate in both figures gives the fraction of the whole rock content which is contributed by each mineral for each REE. The two rocks chosen were 147-MW-61 (CaO = 1.5 percent) and 43-DL-61 (CaO = 3.9 percent), since these two rocks represent the two extremes of CaO content on which major mineral REE data is available.

The REE data on these two rocks is not complete, but will give a good idea of REE distribution in the rocks. The low CaO rock (147-MW-61) contains a trace of monazite and sphene and about .013 percent zircon (Lee, 1972) and probably some ilmenite, magnetite and epidote in addition to the minerals shown in fig. 20. The high CaO rock (43-DL-61) contains .044

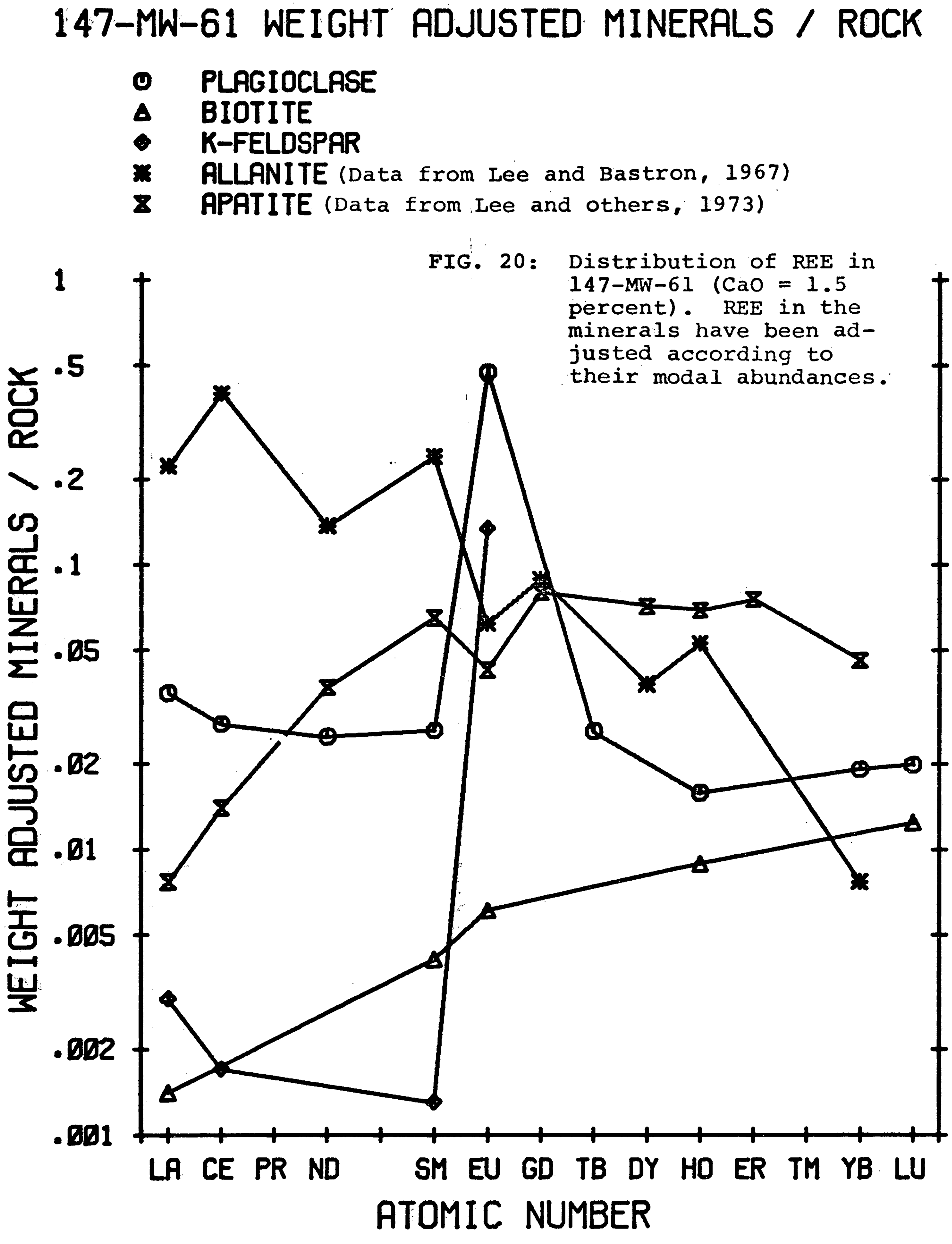


FIG. 20: Distribution of REE in 147-MW-61 (CaO = 1.5 percent). REE in the minerals have been adjusted according to their modal abundances.

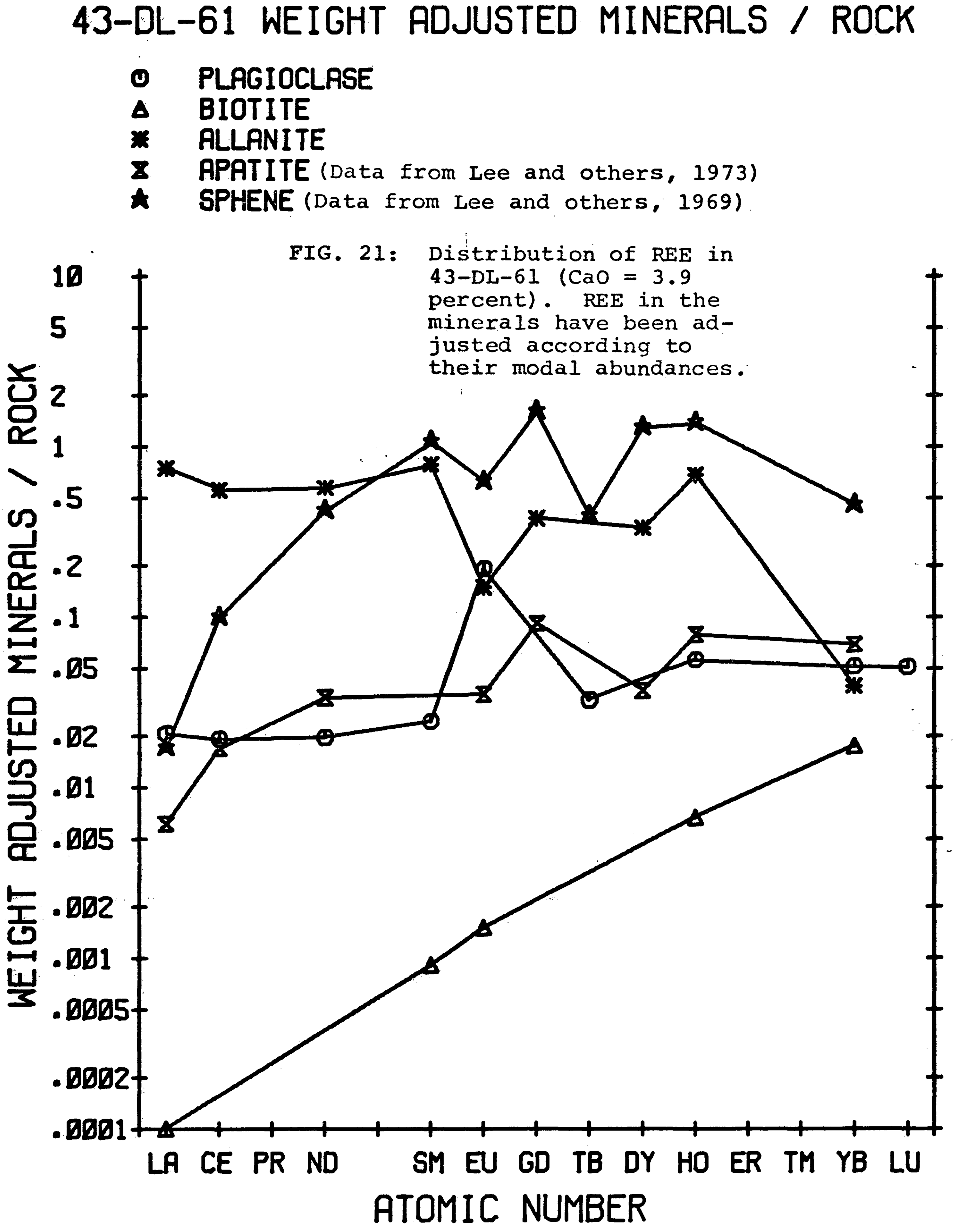


FIG. 21: Distribution of REE in 43-DL-61 (CaO = 3.9 percent). REE in the minerals have been adjusted according to their modal abundances.

percent zircon (Lee, 1972) and some magnetite and epidote in addition to the minerals in fig. 21.

Figure 20 shows that the LREE are primarily contained in the allanite, and probably also in the monazite, Eu is concentrated in the feldspars, while the HREE are predominantly contained in the apatite, with zircon also expected to contain a large portion of the HREE.

Figure 21 shows that there are more of some of the REE in sphene than in the whole rock (value on ordinate >1). A modal abundance that is too large or REE concentrations that are too high could cause this phenomena. The REE values on the sphenes were determined by a semiquantitative spectrographic technique (Lee and others, 1969). The accessory minerals completely dominate this plot. Again the LREE are primarily in the allanite, but here the HREE are concentrated in the sphene. Zircon would also probably concentrate the HREE in this rock. Most of the Eu in the rock is also contained in the sphene, with only about 20 percent in the plagioclase, which comprises about half the rock.

These two plots again illustrate the increased dominance of the REE distribution in these rocks by the accessory minerals as CaO content becomes large, that is, in the rocks that show the strongest effects of assimilation. The dominance of plagioclase over the major mineral REE is also evident.

Causes for the REE Distributions

Before discussing processes active in the production of the REE distributions presented in this report, a few assumptions and factors entering into this discussion should be clarified. The concern here is not to discuss the production of the REE distribution in the parent magma, but rather to examine the reasons for the changes in the REE distributions that are presently seen in the intrusive. The following discussion will assume that the REE distribution of the parent magma was roughly that of the SCIA, as discussed earlier.

Data from Lee and Van Loenen (1971) indicate that the high CaO rocks crystallized before the low CaO rocks, and a variation diagram for the major oxides from the Snake Creek intrusive (fig. 2) plots very near Daly's average andesite-dacite-rhyolite, indicating that for the major elements, assimilation has produced a rock series very similar to the normal differentiation series.

Is the REE data presented here in accordance with a differentiation model? Zielinski and Frey (1970) and Haskin and Haskin (1968) have studied REE distributions in rocks from Gough Island and the Skaergaard intrusion, respectively. Both of these suites of rocks are believed to have formed through fractional crystallization. In the Gough Island rocks, the REE increase in abundance in the sequence from alkalai-olivine basalt to trachyte, and the LREE become increasingly more abundant than the HREE. Europium is strongly depleted in the trachytes. In the Skaergaard intrusion, Haskin and Haskin (1968) conclude that, "The Skaergaard successive liquids become steadily enriched in the REE during solidification of the layered series." They also noted that the fractional crystallization of the magma did not cause any strong trend of changes in the REE pattern as solidification proceeded. These trends are strikingly different from those seen in figs. 7 and 8 for the Snake Creek whole rocks, where the total REE abundance decreases from the high CaO to the low CaO rocks, and the HREE are more favored in the low CaO rocks. These trends imply that fractional crystallization was not the major process involved in producing the REE distributions in the Snake Creek intrusive.

The question of production of the REE distributions is faced with an apparent contradiction: The major elements appear to follow the trends of differentiation while the REE appear to show trends almost the opposite of those expected for differentiation.

Can assimilation of REE from the host rocks have caused these trends? The question of effect of sedimentary rock assimilation on the SCIA was looked at earlier, but not in terms of rocks near the contact with sedimentary rocks, which may have assimilated larger amounts of material. Looking closely at REE concentrations in the quartzite, limestone, and intrusive rocks (Appendix A) indicates that assimilation of REE from the sedimentary rocks was probably not the major cause. Concentrations of La are higher in the high CaO rocks than in the low CaO rocks, but La is more abundant in the quartzite which contacts the low CaO rocks than in the limestone in contact with the high CaO rocks. Ytterbium reaches its highest concentration in the intrusive in the low CaO rocks, which are in contact with quartzite which has higher Yb concentrations than the limestone. The abundance of Yb in the low CaO rocks is about 3 times that found in the quartzite though, so only a small part (less than one-third) of the Yb in the low CaO rocks can be attributed to assimilation of quartzite.

What process could have caused the major elements to show trends similar to differentiation while the REE show trends opposite of that expected from differentiation? Crystallization and uptake of the REE in accessory minerals is consistent with this data. Crystallization of accessory minerals seems to be closely related to assimilation, as noted by Lee and Van Loenen (1971). According to Nockolds (1933) the volatiles in an acid magma are an important factor in contamination because they aid diffusion of material between xenoliths or margins and the magma itself. Evidence of volatiles in the magma is seen in the Snake Creek rocks as increasing abundances of P_2O_5, H_2O, and F in the more mafic phases through incorporation in apatite and biotite. REE are concentrated in the apatite with respect to the whole rocks, but as seen in the last section, the bulk of the REE in the high CaO rocks is associated with allanite, sphene, and probably zircon. Concentrations of the elements found in these minerals, that is, LREE, Ti, and Zr have also been noted in carbonatites (Pecora, 1956), and Nockolds (1933) has stated that the entry of Ti into lime bearing zenoliths is a common phenomenon. Wyatt (1954) and Lee and others (1968) have noted that zircon is typical of hybrid rocks. Lee and Van Loenen (1971) infer that assimilation of limestone was a cause of crystallization of large amounts of Ca bearing accessory minerals, and Lyakhovich (1962) stated that the abundance of Ca bearing minerals in hybrid granites aids the dispersion of the REE into the structures of the Ca bearing minerals.

Examination of figs. 7 and 8, coupled with the above data leaves no question that the REE were transported. Transport of the light REE into the high CaO rocks probably came about in response to one of two conditions: concentration gradients resulting from crystallization of LREE concentrating accessory minerals, or as suggested by Lyakhovich (1962), transport may be a result of the similarity in size of the LREE and Ca^{+2}, enabling LREE to occupy Ca^{+2} sites in the abundant accessory minerals. This transport may have been in the form of diffusion through a volatile, mostly aqueous phase, as suggested by Nockolds (1933) and supported by Lee and Van Loenen (1971).

Concentration of the HREE in the low CaO rocks is probably due to concentration of these elements in a residual aqueous phase. The question of whether an aqueous phase was present in the late crystallizing rocks is difficult to answer on the basis of H_2O data in the rocks, since this data only indicates how much water was fixed in a solid phase. Lee and Van Loenen (1971) show that H_2O increases with CaO content, but this is due primarily to an increase in the modal abundance of biotite. Lee and Van Loenen (1971) do state however, that "Although there is a concentration of volatiles (mainly water) in the final product (the rocks), the P_{H_2O} was not necessarily higher in the more mafic parts of the magma...". The process of concentration of the HREE in an aqueous phase has been documented by Mineyev (1963) and was discussed earlier in relation to the Pole Canyon intrusive rocks and associated aplites.

It appears that these ideas will explain the changes in the REE distributions of the whole rocks, but what about other data? Plagioclase fractionation data discussed earlier indicated that the crystallization of accessory minerals prior to plagioclase crystallization had altered the REE distribution in the liquid phase. Had the major minerals themselves been a product of fractional crystallization as far as the REE are concerned, they should show increasing REE concentrations with decreasing CaO. This was not found to be the case, indicating that at any successive stage of crystallization, the REE concentrating accessory minerals crystallized before the major minerals, altering the REE distribution in the liquid phase. It is also of interest to note that the absolute amount of REE (except Eu) in the major minerals is roughly constant throughout the intrusive. Absolute quantities of La (including estimates for contaminated feldspars in sample 25-DL-61 and biotite in 152-MW-61) in the major minerals are all within about 20 percent of 1.5 ppm while La in the rocks varies from 13 to 79 ppm. Absolute quantities of Yb in the major minerals are all within about 25% of 0.11 ppm, while Yb in the whole rocks changed from 3.5 to 0.83 ppm. Data of this sort has never been noticed before, and its interpretation is difficult. Does it imply a condition in the magma, where above a certain concentration, the REE will be incorporated into the available accessory minerals? Is it a consequence of diffusion whereby the REE stopped moving when concentration gradients no longer existed in the liquid phase? Is it related to special conditions in this assimilated magma? The question cannot be answered with current knowledge of REE behavior.

Changes in La/Yb ratio shown in fig. 19 are compatible with the ideas presented. The trends seen in this figure, especially for the accessory minerals may be explained by transport of La to the high CaO rocks, resulting in an increased La/Yb ratio in these rocks, while depleting La and thus decreasing La/Yb in the low CaO rocks. Concentration of Yb in a residual fluid would serve to make this trend even stronger. The La/Yb trend in the plagioclases has already been discussed and is consistent with the idea of incorporation of the REE in accessory minerals before crystallization of the plagioclase.

The trend of Eu/Eu* shown in fig. 10 is probably caused by a combination of depletion of Eu in the liquid due to plagioclase crystallization in the early crystallizing rocks, and by increasing uptake of Eu in accessory minerals in rocks with more CaO than about 1.5 to 2.0 percent. Data is insufficient to formulate a more quantitative model for interpretation of the Eu data, but it is believed to be significant that the large gap in the trend in fig. 10 occurs at about the same range of CaO where a sharp rise in accessory mineral content is seen (fig. 4).

In summary, it is reasonable to expect that the REE distributions in these rocks would be controlled by the accessory minerals, since as noted previously, between 80 and 98 percent of the REE except Eu are contained in the accessory minerals. The REE distributions in the whole rocks show that the REE were transported in the magma, concentrating the LREE in the high CaO rocks, and the HREE in the low CaO rocks. These trends are the opposite of those expected for differentiation. The LREE were probably transported by diffusion and incorporated in the accessory minerals of the high CaO rocks, while the HREE were concentrated in an aqueous phase and were incorporated into the late crystallizing low CaO rocks. This model for REE behavior is consistent with La/Yb, Eu/Eu*, and major mineral REE data.

CONCLUSIONS

An average REE distribution for the intrusive can be roughly equated to the REE distribution in the parent magma, due to a lack of contact metasomatism, coupled with small changes in the average due to assimilation of REE from the sedimentary rocks. Examination of REE fractionation in the whole rocks with respect to this parent magma REE distribution shows trends the opposite of that expected for normal differentiation. These trends can be attributed to uptake of the REE in the accessory minerals, which contain 80-98 percent of the REE except Eu. Europium displays anomalous behavior, apparently due to reduction to the +2 state. This divalent Eu is concentrated in the feldspars, in all but the highest CaO rocks. Most of the REE that is associated with the major minerals is contained in the plagioclase, and the amounts of REE (except Eu) in the major minerals are roughly constant despite large changes in these amounts in the whole rocks.

The REE data is consistent with transport of the LREE to the high CaO rocks with subsequent incorporation in accessory minerals, while the HREE were probably concentrated in a residual aqueous phase with uptake in the late crystallizing low CaO rocks.

APPENDIX A

Analysis Data

REE concentrations (ppm) in granitoid rocks, mineral separates, sedimentary rock composites, and standard distributions

Whole Rocks

Sample No.	238-MW-61	147-MW-61	151-MW-61	25-DL-61
CaO Content (%)	0.78	1.5	1.8	3.1
La	13.	32.	13.	35.
Ce	52.	76.	36.	61.
Nd	19.	28.	12.	23.
Sm	4.1	5.4	1.9	3.3
Eu	.55	.82	.73	.99
Gd	4.9	4.4	2.2	2.2
Tb	.77	.73	.28	.28
Dy	4.9	4.9	1.9	1.7
Ho	1.1	1.0	.43	.35
Er	3.0	2.8	nd	nd
Yb	3.5	2.6	1.3	.83
Lu	.52	.40	.17	.16
La/Yb	3.7	11.	10.	42.
Σ REE	107.	159.	70.	129.

nd = not detected

APPENDIX A, Con't:

Whole Rocks

Sample No.	152-MW-61	43-DL-61	228-DL-63	135-DL-62
CaO Content (%)	3.2	3.9	4.5	.98 (Pole Canyon)
La	65.	79.	43.	23.
Ce	130.	140.	92.	61.
Nd	43.	47.	33.	23.
Sm	5.2	5.3	5.0	3.3
Eu	1.2	1.4	1.4	.78
Gd	nd	3.5	4.1	nd
Tb	.32	.37	.52	.34
Dy	1.6	2.2	3.2	1.5
Ho	.27	.30	.61	.27
Er	nd	nd	nd	nd
Yb	.94	.92	1.5	.47
Lu	.19	.16	.25	.065
La/Yb	69.	86.	29.	49.
Σ REE	248.	280.	181.	114.

nd = not detected

APPENDIX A, Con't:

Plagioclases

Sample No.	147-MW-61	151-MW-61	25-DL-61	152-MW-61
CaO in Rock (%)	1.5	1.8	3.1	3.2
La	3.0	3.3	7.0	2.1
Ce	5.5	11.	15.	3.8
Nd	1.9	2.1	3.7	nd
Sm	.37	.35	.50	.12
Eu	1.0	1.2	1.5	.64
Gd	nd	nd	nd	nd
Tb	.051	.057	.062	nd
Ho	.041	nd	nd	nd
Yb	.13	.18	.23	nd (.073)*
Lu	.020	.024	.042	.011
La/Yb	23.	18.	30.	29.*
An content (%)	18.	20.	28.	21.

* estimated

nd = not detected

APPENDIX A Con't:

Plagioclases

Sample No.	43-DL-61	135-DL-62
CaO in Rock (%)	3.9	.98 (Pole Canyon)
La	3.3	5.4
Ce	5.5	9.8
Nd	1.9	3.7
Sm	.26	.61
Eu	.52	.83
Gd	nd	nd
Tb	.025	.064
Ho	.035	nd
Yb	.097	.25
Lu	.017	.035
La/Yb	34.	22.
An content (%)	24	17

nd = not detected

APPENDIX A Con't:

Biotites

Sample No.	147-MW-61	151-MW-61	25-DL-61	152-MW-61
CaO in Rock (%)	1.5	1.8	3.1	3.2
La	.46	.47	.62	17.
Ce	nd	1.2	1.4	35.
Nd	nd	nd	nd	13.
Sm	.22	.39	.28	1.8
Eu	.052	.069	.048	.29
Gd	nd	nd	nd	1.3
Tb	nd	nd	nd	.12
Ho	.089	.16	.071	.18
Yb	nd(.24)*	.47	.25	.55
Lu	.047	.088	.049	.12
La/Yb	1.9*	1.0	2.5	31.

* estimated

nd = not detected

APPENDIX A Con't:

Biotites and Muscovite

Sample No.	43-DL-61	135-DL-62	135-DL-62 Muscovite
CaO in rock (%)	3.9	.98 (Pole Canyon)	.98 (Pole Canyon)
La	.059	4.3	1.7
Ce	nd	9.3	4.2
Nd	nd	nd	nd
Sm	.024	.70	.24
Eu	.008	.15	.087
Gd	nd	nd	nd
Tb	nd	.081	nd
Ho	.010	.11	nd
Yb	.165	.30	.13
Lu	nd	.067	.032
La/Yb	.36	14.	13.

nd = not detected

APPENDIX A Con't:

Potassium Feldspars

Sample No.	147-MW-61	151-MW-61	25-DL-61	135-DL-62
CaO in Rock (%)	1.5	1.8	3.2	.98 (Pole Canyon)
La	.54	.36	2.1	1.1
Ce	.71	nd	4.5	1.6
Nd	nd	nd	nd	nd
Sm	.040	.019	.41	.064
Eu	.61	.46	.41	.68
Gd	nd	nd	.43	nd
Tb	nd	nd	.052	nd
Ho	nd	nd	.055	nd
Yb	nd	nd	.16	nd
Lu	nd	nd	.035	nd
La/Yb	--	--	13.	--

nd = not detected

APPENDIX A Con't:

Standard Distributions

Standard Name	SCIA	NASC
La	25.	32.
Ce	61.	73.
Nd	21.	33.
Sm	3.5	5.7
Eu	.82	1.24
Gd	3.2	5.2
Tb	.46	.85
Dy	3.0	5.04
Ho	.64	1.04
Er	--	3.4
Yb	1.8	3.1
Lu	.28	.48
La/Yb	14.	10.
Σ REE	121.	164.

APBENDIX A Con't:

Sedimentary Rock Composites

Sample	Osceola Argillite	Prospect Mt. Quartzite	Pioche Shale	Wheeler Limestone	Pole Canyon Limestone
La	42.	7.0	43.	5.0	3.8
Ce	98.	17.	110.	13.	10.
Nd	46.	8.6	46.	6.5	4.3
Sm	8.5	1.8	8.5	1.5	.76
Eu	1.5	.44	1.7	.35	.14
Gd	nd	nd	nd	nd	nd
Tb	1.1	.25	1.1	.28	.10
Ho	1.5	.40	1.7	.45	.15
Yb	4.0	1.3	4.3	1.1	.38
Lu	.60	.20	.68	.17	.057
La/Yb	11.	5.4	10.	4.5	10.

nd = not detected

APPENDIX B

Duplicate Analyses and Detection Limits

REE concentration in ppm

Interlaboratory Standard Analysis

Sample: USGS Standard Rock G-2

Element	Analysis This Study	Values From Flanagan (1973)*	Average	Standard Deviation	Percent Deviation
La	77.	96 avg	87.	13.	16.
Ce	180.	150 mag	165.	21.	13.
Nd	53.	60 avg	57.	5.0	8.8
Sm	6.9	7.3 avg	7.1	.28	4.0
Eu	1.3	1.5 rec	1.4	.14	10.
Gd	4.1	5 mag	4.6	.64	14.
Tb	.43	.54 rec	.49	.078	16.
Yb	.72	.88 avg	.80	.11	14.
Lu	.12	.11 avg	.115	.007	6.1

* We follow the convention of Flanagan (1973), where avg = average, rec = recommended, and mag = magnitude.

APPENDIX B, Con't:

Duplicate Analyses

Sample: 152-MW-61 Biotite

Element	Original Analysis	Second Analysis	Average	Standard Deviation	Percent Deviation
La	22.	12.	17.	7.1	42.
Ce	43.	26.	35.	12.	35.
Nd	16.	9.2	13.	4.8	38.
Sm	2.1	1.4	1.8	.50	28.
Eu	.31	.26	.29	.035	12.
Gd	nd	1.3	--	--	--
Tb	.11	.12	.115	.007	6.1
Ho	.18	.17	.175	.007	4.0
Yb	.56	.54	.55	.014	2.6
Lu	.13	.10	.115	.021	18.

Sample: 25-DL-61 Plagioclase

La	8.3	5.7	7.0	1.8	26.
Ce	18.	12.	15.	4.2	28.
Nd	4.3	3.0	3.7	.92	25.
Sm	.58	.41	.50	.12	24.
Eu	1.7	1.2	1.5	.35	24.
Tb	.076	.048	.062	.020	32.
Yb	.25	.20	.23	.035	16.
Lu	.042	.032	.037	.007	19.

nd = not detected

APPENDIX B, Con't:

Duplicate Analysis

Sample: 228-DL-63 Whole Rock

Element	Original Analysis	Second Analysis	Average	Standard Deviation	Percent Deviation
La	46.	40.	43.	4.2	9.9
Ce	81.	103.	92.	16.	17.
Nd	31.	34.	33.	2.1	6.5
Sm	5.0	5.0	5.0	--	0.
Eu	1.3	1.4	1.35	.07	5.2
Gd	3.9	4.2	4.1	.21	5.2
Tb	.51	.53	.52	.01	2.7
Dy	3.2	na	--	--	--
Ho	.58	.63	.61	.04	5.8
Er	nd	na	--	--	--
Yb	1.4	1.5	1.45	.07	4.9
Lu	.26	.[illegible]	.25	.02	8.7

nd = not detected

na = not analyzed

APPENDIX B, Con't:

Detection Limits

Element	Detection Limit in ppm for a .1 gm Sample	Detection Limit in ppm for a .5 gm Sample	Absolute Detection Limit in Nanograms	Smallest Amount Detected in Nanograms	Sample
La	.11	.022	11.	7.3	43-DL-61 biotite
Ce	.42	.085	42.	130.	147-MW-61 potassium feldspar
Nd	1.8	.37	180.	1100.	147-MW-61 plagioclase
Sm	.008	.002	.8	2.7	151-MW-61 potassium feldspar
Eu	.009	.002	.9	1.0	43-DL-61 biotite
Gd	1.6	.31	160.	180.	25-DL-61 potassium feldspar
Tb	.024	.005	2.4	12.	43-DL-61 plagioclase
Ho	.058	.012	5.8	1.2	43-DL-61 biotite
Yb	.081	.016	8.1	45.	43-DL-61 plagioclase
Lu	.012	.002	1.2	1.9	152-MW-61 plagioclase

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