TRACE ELEMENT DISTRIBUTIONS AND THE ORIGINS OF SOME NEW ENGLAND GRANITES

by

Grant Buma

SUBMITTED IN PARTIAL FULFILLMENT OF THE
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Signature of Author____
Department of Earth and Planetary Sciences
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Certified by____
Thesis Supervisor

Accepted by____
Chairman, Departmental Committee
on Graduate Students

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ABSTRACT

The Peabody, Cape Ann, and Quincy granites of the "alkaline" series in Massachusetts and the Westerly and Narragansett Pier granites of the sub-alkaline series in Rhode Island have been analyzed for their content of rare-earths (REE), Zr, Hf, Ta, Sc, and Th.

Petrographic and field evidence indicates that the sub-alkaline granites crystallized at a shallower depth and higher P_{H_2O} than the alkaline granites. Heavy REE, Zr, Hf, and Ta are all depleted in the sub-alkaline granites. Such a depletion could be the result of the participation of some phase which concentrates these elements, such as garnet or zircon, in the differentiation of these rocks. Another mechanism might be the removal of these elements in escaping volatiles.

High Th abundances (> 20 ppm) in the sub-alkaline granites indicate that they have undergone more extensive differentiation than the alkaline group.

Large Eu anomalies indicate that feldspar is probably present in the parent material for the alkaline group, thus arguing against upper mantle material as a possible direct source for these rocks. The especially large Eu anomaly and depletion of Sc in the Quincy granite indicate that it has undergone more extensive differentiation than the other alkaline rocks.

Thesis Supervisor: F. A. Frey
Title: Ass't. Professor

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INTRODUCTION

Five New England granites have been selected for study--the Cape Ann, Peabody and Quincy granites of the alkaline series in Massachusetts, and the Westerly and Narragansett Pier granites of the sub-alkaline series in Rhode Island.

The use of the term "alkaline" in relation to these rocks is discussed by Toulmin (1958). For the purposes of this paper "alkaline" refers to granites for which the ratio $(Na_2O + K_2O)/Al_2O_3$ is near one; "subalkaline" refers to granites for which this ratio is considerably less than one.

All five of these granites have been well studied and their geology and petrology have been established. Evidence has been presented that all five are clearly magmatic (Cape Ann and Peabody--Toulmin, 1964; Quincy--Warren, 1913; Westerly and Narragansett Pier--Feininger, 1964). The nature of the origin of these magmas is, however, not so well understood. The purpose of this study is to examine the distributions of selected trace elements and try to understand their behavior in the light of geologic, petrologic and petrographic evidence. It is hoped that the addition of trace element data to the already accumulated knowledge about these granites will help in trying to understand the nature of their source and differentiation. The elements selected for study are as follows: The REE (rare-earth elements), Zr, Hf, Sc, Ta and Th.

Peabody and Cape Ann granites:

The Peabody and Cape Ann granites have been studied by Toulmin (1964). The ages of these two granites are given in table 1.

The Peabody stock comprises approximately 15 square miles of uniform, massive, medium- to coarse-grained rock. The essential minerals are microperthite, quartz and iron-rich amphibole. The color varies from gray to green. The accessory minerals include pyroxene, zircon, magnetite, ilmenite, biotite, sphene, allanite, riebeckite, sulfides, garnet, monazite and some extra-perthitic plagioclase. The modal abundances are included in table 6. (See Appendix 1 fig. B)

Zircon, apatite, allanite and opaque minerals are enclosed poikilitically in the amphibole. Zircon and allanite are surrounded by pleochroic halos caused by the decay of radioactive elements. Zircons are also found included in feldspar. (See Appendix 1 figs. C and E)

Table 1. Radiometric ages for five New England granites

Granite	Age (my)	Method	Reference
Westerly and Narragansett Pier	234	Pb - α	Hurley *et al.* (1960
Westerly	240 ± 12	K-Ar(bt)	Hurley *et al.* (1960)
Peabody	367 ± 12	Rb-Sr(wr)	Zartman (1969)
Peabody	359, 362, 371, 375, 402 - ± 4%	K -Ar(hb)	Zartman (1969)
Peabody	380 ± 20	Pb^{207} -Pb^{206} (zircon)	Zartman (1969)
Cape Ann	433 ± 6	Rb - Sr(wr)	Zartman (1969)
Cape Ann	450 ± 20	Pb^{207}-Pb^{206} (zircon)	Zartman (1969)
Quincy	430, 437, 444, 447, 457	K - Ar(Hb)	Zartman (1969)
Quincy	450 ± 20	Pb^{207} -Pb^{206} (zircon)	Zartman (1969)

Table 2.

Chemical compositions of five New England granites (%)

	Peabody (1)	Cape Ann (2)	Quincy (3)	Westerly (4)	Narragansett Pier (5)
SiO_2	71.55	71.61	74.40	69.19	73.05
Al_2O_3	12.60	11.94	11.95	15.34	14.53
Fe_2O_3	1.38	0.55	2.60	1.08	2.96
FeO	3.28	0.87	1.40	1.44	
MgO	0.11	tr	0.05	0.78	-
CaO	1.12	0.31	0.36	1.98	2.06
Na_2O	3.93	3.80	4.48	4.15	1.72
K_2O	5.34	4.98	4.64	4.51	5.39
TiO_2	0.34	0.25	0.19	0.53	-
P_2O_5	-	-	-	0.14	-
MnO	0.09	tr	0.01	0.03	tr
S	-	-	-	0.02	-
BaO	-	-	-	0.18	-
CO_2	-	-	-	0.08	-
H_2O^+	0.16	0.23	0.36	0.55	0.29
H_2O	-	tr	-	0.11	

---

(1) Average of 2 (toulmin, 1958 and Clapp, 1921).
(2) Dale (1923) (H. S. Washington analyst).
(3) Average of 2 (Warren, 1913).
(4) Flanagan (1969).
(5) Dale (1923).

On the basis of the preceding description zircon was among the earliest minerals to begin crystallizing. Further petrographic examination indicates that feldspar also began crystallizing early followed closely by amphibole with quartz coming out late.

The Cape Ann granite is very similar to the Peabody granite. Field observations confirm the relative ages of these two granites shown in table 1 (Toulmin, 1964). In hand specimen the Cape Ann granite appears to be slightly more fine-grained than the Peabody granite. (See Appendix 1 fig. D) The general mineralogy is about the same for the Cape Ann and Peabody granites, but the Cape Ann granite is not as uniform in composition as the Peabody granite. Fayalite has been reported in thin sections of Cape Ann granite (Toulmin, 1964 and Warren and McKinstry, 1924). Toulmin (1964) presents a more detailed description of Peabody and Cape Ann granites.

The major element compositions of the Cape Ann and Peabody granites are shown in table 2. The similar mineralogical and chemical compositions of the Peabody and Cape Ann granites imply that they are genetically related. Whitney (1969) has come to the same conclusion as a result of studying their melting relationships.

The occurrence of coexisting biotite, fayalite and magnetite, and the unique compositions of the Peabody and

Cape Ann granites are among the reasons these two granites were selected for study. From studies of the feldspars from the Peabody granite Toulmin (1958) has concluded that it probably did not crystallize below about 675°C. The experiments of Rutherford (1969) indicate that the temperature was probably $< 800^\circ C$. This temperature range, coupled with the data of Eugster and Wones (1962) on the stability of biotite coexisting with fayalite, magnetite and quartz, indicate a very low f_{H_2O} during crystallization of the Peabody and Cape Ann granites. Toulmin (1958) has concluded that a maximum P_{H_2O} for the magma which produced these granites would be less than 1000 kgm/cm^2.

The homogeneity and relatively coarse-grained texture of the Peabody granite indicate that it probably crystallized rather slowly and at considerable depth. Gravity studies of the area (Joyner, 1958) indicate that the Cape Ann granite and Beverly syenite are underlain by denser rocks at a rather shallow depth (Toulmin, 1964).

The above description agrees well with what might be expected of a granite which was derived from upper mantle material by differentiation from a basaltic magma (Green and Ringwood, 1967). This hypothesis will be tested against other alternatives.

Quincy granite:

The most recent studies of Quincy granite have been by Quinn and Moore and are summarized in Zen et al. (1968). Other studies include La Forge (1932), Dale (1923), Warren (1913), Loughlin (1911) and Crosby (1900).

The Quincy granite in general is a holocrystalline, gray, medium- to coarse-grained rock, somewhat more fine-grained than the Peabody granite. (See Appendix 1 fig. F) The essential minerals are micro-perthite, quartz, hornblende and aegirite. Accessory minerals include fluorite, zircon, riebeckite, magnetite, aenigmatite, astrophyllite, sphene, hematite, parisite, synchisite, siderite and occasionally calcite. Modal abundances are included in table 5.

The feldspar in the Quincy granite is more turbid than that of the Peabody granite and often contains minute inclusions of magnetite. (See Appendix 1 fig. G) Pink feldspar is also present in altered areas. In the Quincy granite, riebeckite replacing aegirite is common. (See Appendix 1 fig. H) Accessory minerals such as zircon, monazite, parisite and synchisite are concentrated along grain boundaries and in interstitial positions. (See Appendix 1. figs. I and J) For a more detailed description of Quincy granite see Warren (1913).

Close petrographic examination indicates that pyroxene and magnetite were probably among the first minerals to begin crystallizing (Warren, 1913). Feldspar came next, followed by quartz and amphibole, with zircon, monazite, parisite, and synchisite coming out late.

The presence of magnetite and hematite in feldspar and riebeckite replacing aegirite in Quincy granite might indicate that conditions were more oxidizing during crystallization of Quincy granite than during crystallization of Peabody and Cape Ann granites. The more fine-grained texture of the Quincy granite relative to the Peabody granite indicates that it probably crystallized more rapidly and at a shallower depth than the Peabody granite. Warren (1913) offers further evidence that the Quincy granite was intruded at a rather shallow depth and underwent fairly rapid crystallization. He also discusses the association of the Quincy granite with various porphyries and implications that the Quincy may have been associated with volcanism.

The age, chemical, and mineral compositions of the Quincy granite (tables 1 and 2) are similar to those of the Cape Ann granite. Emerson (1917) labeled the Peabody, Cape Ann and Quincy granites all as Quincy granite. One purpose of this study is to determine whether or not the Quincy granite is co-magmatic with the Peabody and Cape Ann granites.

Westerly and Narragansett Pier granites:

The Westerly and Narragansett Pier granites have been studied by Feininger (1964). Quoting Feininger: "Narragansett Pier Granite is a medium-grained, equigranular, granitoid, reddish pink, massive to weakly foliated rock." There are numerous pegmatites in the Narragansett Pier granite in contrast to the lack of pegmatites in the alkaline group.

The essential minerals are microcline, plagioclase, quartz and biotite. The accessory minerals include zircon, muscovite, chlorite, rutile?, magnetite, ilmenite, allanite, apatite, epidote, monazite, and sphene. Modal abundances are included in table 4. (See Appendix 1 fig. K)

Pleochroic halos surrounding inclusions of zircon or allanite in biotite are common. (See Appendix 1 fig. L) Muscovite, usually associated with biotite, is abundant and often occurs in quite large grains. (See Appendix 1 figs. M and N) Magnetite is ubiquitous and often found concentrated along grain boundaries in biotite. (See Appendix 1 figs. N and M)

According to the above description zircon was probably among the first minerals to begin crystallizing, and was followed closely by biotite and plagioclase. Perthite probably came next followed by quartz and magnetite. The large size of the muscovite grains indicate that it might also have been a primary mineral, in which case it probably would have crystallized about the same time as the biotite or before. This, however, is open to debate.

The Westerly granite is a dike rock intimately associated with the Narragansett Pier granite. Quoting Feininger it is "a fine-grained, light gray, massive to rarely very feebly foliated, exceedingly uniform rock." The general mineralogy of the Westerly granite is similar to that of the Narragansett Pier granite, except that calcite is included among the accessory minerals in Westerly granite and monazite is not. (See Appendix 1 fig. 0)

As was found in the Narragansett Pier granite, large muscovite grains are abundant in Westerly granite (See Appendix 1 fig. P) and zircons enclosed in biotite are surrounded by pleochroic halos. (See Appendix 1 fig. Q) Some magnetite is found concentrated along grain boundaries in biotite from Westerly granite similar to that found in Narragansett Pier granite, but there are also abundant irregular blebs of magnetite which do not appear to be directly associated with biotite. (See Appendix 1 figs. R and Q) A more detailed description of Westerly and Narragansett Pier granites is given by Feininger (1964).

Following the above description, paragenesis for the

Westerly granite is probably similar to that given for the Narragansett Pier granite, except that a considerable amount of magnetite may have crystallized early rather than late.

The age and chemical compositions of the Westerly and Narragansett Pier granites are quite similar as shown in tables 1 and 2 respectively. These similarities between the Westerly and Narragansett Pier granites in addition to those discussed above, indicate that these two granites are genetically related. Quinn (1957) has come to the same conclusion as a result of studying the field relations and radiometric ages of Westerly and Narragansett Pier granites.

The Narragansett Pier and Westerly granites were selected for study because they represent a direct contrast to the alkaline group in both age and composition. The presence of muscovite indicates that f_{H_2O} was probably fairly high during crystallization of Westerly and Narragansett Pier granites. It was certainly higher than it was during crystallization of granites of the alkaline group. Feininger (1964) has indicated that P_{H_2O} during crystallization of Westerly and Narragansett Pier granites was close to 5100 kg/cm^2. The presence of pink feldspar in the Westerly and Narragansett Pier granites and large magnetite crystals in the Westerly granite (Moore, 1959) could mean that conditions were more oxidizing during crystallization of these two granites than they were during crystallization of the

Peabody and Cape Ann granites.

The fine grained texture of Narragansett Pier and Westerly granites indicates that they were probably intruded at a rather shallow depth and crystallized fairly rapidly (Feininger, 1964). Whitney (1969) has placed the temperature of crystallization close to 700°C as a result of studying the melting relations of the Westerly granite.

The above description is similar to what would be expected for a granite which resulted from partial fusion of crustal material (Turner and Verhoogen, 1960 and Feininger, 1964). This hypothesis will be tested against other alternatives.

As described above, the two groups of granites apparently crystallized under distinctly different physical and chemical conditions. The trace elements studied in this research may reflect these crystallization conditions in addition to reflecting the magma source.

ANALYTICAL METHOD

Three samples were collected from different localities within each pluton. The sample localities are described in Appendix 1 and shown on the map in fig. A.

An instrumental neutron activation technique was used similar to that described by Gordon et al. (1968). Refinements were made on Gordon's method by analyzing the U.S.G.S. standard rock G-2 twice. The results are shown in table 3 along with the rest of the whole-rock samples. The estimated analytical errors for the whole-rock analyses are $\leq$ 10% for all elements except Lu and Zr for which the error is $\leq$ 20%; Lu because of its low abundance and Zr because the Zr^{95} peak which is analyzed is also a fission product of U^{235} (See Appendix 2). The ± values reported are $\frac{1}{2}$ the difference between the two runs of G-2 and all fall within the estimated error. A more detailed account of the analytical errors is given in Appendix 2.

ANALYTICAL RESULTS

The rare earths:

Outlines of rare-earth geochemistry have been presented by Rankama and Sahama (1950), Goldschmidt (1954) and Ahrens (1964). A relatively complete summary of rare-earth data has been presented by Haskin et al. (1966). Studies of rare-earth distributions in coexisting mineral phases in granitic rocks are scarce; three important papers in this area are by Gavrilova and Turanskaya (1958), Towell et al. (1965) and Chase et al. (1963).

Table 3

Trace Element Abundances in Five New England Granites

Values represent averages of three samples analyzed from each pluton (ppm)(1).

	G-2(2)	G-2(3)	Westerly	Narragansett Pier	Quincy	Peabody	Cape Ann
La	84 ± 2	85 ±2	87 ±13	137 ± 3	89 ± 13	95 ± 7	71 ± 7
Ce	167 ± 4	168.5 ±0.5	174 ±28	257 ± 3	212 ± 29	219 ±17	169 ±12
Sm	7.3 ± 0.5	7.4 ±0.5	7.2 ± 0.7	10 ± 1	20 ± 3	18 ± 1	15 ± 1
Eu	1.37± 0.05	1.29±0.01	1.12± 0.25	1.65± 0.12	0.81± 0.03	1.46± 0.12	1.52± 0.26
Tb	0.52± 0.05	0.40±0.03	0.44± 0.07	0.54± 0.06	2.2 ± 0.3	2.1 ± 0.2	2.0 ± 0.2
Dy	2.05	2.3 ±0.3	2.7 ± 0.3	2.2 ± 0.3	14 ± 2	13 ± 1	18 ± 3
Yb	0.8 ± 0.2	0.56±0.05	0.84± 0.18	0.40± 0.04	8.9 ± 2.1	5.1 ± 0.8	5.2 ± 0.7
Lu	0.18± 0.08	0.10±0.02	0.16± 0.05	0.10± 0.01	1.4 ± 0.2	0.96± 0.10	0.86± 0.07
Hf	8.4 ± 0.5	8.26±0.02	7.05± 1.65	7.94± 0.47	22.8 ± 7.2	18.2 ± 2.3	13.7 ± 1.7
Ta	0.82± 0.1	0.80±0.04	0.92± 0.19	0.22± 0.03	5.3 ± 0.8	3.4 ± 0.5	3.4 ± 0.5
Sc	3.05± 0.2	3.12±0.02	2.87± 0.05	2.36± 0.30	0.27± 0.03	2.59± 0.83	1.23± 0.39
Zr	312 ±30	313 ±1	315 ±78	312 ± 9	936 ±279	772 ±58	448 ±64

Table 3 (Cont'd)

Trace Element Abundances in Five New England Granites

Values represent averages of three samples analyzed from each pluton (ppm)(1).

	G-2(2)	G-2(3)	Westerly	Narragansett Pier	Quincy	Peabody	Cape Ann
Th	24.5±1.4	23.7 ±0.3	38.5 ±15.4	59.6 ±15.7	14.2 ±1.4	13.9 ±2.0	13.1 ± 3.0
$\frac{Zr}{Hf}$		38	44	39	41	43	33
$\frac{Th}{Zr}$		0.12	0.19	0.015	0.018	0.029	
$\frac{K}{Th}$(4)		1340	636	2300	2710	2680	
$\frac{Eu}{Eu^*}$		0.59±0.16	0.63± 0.04	0.14 ± 0.02	0.28 ±0.01	0.35 ±0.12	

(1) The ± values for all but G-2 represent the average deviation from the mean for the three samples analyzed from each pluton (Daniels et al, 1962).

(2) Values reported in the literature (Flanagan, 1969).

(3) From this study.

(4) K values from Toulmin (1964).

Whole-rock analyses:

Figure 1 shows the limits of rare-earth distributions of several composite and granite averages reported in the literature. The values are plotted on a log scale and are normalized to chondrites and La = 100. This is the general form of rare-earth distributions obtained from highly differentiated acid igneous rocks. Also shown in fig. 1 are the limits of the rare-earth distributions of 16 individual granites.

If one accepts chondrites as a model for the primordial earth (Aller, 1961 and 1965), it is apparent that all of the REE have been enriched, with the lighter ones being more enriched relative to the heavier ones. It is also apparent that the abundances of the heavy REE are more variable than those of the light REE; therefore, the heavy REE will probably prove to be the most useful and most sensitive as geochemical indicators in granitic rocks.

The whole-rock distributions of the five granites studied in this paper are shown in fig. 2. The variation in the abundances of heavy REE divides them neatly into two groups. The difference in the abundances of heavy REE and in the magnitudes of the Eu anomalies indicates a different source or crystallization history.

To illustrate that the variation of heavy REE shown

Fig. 1. Dashed lines indicate an envelope for a family of curves representing RE values of 8 average and composite granites normalized to chondrites and La = 100. Solid lines indicate an envelope of a family of curves representing the RE values of 16 analyses of individual granites. References:

Haskin et al. (1966)
Haskin et al. (1968)
Fleischer (1965)
Nagasawa (1970)

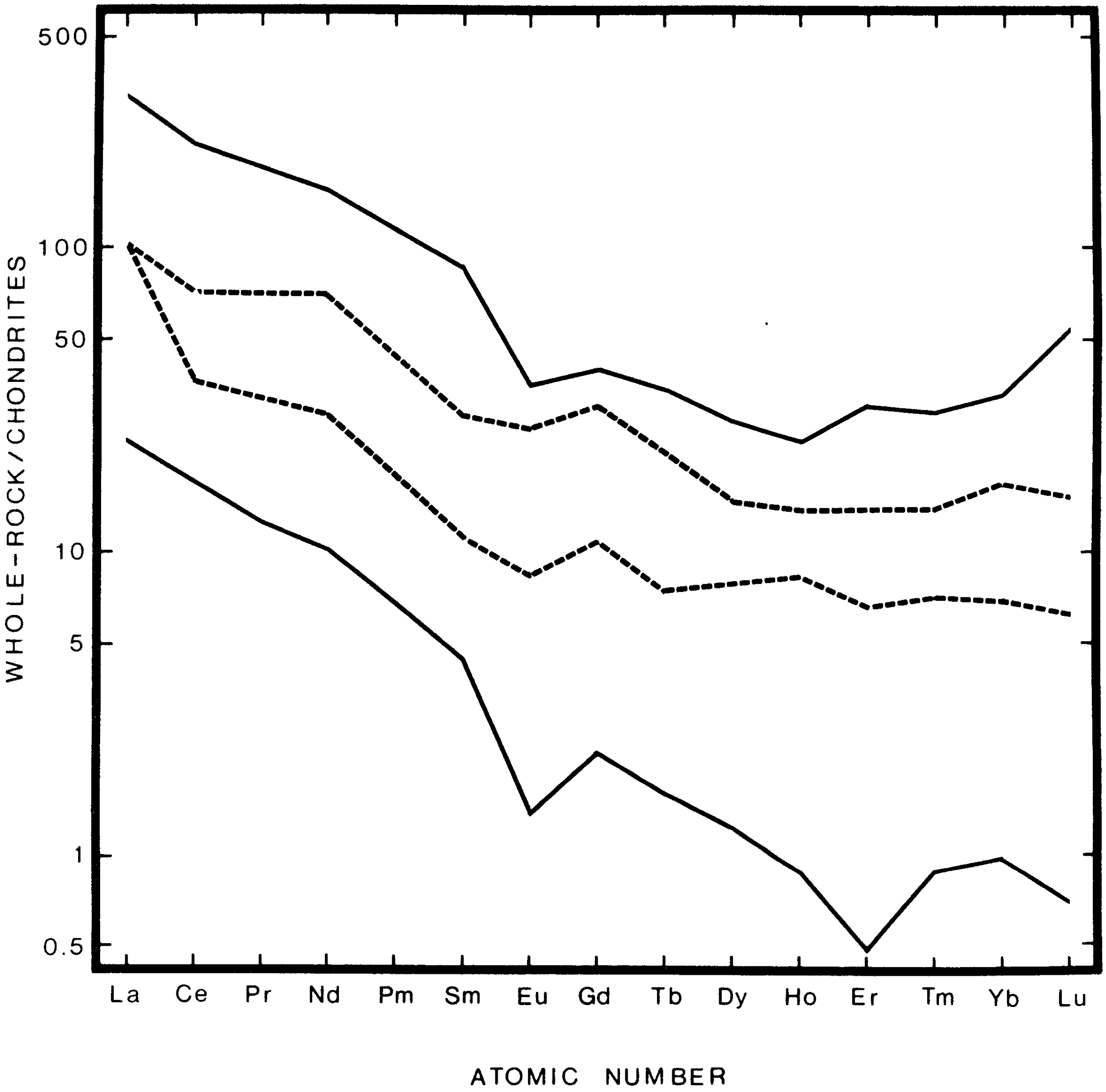
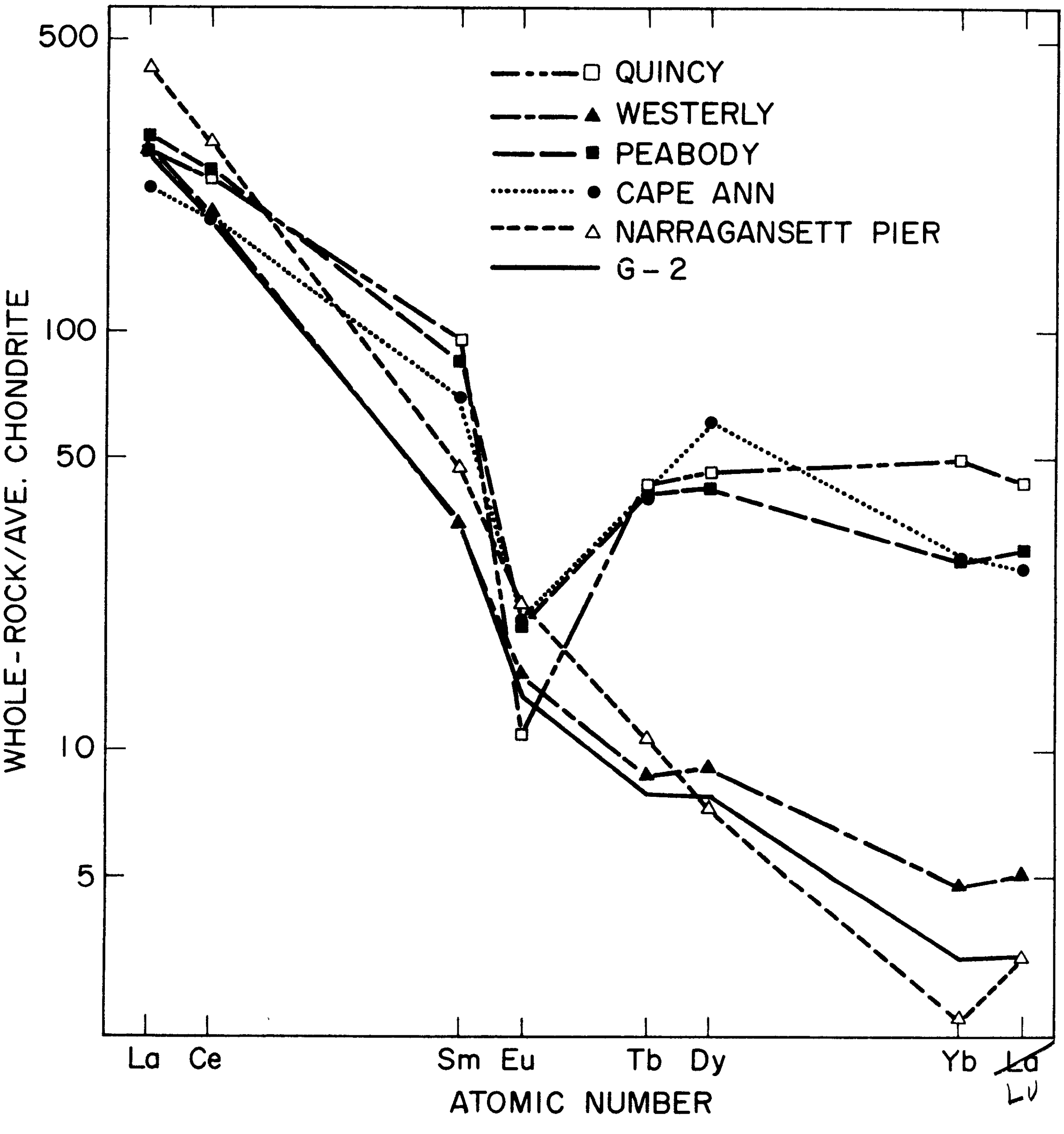

500
100
50
10
5
1
0.5
WHOLE-ROCK/CHONDRITES
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
ATOMIC NUMBER

Fig. 2. Rare earth abundances of 5 New England granites normalized to chondrites.


500
100
50
10
5
WHOLE-ROCK/AVE. CHONDRITE
□ QUINCY
▲ WESTERLY
■ PEABODY
● CAPE ANN
△ NARRAGANSETT PIER
G-2
La
Ce
Sm
Eu
Tb
Dy
Yb
~~La~~
Lu
ATOMIC NUMBER

here is not unique with these granites, in fig. 3 (Σ heavy RE) / (Σ RE) is plotted against various parameters for these five and three other granites for which both major element and rare earth data are available.

There is insufficient data available for a detailed discussion of all these trends, but one might speculate for example, that the negative trends obtained in the P_2O_5 and CaO plots reflect the apatite and monazite content of the various rocks, as they do for the five granites studied in this paper. The abundances of these two accessory minerals will have a significant impact on the whole-rock distribution of REE because these minerals generally contain a major portion of the REE in the rock. See fig. 7 and Lyakhovich (1967).

It should be clear from the above that variation of different parameters in granites is accompanied by a variation in the abundances of heavy REE.

Both the alkaline and sub-alkaline granites exhibit Eu anomalies; although that of the alkaline group is much more prominent, the absolute abundances in both groups are similar.

Mineral fraction analyses:

The data from the analyses of the mineral fractions is tabulated in tables 4, 5 and 6, and plotted normalized to

Fig. 3. Fractionation of REE according to variation in selected components.

$\Sigma HRE = Tb + Yb + Lu$

$\Sigma RE = La + Sm + Eu + Tb + Yb + Lu$

References:

Rubidoux -- Larsen (1948), Haskin et al. (1966)
Wausau -- Peck (1953), Haskin et al. (1966)
Saganaga -- Grout (1929), Haskin et al. (1966)

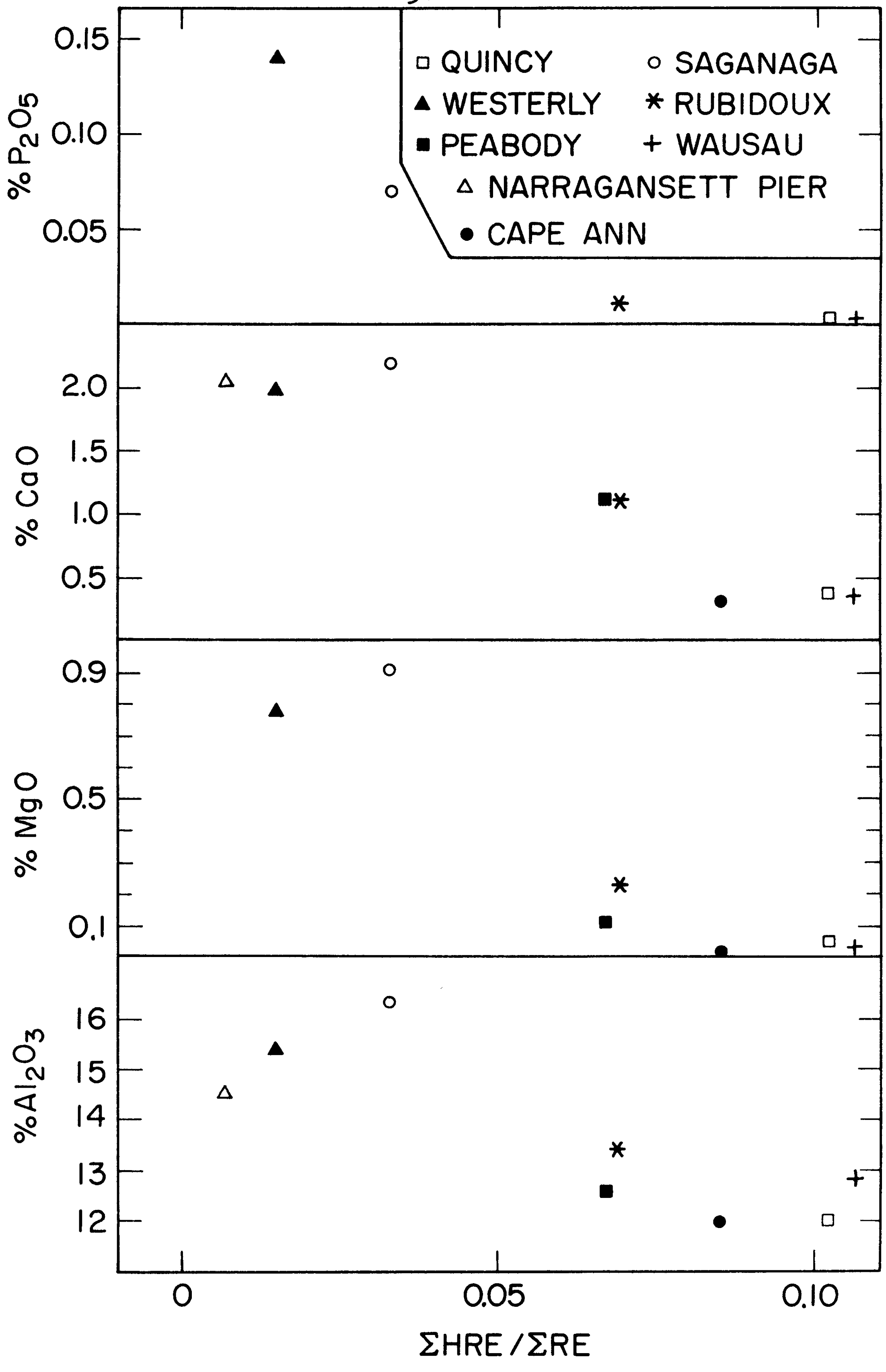

□ QUINCY
○ SAGANAGA
▲ WESTERLY
* RUBIDOUX
■ PEABODY
+ WAUSAU
△ NARRAGANSETT PIER
● CAPE ANN
% P_2O_5
0.15
0.10
0.05
% CaO
2.0
1.5
1.0
0.5
% MgO
0.9
0.5
0.1
% Al_2O_3
16
15
14
13
12
0
0.05
0.10
ΣHRE / ΣRE

Table 4. Narragansett Pier Mineral Fractions* (ppm)

	Plagioclase	K-Spar	Quartz	Biotite	Magnetite** Ilmenite	Westerly Feldspar
Modal Abundance (%)	35.0	30.0	27.0	5.5	1.0	
La	22	9	1	141	64	8
Ce	38	13	2	315	~101	13
Sm	1.5	0.5	0.1	11	9.9	0.5
Eu	0.76	1.16	0.04	0.95	0.48	0.69
Tb	0.07	–	0.01	0.60	0.30	0.05
Dy	≤ 0.6	≤ 0.3	0.1	2.7	1.3	≤ 0.2
Yb	0.12	0.01	0.05	0.74	1.1	0.17
Lu	0.02	0.01	0.01	0.39	0.13	0.04
Hf	1.64	0.56	1.74	23.5	27.7	0.70
Ta	0.01	0.03	0.04	23.4***	15.9	0.01
Sc	0.29	0.07	0.03	46.4***	12.9	0.10

Table 4. (cont'd) Narragansett Pier Mineral Fractions* (ppm)

	Plagioclase	K-Spar	Quartz	Biotite	Magnetite** Ilmenite	Westerly Feldspar
Zr	78	59	45	666	639	54
Th	6.0	2.0	1.1	92.3	39.5	5.7
Zr/Hf	48	105	26	28	23	77
Th/Zr	0.077	0.034	0.024	0.14	0.062	0.11

* Errors are ~5% greater than for the whole-rock analyses except for the magnetite fraction, for which the error is greater due to background problems.

** Relative values only.

*** Values appear high from balance calculations.

Table 5. Quincy mineral fractions (ppm)*

	Feldspar-Quartz	Amphibole	Pyroxene	Magnetite-Ilmenite	Heavy Mineral (G.>3.3)
Modal Abundance (%)	91.1	6.5	2.4	<1	<1
La	15	169	277	4	4260
Ce	36	475	687	-	9270
Sm	3.8	40	94	0.8	868
Eu	0.16	1.32	2.39	<0.03	34.8
Tb	0.41	4.5	8.2	0.23	143
Dy	-	22	56	-	1060
Yb	1.7	29	43	0.17	760
Lu	0.25	6.3	8.1	0.04	115
Hf	3.94	12.5	87.6	3.13	6360
Ta	1.7	4.1	9.1	0.10	181

Table 5. (Continued) Quincy mineral fractions (ppm)*

	Fedspar-Quartz	Amphibole	Pyroxene	Magnetite-Ilmenite	Heavy Mineral (G.>3.3)
Sc	0.01	3.97**	1.79	<0.20	0.07
Zr	175	513	2100	<295	266000
Th	6.3	11.2	30.8	1.1	798
Zr/Hf	44	41	24	94	42
Th/Zr	0.036	0.022	0.015	>0.0037	0.0030

* Errors under Table 4.

** Value appears high in mass balance calculations.

Table 6. Peabody mineral fractions (ppm)*

	Feldspar	Quartz**	Amphibole	Heavy Minerals (G.>3.0)
Modal Abundance (%)	62.1	28.2	6.5	<0.3
La	9	5	1470	338
Ce	18	10	-	684
Sm	1.5	0.7	276	68
Eu	1.22	0.43	6.69	6.92
Tb	0.17	0.75	22	24
Dy	<1	0.6	93	231
Yb	0.55	0.37	49	321
Lu	0.10	0.04	3.7	68
Hf	0.97	43.9	60.8	9130

Table 6. (Continued) Peabody mineral fractions (ppm)*

	Feldspar	Quartz**	Amphibole	Heavy Minerals (G.>3.0)
Ta	0.33	2.0	28	19
Sc	0.10	0.50	31.3	5.01
Zr	74	8	2150	371000
Th	0.8	0.7	159	2450
Zr/Hf	76	18	35	41
Th/Zr	0.011	0.088	0.074	0.0066

* Errors under Table 4.

** Relative values only.

whole-rock values in figs. 4, 5 and 6. The error for the mineral fraction data is in general ≈ 5% greater than that for the whole-rock analyses. The error for the magnetite fractions is larger because of background problems. The whole-rock data allowed one to distinguish easily the two groups of rocks, but as illustrated by the contrast between figs. 4 and 5, the mineral fraction data allow one to distinguish more clearly individual rocks from the same group.

The Quincy mineral fractions exhibit much less relative variation in the abundances of the REE compared to those from the Peabody granite.

The subdued fractionation behavior observed in the mineral fractions from the Quincy granite is probably indicative of a highly immobile environment and of rapid crystallization which would not allow much time for equilibration. Such conditions might be found in a dry magma which was intruded at a relatively shallow depth.

The heavy mineral fraction from the Peabody granite is >95% zircon, and the enrichment of this fraction in the heavy REE is in agreement with the findings of other investigators (Lyakhovich, 1962 and Nagasawa, 1970). The depletion of the heavy REE in the amphibole fraction of the Peabody is probably a reflection of that depletion in

Fig. 4. Rare-earth abundances in selected mineral fractions from Peabody granite normalized to whole-rock. The absolute abundances of the quartz fraction are uncertain, but the relative values should be good.

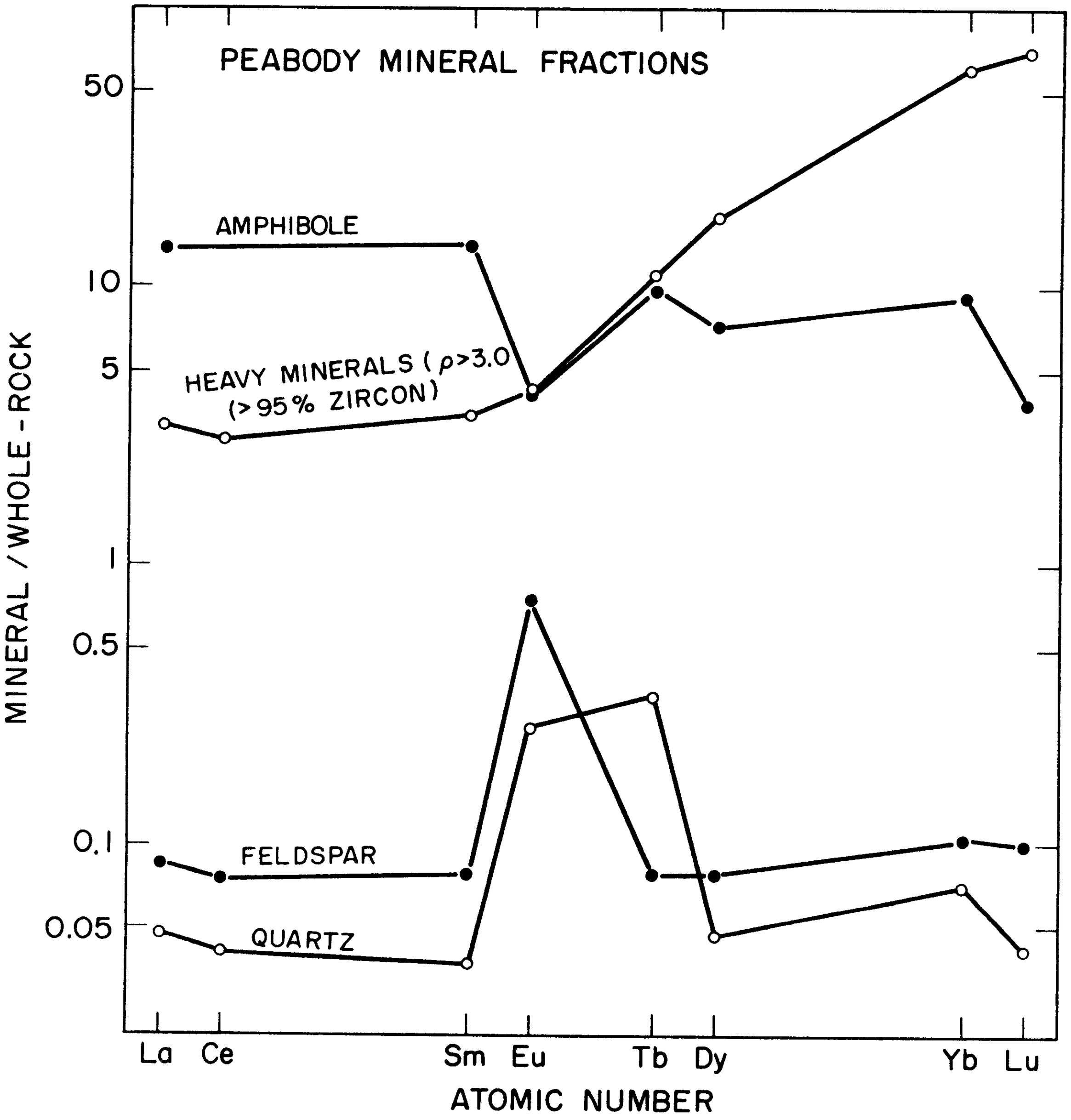

PEABODY MINERAL FRACTIONS
AMPHIBOLE
HEAVY MINERALS (ρ>3.0
(>95% ZIRCON)
FELDSPAR
QUARTZ
50
10
5
1
0.5
0.1
0.05
MINERAL / WHOLE - ROCK
La
Ce
Sm
Eu
Tb
Dy
Yb
Lu
ATOMIC NUMBER

Fig. 5. Rare-earth abundances in selected mineral fractions from Quincy granite normalized to whole-rock.

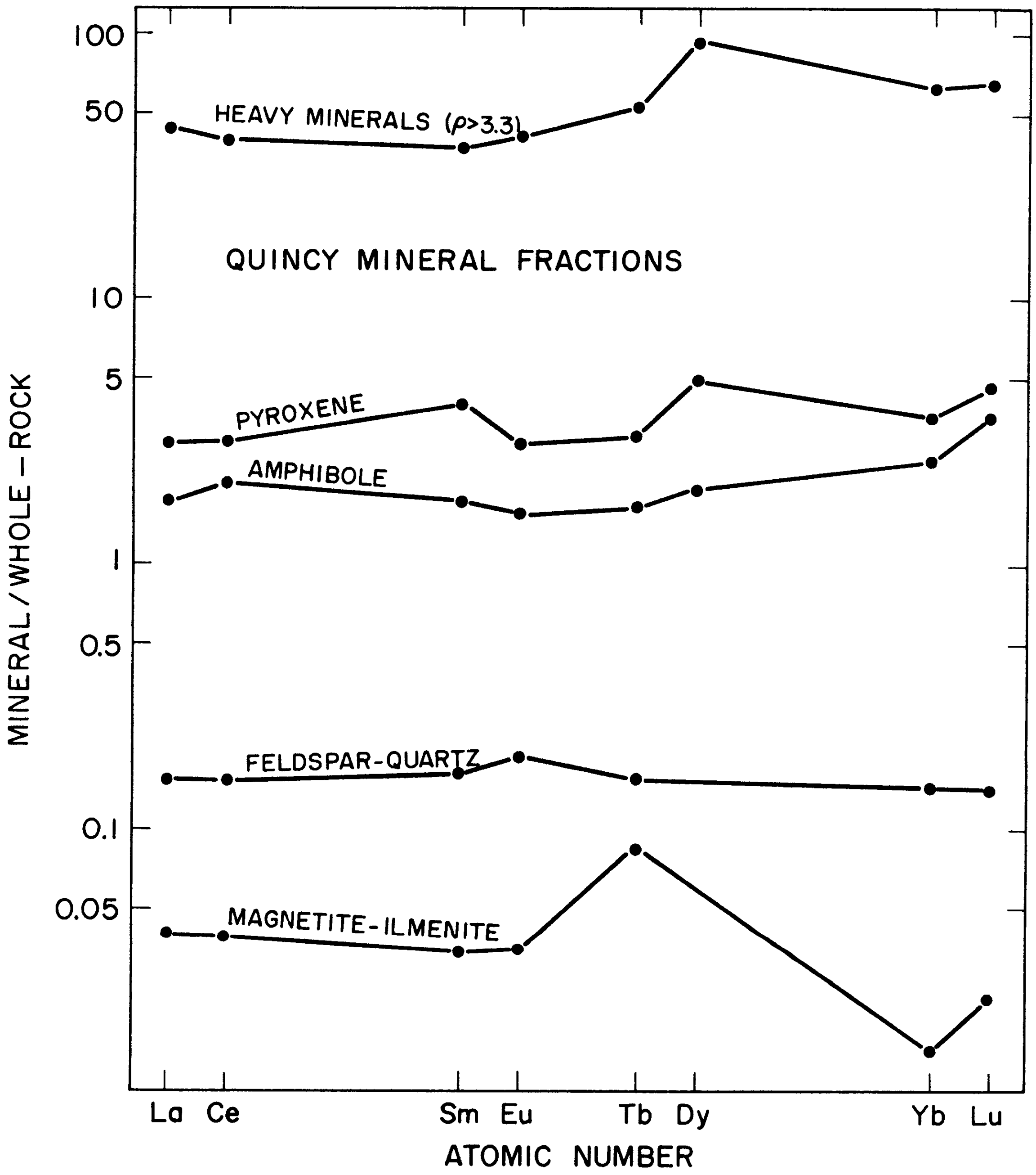
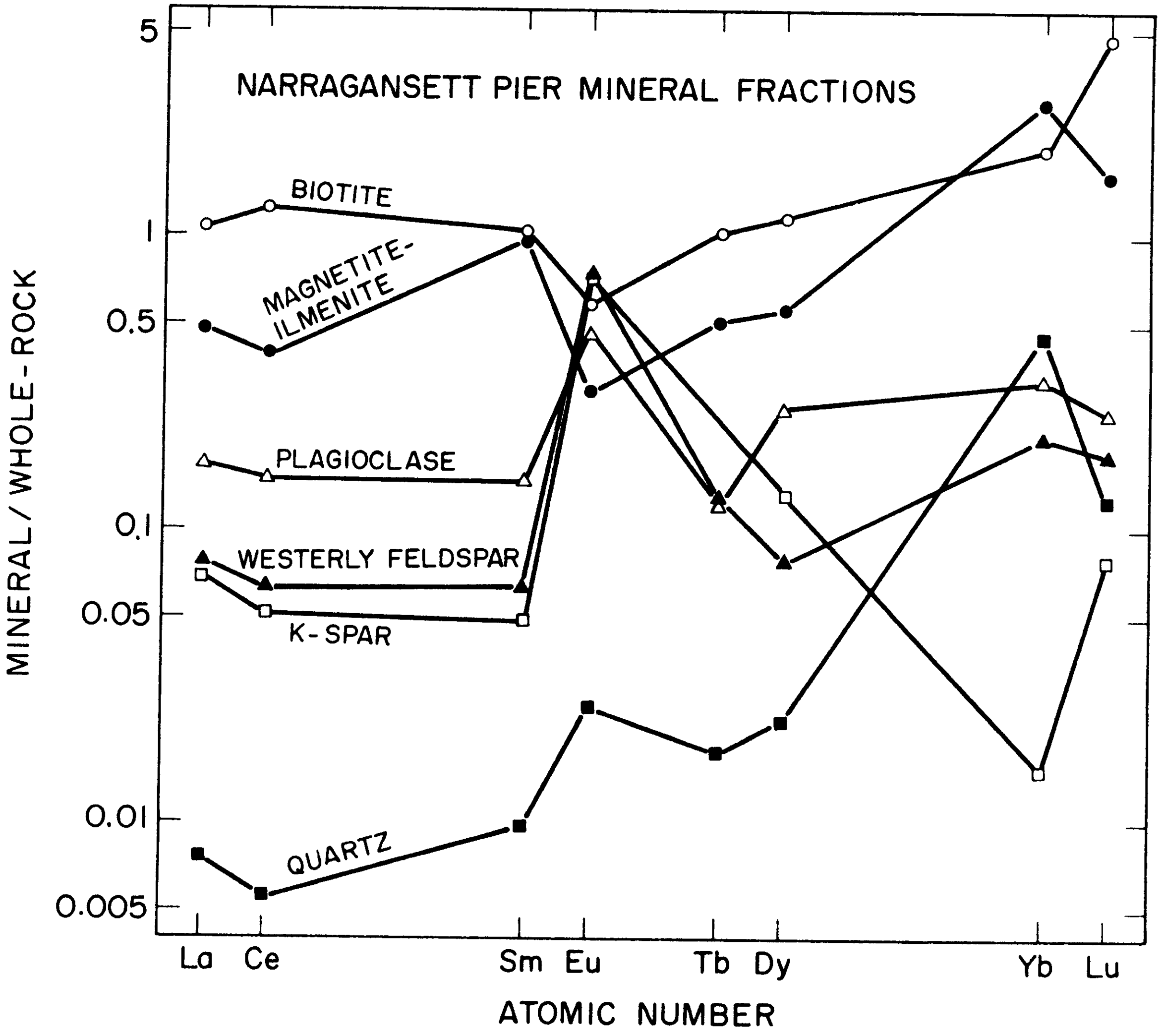

100
50
10
5
1
0.5
0.1
0.05
MINERAL / WHOLE - ROCK
HEAVY MINERALS (ρ>3.3)
QUINCY MINERAL FRACTIONS
PYROXENE
AMPHIBOLE
FELDSPAR-QUARTZ
MAGNETITE-ILMENITE
La
Ce
Sm
Eu
Tb
Dy
Yb
Lu
ATOMIC NUMBER

Fig. 6. Rare-earth abundances from Narragansett Pier granite normalized to whole-rock. Included is a feldspar fraction from Westerly granite. The absolute abundances of the magnetite-ilmenite fraction are uncertain, but the relative values should be good.


NARRAGANSETT PIER MINERAL FRACTIONS
BIOTITE
MAGNETITE-ILMENITE
PLAGIOCLASE
WESTERLY FELDSPAR
K-SPAR
QUARTZ
MINERAL / WHOLE - ROCK
5
1
0.5
0.1
0.05
0.01
0.005
La
Ce
Sm
Eu
Tb
Dy
Yb
Lu
ATOMIC NUMBER

the melt resulting from the crystallization of zircon. Such a depletion argues against contamination of the amphibole by zircon. An examination of Th/Zr ratios also supports this argument (Adams et al., 1959). (Appendix 2)

The heavy mineral fraction from the Quincy, on the other hand, although predominantly zircon, also contained considerable amounts of parisite and synchisite, both of which concentrate light REE (Fleischer, 1965). This might explain the much less pronounced enrichment in heavy REE compared with the heavy mineral fraction from the Peabody.

The mafic minerals from the Quincy are slightly enriched in the heavy REE, which agrees with the findings of others (Towell et al, 1965). This is probably the normal trend for mafic minerals, because these mafics crystallized before the zircon as explained earlier. The negative Eu anomalies in the mafic minerals are a result of the concentration of Eu in feldspars as shown in fig. 7. Notable is the marked difference in size of the Eu anomaly from the Quincy feldspar fraction and that from the other feldspar fractions.

The mineral fractions from the Narragansett Pier granite exhibit much more pronounced relative fractionation of the REE, with all of the fractions behaving in the classical manner which one would expect. This behavior is undoubtedly due to the presence of water allowing an increased degree of equilibration. Here, for example, is field illustration of the work of Schnetzler and Philpotts (1970) showing an increased positive Eu anomaly with decreasing An content of feldspars. (The Westerly feldspar fraction is mostly K-spar.)

Quartz might serve well as an indicator reflecting the composition of the late stage magma, because it contains so little RE and it is not likely that REE substitute into the structure, but are probably concentrated in fluid inclusions. The RE distribution of the Peabody quartz fraction does not vary much from the whole-rock distribution; the Eu anomaly probably arises from feldspar contamination. The Narragansett Pier quartz fraction shows a marked enrichment in the heavy REE. Before this kind of data can be used as evidence of the composition of late stage fluids, more work must be done to determine the exact nature of the inclusions in the quartz. Examination of the Th/Zr ratios argue against contamination of the quartz by zircon (Adams et al., 1959). (Appendix 2)

It is possible that magnetite might be used in a manner similar to the quartz, but again one must determine the nature of the occurrence of lanthanides in magnetite. The RE distribution of the magnetite fraction from the Quincy granite is not much different from that of the whole rock.

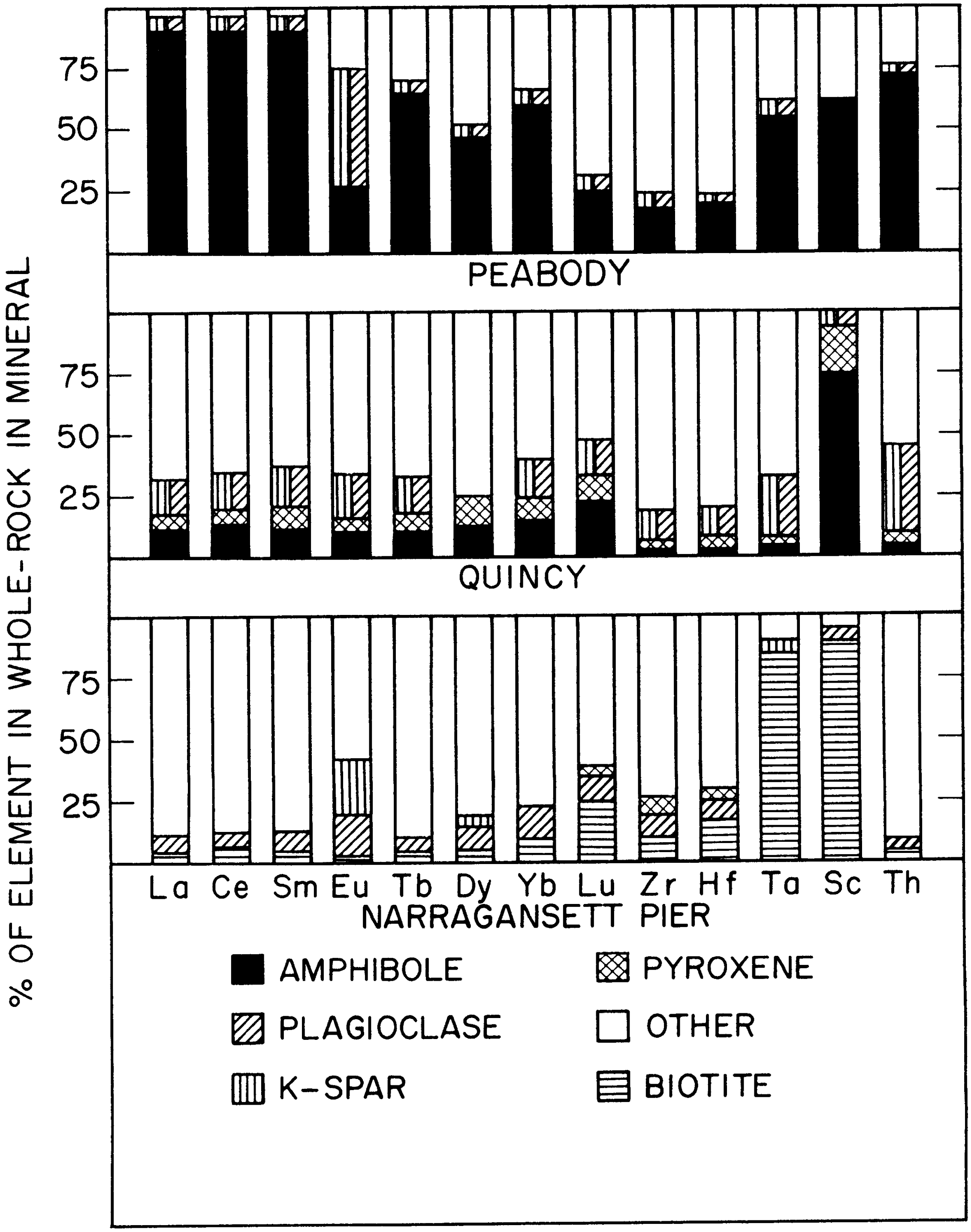
This is certainly what one would predict, knowing that the magnetite crystallized early. The RE distribution of the magnetite fraction from the Narragansett Pier granite, on the other hand, is enriched in the heavy REE similar to the quartz fraction. It is not clear in this case whether this distribution is a reflection of the late-stage fluids or merely a result of the magnetite replacing biotite. In any case the RE distributions of both quartz and magnetite do vary considerably.

The smooth distribution of Eu in the heavy minerals from the Peabody granite and the very small Eu anomaly in the feldspar from the Quincy granite suggest that the large depletion in Eu shown by the whole-rock was already characteristic of the melt by the time these minerals began crystallizing.

There is no ready explanation for the Tb anomaly in the quartz fraction from the Peabody granite and the magnetite fraction from the Quincy granite.

Figure 7 shows the percentages of the whole-rock abundance of each element in the various minerals. In the Peabody granite, amphibole dominates the distribution of REE except for Eu which is concentrated in the feldspar. The Quincy and Narragansett Pier distributions are dominated by accessory minerals. Feldspars are more important than

Fig. 7. Percent of elements in whole-rock in each mineral fraction. The Ce value in the amphibole fraction from the Peabody granite was extrapolated from the La and Sm values. The following values were determined by subtraction from other values listed because the analytical results were known to be high: Ta and Sc in biotite from Narragansett Pier, and Sc in amphibole from Quincy granite. Values $< 2.5\%$ are not shown.


% OF ELEMENT IN WHOLE-ROCK IN MINERAL
75
50
25
PEABODY
75
50
25
QUINCY
75
50
25
La
Ce
Sm
Eu
Tb
Dy
Yb
Lu
Zr
Hf
Ta
Sc
Th
NARRAGANSETT PIER
AMPHIBOLE
PYROXENE
PLAGIOCLASE
OTHER
K-SPAR
BIOTITE

In the Peabody granite and pyroxenes are less important than even feldspar.

Zirconium and hafnium:

The geochemistry of Zr and Hf has been reviewed in a compilation by Vlasov (1964). These two elements are useful because they are almost identical in size, and any process capable of separating them would have to be associated with minor differences in their chemistry.

The whole-rock Zr/Hf ratios are nearly constant. The ratios are determined by the zircons which contain the major portion of both elements in the rocks. The values are in good agreement with those found by other investigators (Vainshtein et al., 1959 and Kosterin et al., 1960). It will be noticed that $Zr/Hf_{\text{Peabody}} > Zr/Hf_{\text{Cape Ann}}$ and $Zr/Hf_{\text{Westerly}} > Zr/Hf_{\text{Narragansett Pier}}$ indicating that Zr/Hf ratios increase toward the end of the magmatic process. This is in agreement with the findings of others (Gerasimovskii et al., 1962). It should also be noted that the whole-rock abundances of Zr and Hf shown in table 3 follow the same bimodal distribution as the heavy REE. This suggests that the enrichment of Zr and Hf may be affected by the same mechanism which caused the enrichment of the heavy REE.

The Zr/Hf values for the three groups of mineral fractions are given in tables 4, 5 and 6. As has been found by other investigators (Vlasov, 1964), a considerable amount of Hf is dispersed among the mafic minerals. The feldspars show some preference for Zr over Hf. Quartz shows significant enrichment in Hf. On the basis of ionic size, it is not likely that these elements substitute into the structure of quartz, but are probably concentrated in the inclusions. Magnetite is the only mineral that shows any significant variation. In the Narragansett Pier, where magnetite is considered to have crystallized out late, it is enriched in Hf similar to biotite and quartz; however, in the Quincy, where it crystallized early, it is enriched in Zr similar to feldspar. This could indicate that the Zr/Hf ratio changes during crystallization.

Realizing that feldspars crystallized early, the above description appears to indicate that the early magmas all had high Zr/Hf ratios which were lowered considerably by the precipitation of zircon, leaving a late stage fluid enriched in Hf. Such an interpretation, however, would require the removal of Zr from the magma. If Zr were indeed removed from the magma by some late stage process, one would expect to find high Zr/Hf ratios in granite pegmatites, but instead one finds just the opposite

(Vainshtein et al., 1959, and Lyakhovich and Shevaleevskii, 1962).

Perhaps a better explanation of the high early ratios is that they reflect the greater stability of Hf complexes relative to those of Zr (Kukharenko et al., 1960), rather than the relative abundances in the melt. If this were the case one would expect to see anomalously low Hf abundances in feldspars and Quincy magnetite rather than high Zr values. Examination of tables 4, 5 and 6 shows that this is indeed the case.

Tantalum:

Little new information has been added to the accumulated knowledge of Ta geochemistry since the study of Rankama (1944). A more recent summary of Ta geochemistry can be found in Vlasov (1964). Tantalum has generally been considered to be enriched in residual liquids (Rankama, 1944), forming complexes such as TaF_5. This observation is confirmed by the whole-rock data shown in table 3 for the Westerly and Narragansett Pier granites. The Cape Ann and Peabody values however, are identical. These whole-rock values also appear to agree well with those of others (Rankama, 1944 and Vlasov, 1964).

Tantalum also seems to follow the bimodal distribution between the two groups of rocks, similar to that observed for the heavy REE. This could be an indication that Ta and heavy REE abundances were controlled by similar mechanisms. It should be noted that the Narragansett Pier, which is most depleted in heavy REE is also most depleted in Ta, and the Quincy, which is most enriched in the heavy REE is also most enriched in Ta. The formation of Ta-halide complexes and the concentration of Ta in garnet, zircon and melanocratic minerals is discussed by Vlasov (1964).

Enrichment of Ta in residual liquids is not strictly true for problems of paragenesis. Znamenskii (1962 and 1957) has found micas to be the principal concentrators of Ta, and this observation is born out by the data shown in fig. 7. Magnetite which formed early in the Quincy granite does not contain much Ta, but magnetite replacing biotite in the Narragansett Pier granite contains considerably more. Most of the Ta is found dispersed among the mafic and heavy minerals in the same fashion as the heavy REE, and is in agreement with the findings of others (Vlasov, 1964).

From the evidence presented thus far, it appears that the same principles which govern the behavior of the heavy REE during the magmatic process may be applied to Ta also with respect to the whole-rock behavior; the crystallochemical effects, however, must be modified to account for the difference in size and charge.

It is to be noted that Ta seems to prefer K-spar to plagioclase and pyroxene to amphibole in these rocks. The preference for K-spar is probably just a reflection of K-spar crystallizing later than plagioclase; however, the preference for pyroxene over amphibole is probably due to a crystallographic preference and agrees with the data of Kukharenko et al. (1961).

Scandium:

The geochemistry of Sc has been summarized by Norman and Haskin (1968). The crystal chemistry of Sc is discussed by Frondel (1968). The data presented here confirm their conclusions, and are in good agreement with the findings of other investigators (Borisenko, 1959).

The abundance of Sc usually reflects the abundance of mafic minerals which concentrate Sc (Vlasov, 1964). The data shown in fig. 7 seem to confirm this idea, however, an attempt to correlate whole-rock Sc abundances in these rocks with modal abundance of mafics fails because of the marked depletion of Sc in the Quincy granite.

Scandium is not found in feldspars, probably due to crystallochemical reasons (Norman and Haskin, 1968). Its low abundance in quartz and the heavy mineral fraction of the Quincy granite indicate that it was depleted in the late stage fluids. Although Sc may be found concentrated in some pegmatite veins, this does not refute the above argument. Several mechanisms are available to explain such concentrations, given the above conditions (Vlasov, 1964; Schaller et al., 1962 and Neumann, 1961). The occurrence of Sc in the magnetite fraction of the Narragansett Pier granite is probably a reflection of its concentration in the biotite which the magnetite is replacing. The abundance of Sc in the heavy mineral fraction of the Peabody granite demonstrates its ability to substitute ismorphously for Zr in the zircon structure (Vlasov, 1964). The low Sc abundances in the pyroxene and amphibole fractions of the Quincy granite probably indicate that the abundance of Sc was low in the initial melt.

According to Vlasov (1964) Sc is quite mobile during post-magmatic alteration processes. There is some evidence, such as riebeckite replacing aegirite (Appendix 1 fig. H), that such a process might have been responsible for the marked depletion of Sc in the Quincy granite.

Thorium:

The geochemistry of Th is discussed by Rogers and Adams (1969) and Adams et al. (1959). The crystal chemistry of

Th has been discussed by Frondel (1956). The values for the whole-rock analyses presented here are in good agreement with the data of other investigators (Rogers, 1963). The value for the Narragansett Pier granite seems quite high but is comparable to that of the Conway granite in New Hampshire (Adams et al., 1962 and Rogers et al., 1965), also a young granite (Triassic) (Toulmin, 1961).

According to Rogers and Adams (1969), in a large number of differentiation sequences described by Peterman, there was only one in which the Th content decreased towards the younger rocks. This observation is confirmed by the Th values for the Peabody and Cape Ann granites, but not by those from the Westerly and Narragansett Pier granites. Other such reversals of the normal trend have been reported (Larsen and Gottfried, 1960).

According to Rogers and Adams (1969) "The tendency of Th to be incorporated in primary minerals in igneous rocks reduces its ability to concentrate in late-stage fluids." This effect could be enhanced even further by the formation of thorite (Ahrens et al., 1967). Mass balance calculations show that for the Peabody granite > 75% of the Th is in the rock forming minerals, however, in the Quincy granite only ≈ 44% of the Th is in the rock-forming minerals, and in the Narragansett Pier granite only ≈ 10% of the Th is accounted for in the rock forming minerals. At the same time the abundance of accessory minerals such as monazite, allanite, thorite and etc. increases in the order: Peabody < Quincy < Narragansett Pier. If thorite is controlling the abundance of Th in the sub-alkaline group then the data could be explained simply by a lower abundance of that mineral in the Westerly than in the Narragansett Pier (Feininger, 1964). This could result if during differentiation in the magma chamber, thorite began to form and during segregation remained with the more crystalline portion of the magma which was eventually intruded as the Narragansett Pier granite while the more fluid portion, relatively depleted in Th but enriched in the other trace elements, was intruded pene-contemporaneously as the Westerly granite (Quinn, et al., 1957).

The same bimodal distribution of Th between the two groups is apparant, but the magnitudes are opposite to those of the other trace elements. This is probably a reflection of the difference in the abundance of high-thorium accessories such as thorite. The credibility of the "thorite hypothesis" is enhanced by the high Th/U ≈ 12.5 for the Westerly granite (Flanagan, 1969 and Ahrens et al., 1967) because thorite type minerals have high Th/U ratios.

The constant ratio of K/Th ≈ 3000 for igneous rocks and sediments has been noted by Heier and Rogers (1963) and Pliler and Adams (1962) respectively. According to this criterian the data for the alkalic group appears normal, but the sub-alkaline group are considerably enriched in Th as was discussed earlier. The marked enrichment in the Narragansett Pier relative to the Westerly is another point in favor of the "thorite hypothesis".

The mineral fraction data are given in tables 4, 5 and 6. Notable is the lack of Th in quartz indicating its depletion in the late stage fluids as discussed above. This claim is further substantiated by the low Th/U ratios for quartz reported by other investigators and summarized in Rogers and Adams (1969). The absolute abundances reported here for quartz are in good agreement with the findings of others as well as most of the abundances reported for the other mineral fractions (Rogers and Adams, 1969). The values for the amphibole fraction from the Peabody granite and the biotite fraction from the Narragansett Pier granite are high compared to the values compiled by Rogers and Adams. The ranges which they report for these two minerals are as follows: biotite 0.5--50 ppm and hornblende 5--50 ppm.

The value for the magnetite fraction from the Narragansett Pier is high probably because it is replacing biotite. The biotite is high because it crystallized early and because of the mutual substitution capabilities between Th^{+4} and Fe^{+3} (Frondel, 1956). Not much Th is contained in feldspars and the nature of the occurrence of what Th is found in feldspars is not certain (Rogers and Adams, 1969). The Th concentration in the feldspars from the Quincy granite is probably a result of rapid crystallization (Adams et al., 1959). The preference of Th for Ca sites as discussed by Frondel (1956), however, is apparant from the relative concentrations in plagioclase and K-spar fractions from the Narragansett Pier granite. The heavy mineral fractions are high because of the close geochemical coherence of Th^{+4}, Ce^{+4} and Zr^{+4}. The higher value for the heavy mineral fraction from the Peabody is a result of two things: (1) The heavy mineral fraction from the Peabody is almost pure zircon while that from the Quincy contains considerable parisite and synchisite. Due to a greater similarity in size and charge, Th^{+4} can more easily replace Zr^{+4} in zircon than any of the trivalent REE in parisite and synchisite. (2) The zircons in the Peabody crystallized earlier than the heavy minerals from the Quincy.

APPLICATIONS OF TRACE ELEMENT DATA TO THE ORIGIN OF GRANITES

The origin of granitic rocks is a long-standing controversy (Turner and Verhoogen, 1960). There are essentially two things to consider in the case of magmatic rocks, such as the ones described in this paper: the source of parent material and differentiation of that material to form a granite. There are essentially two possible sources of parent material from which a magma could be derived: upper mantle material or deeply buried crustal rocks. The possible differentiation processes include complete fusion of source material followed by fractional crystallization, partial melting of parent material or both. The formation of a granite by fractional crystallization from a basaltic magma is discussed by Bowen (1928) and the production of a basaltic magma from upper mantle material is discussed by Green and Ringwood (1967 and 1967a).

Fractional Crystallization of basalt:

Both groups of granites studied in this paper exhibit Eu anomalies as mentioned earlier. The selective removal of Eu is consistent with the theory of a mantle derived granite, because basalts contain a large amount of feldspar. The size of the Eu anomalies, however, is a matter of additional concern if fractional crystallization is to be called upon for differentiation of the magma. The following formulation describes the degree of fractionation that will occur between two elements during fractional crystallization (Schilling and Winchester, 1967):

$C_{Sm,L}/C_{Eu,L} = (C_{Sm,A}/C_{Eu,A})(1-X)^{D(Sm)-D(Eu)}$

where $C_{Sm,L}$ = concentration of Sm in the residual liquid

$C_{Sm,A}$ = average Sm content of the system.

X = fraction that has crystallized.

$D(Sm)$ = Partition coefficient of Sm between solid and liquid phases.

The granite data presented here was subjected to this treatment. In the case of the granites considered here it was necessary to use the average of the Sm and Tb distributions to take into account the slope of the chondrite normalized RE distribution. The value of 0.03 was used for D(Sm) and D(Tb) in plagioclase (Schnetzler and Philpotts, 1970). A limiting value of 0.438 was used for D(Eu) in plagioclase (Schnetzler and Philpotts, 1970). The following results were obtained which indicate the percent of parent magma of chondritic composition that would have to crystallize as feldspar to account for the observed Eu anomaly:

Peabody - X = 96.4%

Cape Ann - X = 94%

Quincy - X = 99.3%

Narragansett Pier - X = 77%

Westerly - X = 80%

If data on the Skaergaard intrusion (Haskin, 1968a) is subjected to the same treatment, 55% of the "chilled marginal gabbro" is required to crystallize as feldspar to account for the observed Eu anomaly in the "transgressive hedenbergite granophyre". Assuming a parent basalt with $\approx$ 17% Al_2O_3 (Wager and Brown, 1968), and a feldspar composition ($\approx$ An_{90}) which will allow the maximum amount of feldspar to crystallize from the parent, mass balance calculations indicate that no more than 62% of the parent basalt could crystallize as feldspar.

The results of these calculations agree well when applied to the Skaergaard intrusion, but it is clear that such a one step model is not adequate for the granites studied here. The above calculations do agree, however, if several steps are considered in the differentiation process, which result in parent liquids of different compositions than the original magma. Such a process might involve liquid immiscibility (Philpotts, 1970) or a stepwise fractional crystallization sequence (Zielinski and Frey, 1970).

Regardless of the model employed, the above calculations will agree in the case of the alkaline granites only if the granites represent a very small percentage of the parent magma. The available field evidence does not indicate that such is the case.

Partial melting:

A model involving partial-melting or a combination of partial-melting and fractional crystallization might be more reasonable (Gast, 1968). Such a model would require that the parent material for the alkaline group contain feldspar. This rules out upper mantle material as a possible direct source.

Whether one accepts the trace element distributions of chondrites, basalts, or sediments (Haskin et al., 1966a) as representative of the source material from which these five granites were derived, it is evident from the RE distributions that the sub-alkaline rocks are the more highly fractionated and that the relative depletion of heavy REE must be explained. When the RE distributions of all five granites are compared to those in fig. 1, again the sub-alkaline group deviates from the average granites. This implies that either the source material or the crystallization history or both were different for the sub-alkaline group than for the alkaline group.

One method of explaining the depletion of heavy REE is the presence of a phase such as garnet or zircon, which concentrates heavy REE (Lyakhovich, 1962). Garnet is a good choice because it is present in upper mantle material such as eclogite, and in metamorphosed sediments of the area (Quinn, 1963). From Whitney (1969 a melting range of 700-900°C seems reasonable. From Wones and Eugster (1965) a range of $10^{-22} < \log f_{O_2} < 10^{-9}$ is apparant. Under these conditions it is reasonable to expect garnet to be stable (Hsu, 1968). The existence of denser material underlying the Peabody granite has been substantiated by geophysics as discussed earlier. It is immaterial whether the garnet participates as a residue during partial melting or crystallizes early and settles out of the magma, as the result is the same--the residual liquid is depleted in heavy REE.

Using the distribution coefficients given by Gast (1968), it could be argued that the RE distributions in the sub-alkaline group are similar to what would be expected from partial melting of a parent material containing garnet. This could be either upper-mantle material or crustal material.

Although zircons are a less likely choice, they must be considered because they are present as a phase in all five granites. Quinn (1943) has reported crystal settling of zircons in the Westerly granite. The modal abundance of zircons in the sub-alkaline rocks is less than in the alkaline rocks as mentioned earlier. Perhaps the higher f_{H_2O} during crystallization of the sub-alkaline rocks resulted in a more fluid magma which allowed zircons to settle out. If the whole-rock RE values of the Peabody granite were assumed to be representative of the melt from which the Westerly granite was formed, and zircons of the same RE composition as those from the Peabody granite began to precipitate from the assumed melt, the precipitation and removal of ≈ 1.39% of the assumed melt as zircon would be sufficient to account for the difference in heavy RE abundances between the Westerly and Peabody granites. Objections may be raised to such an argument on the grounds that the zircons may never reach a size large enough to allow them to settle out of a silicate melt. More data is needed, however, before this claim can be substantiated. (See Shaw, 1965)

A better model than crystal settling of zircons, might involve partial melting of parent material containing zircons. Zircons are more refractory than garnets (Hsu, 1968 and Weast, 1968). The greater depletion of heavy REE in the sub-alkaline group might be due to partial melting of parent material that contained a greater amount of zircon than the parent material from which the alkaline rocks were derived. Crustal derived material generally contains more zircons than material derived from the upper-mantle.

The lower abundance of Zr and Hf in the sub-alkaline rocks relative to the alkaline group bolsters the argument that zircon may have participated in differentiation of the sub-alkaline rocks. Tantalum is known to be concentrated in both zircon and garnet (Vlasov, 1964) and thus the bimodal distribution of Ta would agree well with all models just discussed. Scandium is not affected because it is dispersed among the rock-forming minerals. The bimodal distribution of Th abundances is controlled by the modal abundance of high Th minerals such as thorite.

The influence of volatiles:

Another mechanism, which is independent of the source mechanism, for removal of heavy REE, is removal in late stage volatiles (Beeson and Goles, 1970). Mineyev (1963) has established the greater mobility of the heavier REE due to the greater stability of their complexes relative to those of the lighter REE. Petrographically, the fine grained texture of the sub-alkaline granites implies rapid cooling, probably at a rather shallow depth (Feininger, 1964). Under these conditions it is conceivable that a considerable amount of the heavy REE could be carried off in the escaping volatiles (Nagasawa, 1970). If this is indeed the case one would expect the pegmatites to be enriched in heavy REE. According to Kalita (1959) the latest stage of fluids that formed the pegmatites of northwestern and southwestern Karelia were enriched in the heavy REE.

On the other hand, the more coarse grained alkaline rocks probably crystallized more slowly and at a greater depth than the sub-alkaline rocks. In addition to these physical factors, it has already been established that the alkaline rocks probably crystallized under much dryer conditions than the other two granites--a factor which could contribute to a more alkaline chemical environment as reflected in the presence of peralkaline minerals (Toulmin, 1958). This interpretation is also in agreement with the data of Hemley (1959). It is known that RE complexes tend to break down in an alkaline environment (Ahrens, 1964) and this could result in a greater retention of heavy REE.

Zirconium and Hf are also known to form halide complexes, and their abundances could be explained by this mechanism also. According to Tugarinov et al. (1956), fluoride complexes of Zr are more stable than those of Hf. Butler and Thompson (1965) have suggested that due to the large difference in the atomic weights, a model involving gaseous diffusion could result in a greater mobility for Zr. On the basis of these two facts the removal of proportionately more Zr than Hf from a magma might be possible. In connection with the earlier discussion of Zr/Hf ratios, this argument could be used to indicate that the high Zr/Hf ratios implied for the early magmas were real. Such high initial ratios could be explained by partial-melting of a parent material where some melanocratic mineral such as pyroxene resisted melting, because Hf is known to be concentrated in pyroxene as discussed earlier.

Fluoride complexes of Ta such as TaF_5 have been mentioned earlier. The behavior of Ta in the mechanism under consideration here, would be similar to that of the heavy REE, Zr and Hf. The higher abundance of Ta in the heavy mineral fraction from the Quincy than in the heavy mineral fraction from the Peabody could be used to argue for late stage enrichment of Ta in a volatile phase, because the heavy minerals from the Peabody granite crystallized earlier than the heavy minerals from the Quincy granite. Scandium and Th tend to become dispersed in solid phases rather than being enriched in residual liquid or volatiles, and are therefore unaffected by this mechanism.

Possible sources:

On the basis of present knowledge all of the mechanisms described thus far could operate equally well regardless of the source. Due to large Eu anomalies, it is unlikely that upper mantle material is the direct source of the alkaline granites. The geochemistry of Ta in sediments has not been investigated yet, but the scanty analyses by Rankama (1944) offer no reason to refute a sedimentary origin for any of these granites. The abundance of Sc in sediments and gabbros is comparable, and it does not appear as though Sc could be used to determine whether a granite was derived from gabbroic or sedimentary material.

The Th abundances for sediments (Rogers and Adams, 1969) are a little higher than those for projected upper mantle material (Lovering and Morgan, 1963), but both are quite low compared to granites. The Th/U ratios of both are also quite low. About all that can be said with respect to source of parent material is that the high Th/U ratio and high Th abundances of the sub-alkaline group indicate that they have probably experienced more extensive differentiation than the alkaline group.

Evolution of Quincy granite:

In an earlier section it was implied that the Quincy granite might be different from the Peabody and Cape Ann granites. The description given earlier implied that it may have crystallized under more oxidizing conditions than the Peabody and Cape Ann granites. If this were true, it could account for the small Eu anomaly in the feldspar from the Quincy granite, because the dominant species of Eu in the melt would be Eu^{+3}. Under these conditions, Eu would behave similarly to the other REE. The unusually low abundance of Sc in the Quincy granite was also mentioned earlier. Because Sc tends to become dispersed among the rock-forming minerals, this might be used to argue that the Quincy has undergone more extensive differentiation than the Cape Ann and Peabody granites. The magnitude of the Eu anomaly in the Quincy whole-rock sample is significantly larger than that of any of the other granites. This also could be used to argue that the Quincy has undergone more extensive differentiation than the Cape Ann or Peabody granites.

SUMMARY AND CONCLUSIONS

The heavy REE, Zr, Hf, and Ta all exhibit similar bimodal distributions between the two groups of granites, indicating that they are all responding similarly to certain geochemical conditions.

Two models for the evolution of both groups of rocks are consistent with the trace element data: (1) Partial melting and/or fractional crystallization of some phase such as garnet or zircon which concentrates heavy REE, Zr, Hf, and Ta; (2) removal of these elements in escaping volatiles.

A model involving fractional crystallization exclusively cannot be ruled out but a combination of field evidence and trace element data indicate that such a model is unlikely for the alkaline group.

Large Eu anomalies indicate that parent material for the alkaline group probably contained feldspar and that partial-melting of parent material containing garnet was probably involved. The greater magnitude of the Eu anomaly and depletion of Sc in the Quincy granite indicate that it has undergone more extensive differentiation than the other alkaline rocks.

SUGGESTIONS FOR FUTURE WORK

The next logical step to further understanding of these granites would be the analysis of pegmatite veins to test the theory of volatile transport.

Because the accessory minerals have such a profound influence on the trace element distributions of these rocks, further study of the accessory minerals is warranted. Such a study should include extensive crystallographic studies and quantitative mineral separations.

Because of the variability in trace element distributions in quartz and magnetite, these minerals show promise of being geochemical indicators. For this reason microprobe studies of these minerals are warranted to determine the nature of the trace element occurrences.

A study of the oxidation state of Eu in feldspars from Quincy and Peabody granites could be useful in determining whether or not Eu can be used as an indicator of oxidation potential of a melt. Cathode luminescence may prove helpful in this regard.

It is clear that the geochemistry of Ta in sediments should be investigated.

There is a great deal of work yet to be done on the stabilities of various complex ions and the determination of which complexes could be expected to form in a silicate melt.

In future work it is suggested that the analysis for Dy be abandoned because of the high levels of radioactivity that must be handled to obtain meaningful numbers. Instead of Dy, a later count on a small high-resolution detector (LEPS) could be done to obtain 242-day Gd^{153}. The 103 kev peak can be resolved instrumentally from the 100 kev peak of 115 day Ta^{182} on a small detector.

ACKNOWLEDGEMENTS

I would like to thank especially Professors F. A. Frey and D. R. Wones who inspired this study, for their patience, encouragement, and many valuable comments and discussions. Many helpful conversations were also had with Robert Zielinski, Charles Spooner, Richard Copeland, Don Skibo, John Reid, and Prof. H. W. Fairbairn, of the geology department, and with Prof. W. B. Walters, Prof. G. E. Gordon, W. H. Zoller, P. K. Hopke, E. S. Macias, and Michal Kay of the nuclear chemistry department at M.I.T.

I am indebted to Mr. Y. S. Nikhauj and Prof. R. S. Naylor for their help and for supplying some of the mineral fractions. I also appreciate the help rendered in the laboratory by Mr. L. Lopez.

I am grateful to Julie Golden and the people in Graphic Arts for their help in preparing the figures, and to Mary McIntosh and Maureen Howley for typing the tables. My most sincere gratitude goes to my wife Nancy, who typed the manuscript, for her patience and cooperation.

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APPENDIX 1

Sample Locations:

Three samples were collected from each pluton. An effort was made to get a reasonable geographic distirubiton of sampling sites in order to obtain a representative composition for the pluton as a whole. In each case an attempt was made to sample from a quarry or road cut or location where a fresh, unweathered sample could be obtained. The localities are shown in fig. A and described more fully as follows:

Peabody granite:

P-3 - Near Peabody school in Peabody.

P-4 - Quarry on north side of Rt. 128 approximately 1 mile east of Rt. 1.

P-6 - North side of road cut just off Rt. 128 on the east side of Lynnfield and south side of Suntaug lake.

Cape Ann granite:

C-1 - Road cut north side of Rt. 128 across from Mt. Ann Park.

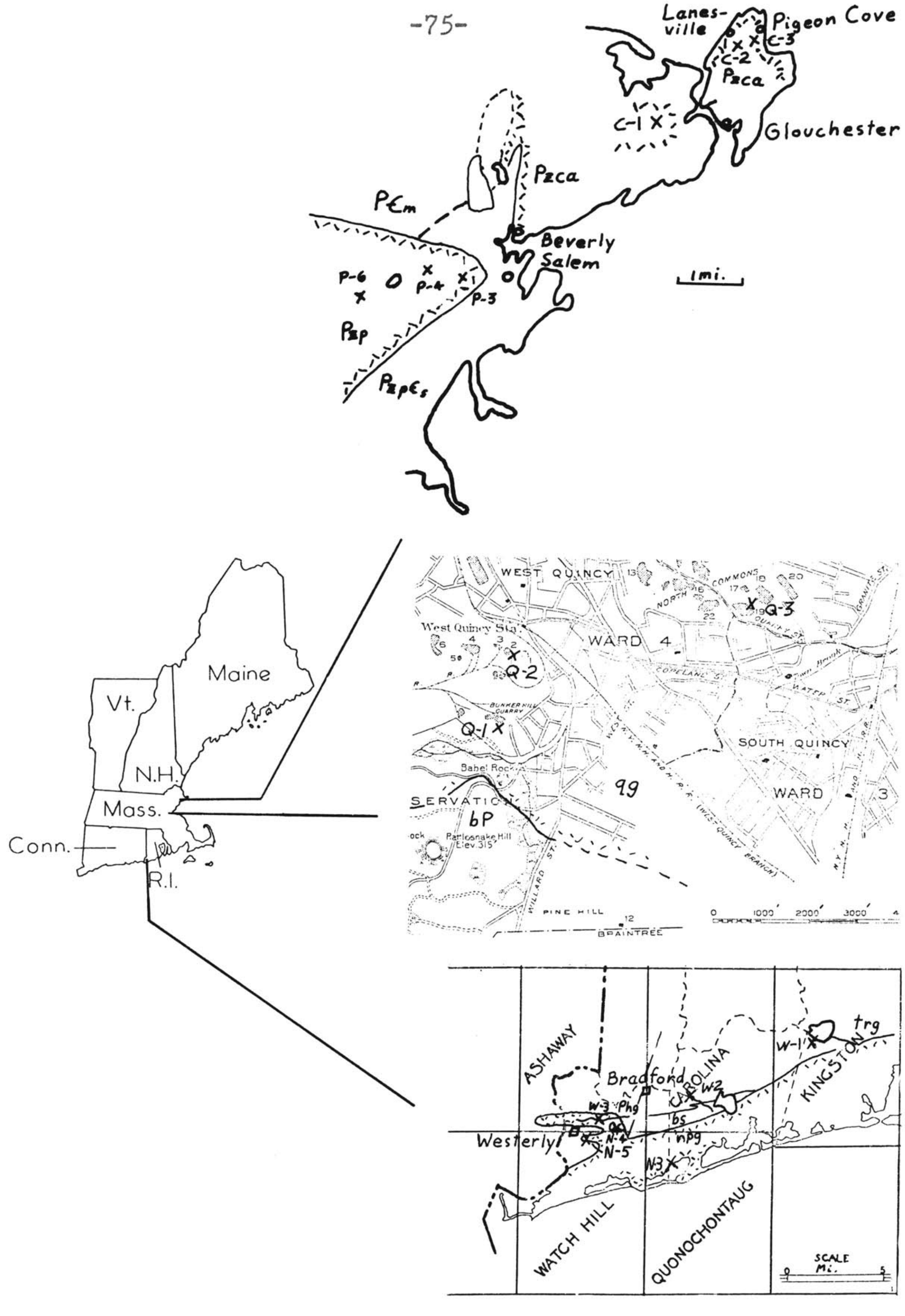
C-2 - Quarry south of Lanesville off High Str. and south of Barker Str.

Fig. A

SAMPLE LOCATIONS

Symbols:

Phg - Hope Valley Alaskite Gneiss
npg - Narragansett Pier Granite
trg - Tenrod Granite
bs - Blackstone Series
Pzca - Cape Ann Granite
P€m - Marlboro Formation
Pzp - Peabody Granite
Pzp€s - Salem Gabbro-Diorite
qg - Quincy Granite
bp - Blue Hills Porphyry
Phg - Potter Hill Granite


Lanes-ville
Pigeon Cove
C-3
C-2
Pzca
C-1
Gloucester
Pzca
P€m
Beverly
Salem
1mi.
P-6
P-4
P-3
Pzp
Pzp€s
Maine
Vt.
N.H.
Mass.
Conn.
R.I.
WEST QUINCY
COMMONS
Q-3
West Quincy Sta.
WARD 4
Q-2
BUNKER HILL QUARRY
Q-1
Babel Rock
SOUTH QUINCY
qg
SERVATION
bP
Rattlesnake Hill Elev 315
WARD 3
PINE HILL
BRAINTREE
0 1000 2000 3000 4
ASHAWAY
Bradford
CAROLINA
KINGSTON
trg
W-1
W2
W-3
Phg
bs
npg
Westerly
N-4
N-5
W3
WATCH HILL
QUONOCHONTAUG
SCALE Mi.
0
5

C-3 - Pigeon Hill quarry at the end of Pigeon Hill Str.

Quincy granite:

Q-1 - Bunker Hill quarry.

Q-2 - Quarry #2 in Dale (1923) near West Quincy Station.

Q-3 - Quarry #19 in Dale (1923) just off Quarry Str. near North Commons.

Narragansett Pier granite:

N-3 - Ellery House belonging to John Wood on the beach just east of the town line between Charlestown and Westerly.

N-4 - Chapman Pond boat landing in Westerly.

N-5 - Approximately ½ mile west of Catto quarry in Westerly.

Westerly granite:

W-1 - A small pit southeast of Worden Pond just off Pond Road.

W-2 - John B. Sullivan quarry (Chayes & Suzuki, 1963).

W-3 - Abandoned quarry. Stop #2 of trip G, N.E.I.G.C. #55, 1963 (Quinn et al., 1963).

Sample Preparation (Whole-rock):

In each case > 10 lb. of rock were collected to insure proper sampling. These samples were broken into chunks that weighed ≈ 1 lb. each. One chunk was chosen and run through two jaw crushers and a pulverizer with great care being taken not to lose any fines or other fractions. The whole sample was saved at all times. The pulverized sample was then run through a sample splitter to get a working size split representative of the whole. Once obtained, this split was ground to a fine powder and homogenized in a pica blender.

Sample Preparation (Mineral separates):

The pulverized whole-rock samples were washed in water and run through seives separating them into fractions: > 35 mesh, < 35 & > 60 mesh, < 60 & > 200 mesh and < 200. Magnetite and ilmenite were then removed from the third fraction by means of a hand magnet. The remainder was run through a Franz isodynamic separator, and several heavy liquid separations. The liquids used were bromoform (G. ≈ 3.0), diiodomethane (G. ≈ 3.3) and clerici solution (G. ≈ 4.0). Portions of spec-pure silica were also run through the same circuit to be analyzed along with the minerals. Prior to analysis, all samples were identified by X-Ray diffraction. A detailed description of the samples follows:

Quincy granite:

All fractions taken from whole-rock #Q-3.

Q-3-A -- Amphibole. Hand picked. +35 mesh. ≈ 99% pure. 0.24591 gm.

Q-3-P -- Pyroxene. Hand picked. +35 mesh. Intergrown with amphibole. ≈ 95% pure. 0.23013 gm.

Q-F -- Feldspar - quartz. ≈ 50% feldspar and 50% quartz with very mild oxide staining. ≈ 99.5% pure. 0.65412 gm.

Q-H -- Heavy minerals (G. > 3.3). X-ray indicates that zircon is dominant with some undetermined contaminant. Some pyroxene and magnetite contamination. 0.06735 gm.

Q-M -- Magnetite - ilmenite. Minor quartz and feldspar contamination and mild oxide staining. ≈ 99% pure. 0.0533 gm.

Peabody granite:

All fractions from whole-rock #P-4.

P-4-A -- Amphibole. Hand purified. -60 mesh. Possible impurities include feldspar, zircon, quartz and pyroxene. 90-95% pure. 0.20258 gm.

P-F -- Feldspar. Fairly homogenous perthitic feldspar with some quartz and minor oxide staining. ≈ 85% pure feldspar. 0.64142 gm.

P-Q -- Quartz. Hand picked. +35 mesh. Very minor magnetite and oxide staining. > 95% pure. 0.12919 gm.

P-H -- Heavy minerals (G. > 3.0). -60 mesh. Almost no opaques. X-ray indicates that zircon is dominant with some undetermined contaminant. > 95% zircon. 0.0721 gm.

Narragansett Pier Granite:

All fractions except quartz fraction were donated by Prof. R. S. Naylor (M.I.T.) and were taken from his sample #RGQ-2, collected at the same site as W-3.

NB -- Biotite. Hand purified. Possible impurities include quartz, feldspar, zircon and white mica. > 99% pure. 0.17471 gm.

NM -- Magnetite - ilmenite. Hand purified. Possible impurities include feldspar, quartz and oxide staining on magnetite. > 98% pure. 0.25775 gm.

NPL -- Plagioclase. Sample labeled "fourth sink" of feldspar separation (R. S. Naylor). -60 mesh

Impurities appear to be largely K-spar and quartz with traces of iron oxide and mica. ≈ 75% pure. 0.65204 gm.

NO_r -- K-spar. Sample labeled "seventh sink" of feldspar separation (R. S. Naylor). Impurities appear to be largely quartz and plagioclase with traces of mica and iron oxide. 85-90% pure. 0.5889 gm.

NQ -- Quartz. Hand picked from whole-rock #N-5. Very minor feldspar contamination. > 99% pure. 0.15225 gm.

Westerly granite:

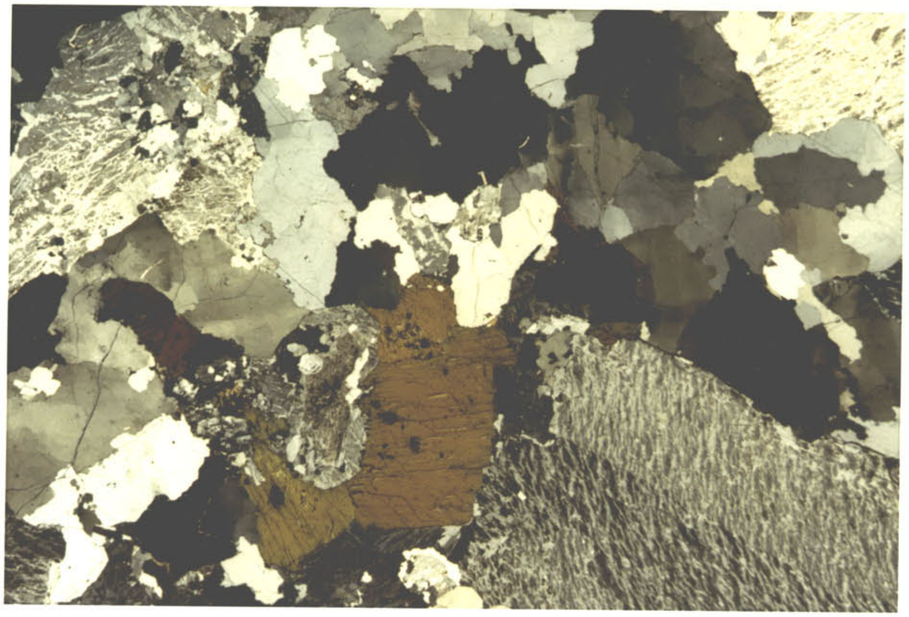
Only one sample which was donated by Prof. R. S. Naylor (M.I.T.) from his sample marked RGQ-1 and collected at the same locality as W-3. Impurities are quartz and iron oxide staining. X-ray indicates that it is mostly K-spar. > 99% pure. 0.65577 gm.

Sample description:

The following pages contain photographs showing the petrographic fabric of each rock and features alluded to in the text. Fig. S shows the compositions of the five granites studied in this paper plotted on a quartz-plagioclase-microcline ternary diagram.

Fig. B. Peabody granite in thin section with crossed nicols. Scale = 14 mm across photo.

Fig. C. Zircons in Peabody granite. Scale = 1.25 mm across photo.



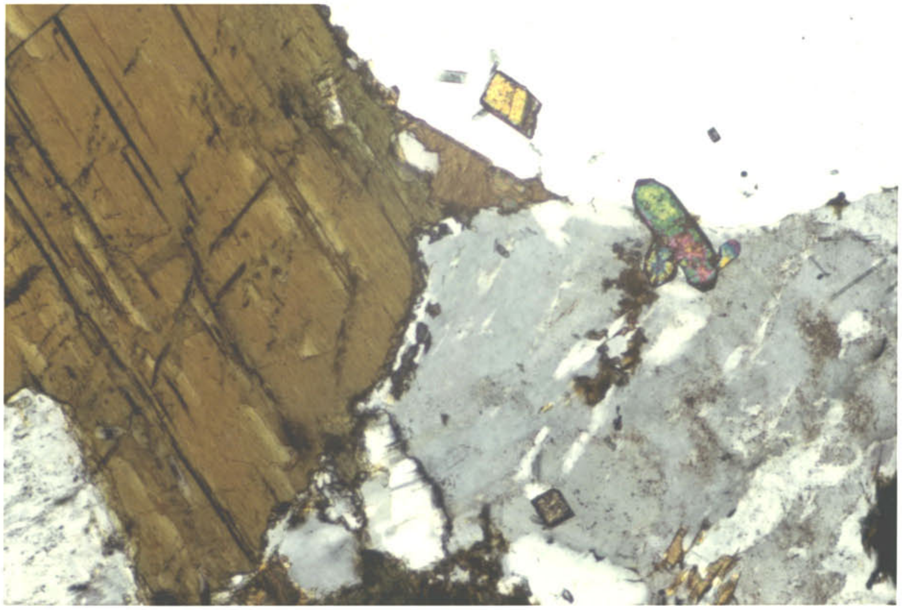
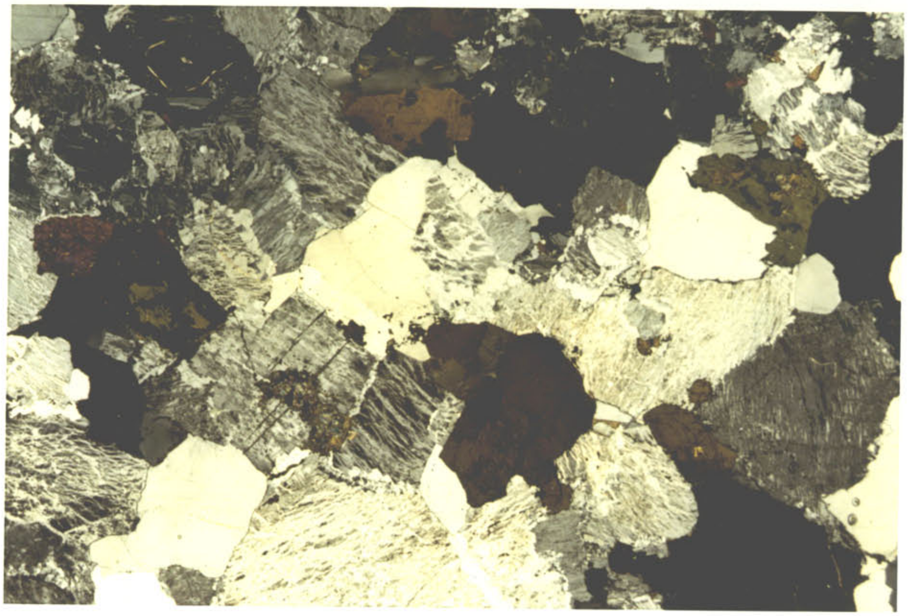


Fig. D. Cape Ann granite in thin section with crossed nicols. Scale = 14 mm across photo.

Fig. E. Amphibole from Cape Ann granite under crossed nicols showing poikilitically enclosed zircons with pleochroic halos. This feature is typical of both Peabody and Cape Ann granites, with the zircons being more abundant in the Cape Ann amphibole than in the Peabody amphibole.



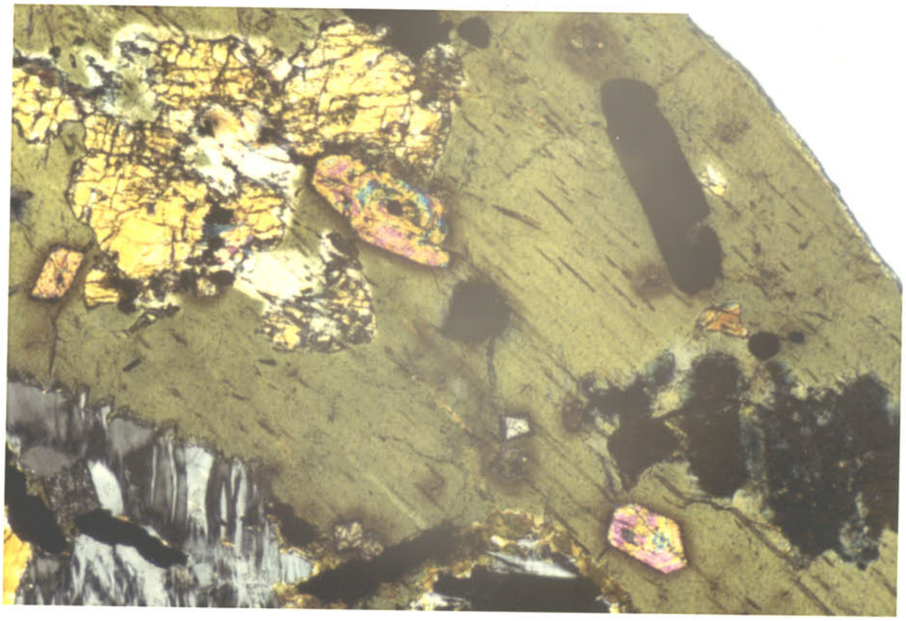
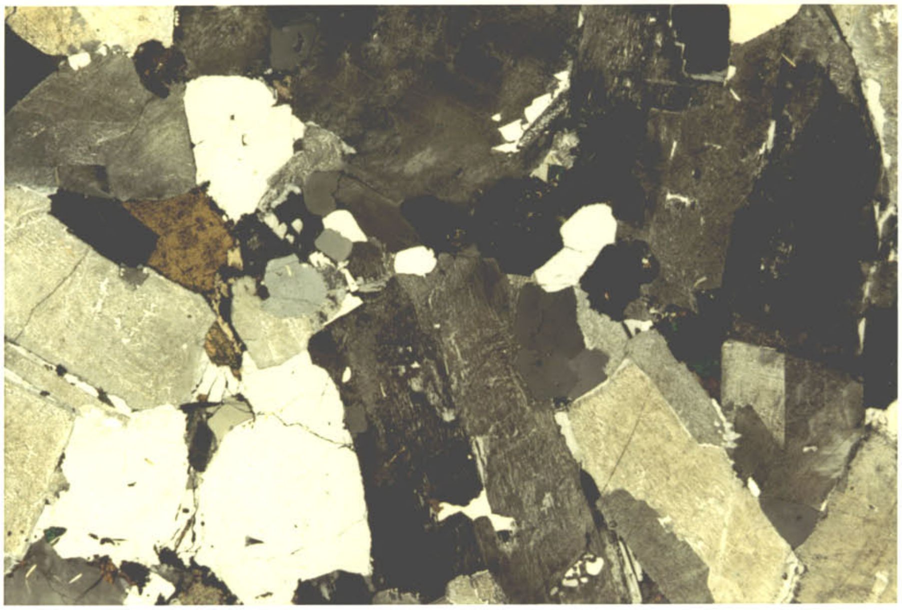


Fig. F. Quincy granite in thin section with crossed nicols. Scale = 14 mm across photo.

Fig. G. Minute inclusions of magnetite in turbid feldspar from Quincy granite. Scale = 0.2 mm across photo.



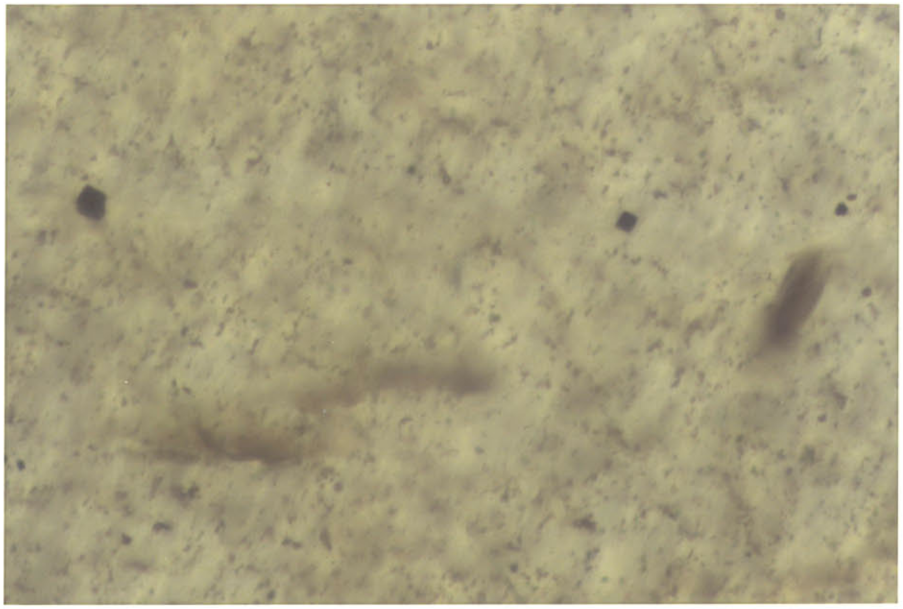
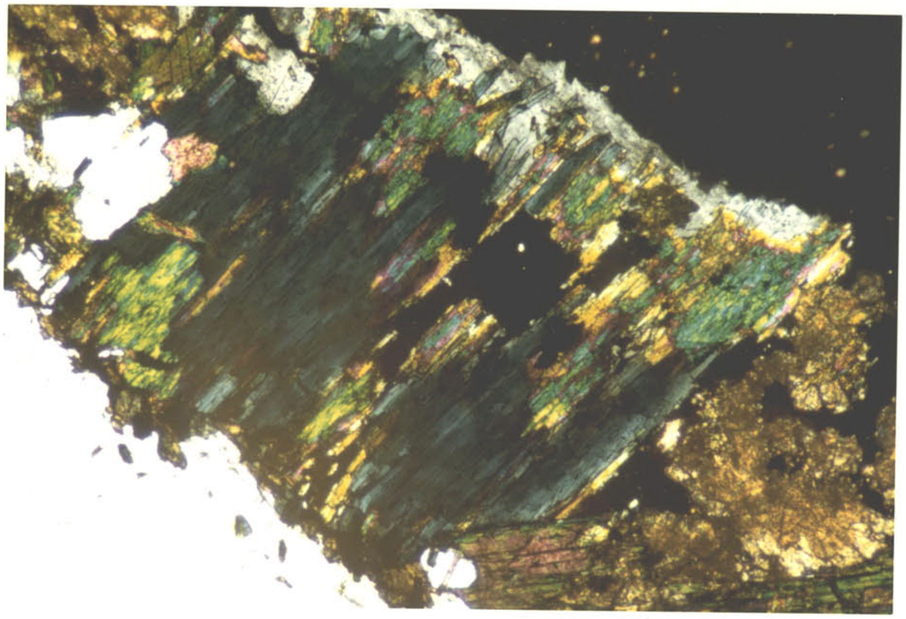


Fig. H. Thin section view with crossed nicols of riebeckite replacing aegirite in Quincy granite. Scale = 1.25 mm across photo.

Fig. I. Thin section view with crossed nicols of parisite and synchisite concentrated along boundaries between grains of feldspar in Quincy granite. Scale = 1.25 mm across photo.



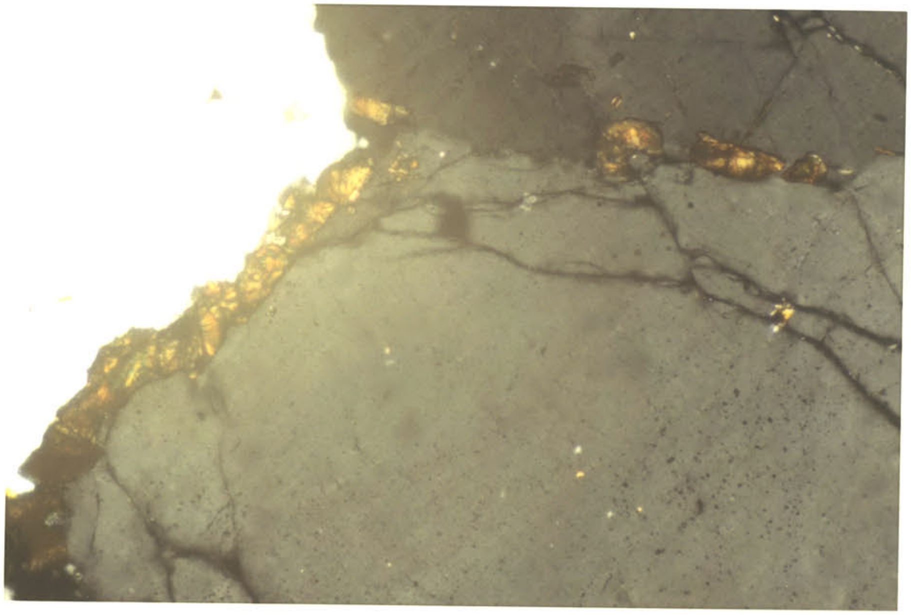
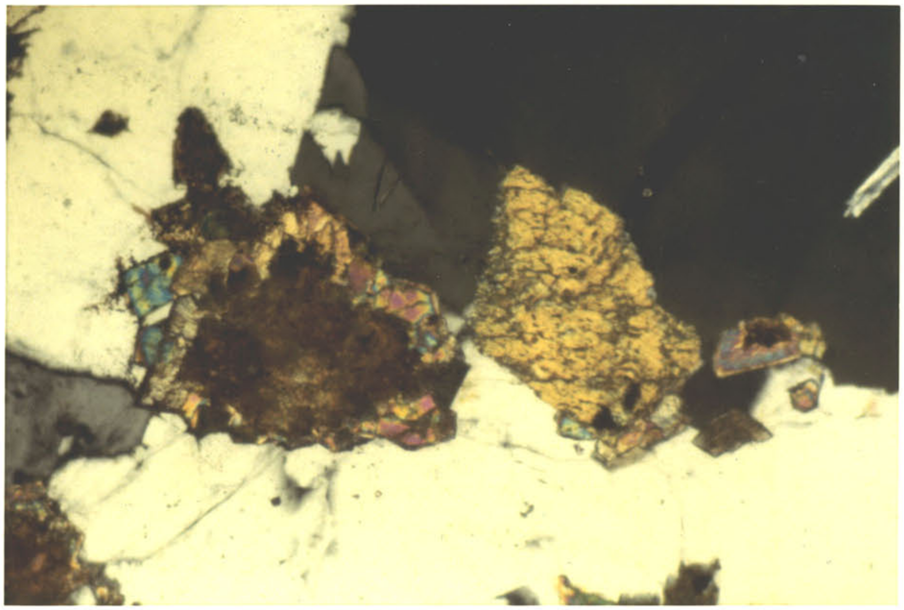


Fig. J. Thin section view with crossed nicols of zircon, parisite and synchisite clustered in an interstitial position between grains of feldspar and quartz in Quincy granite. Scale = 1.25 mm across photo.

Fig. K. Narragansett Pier granite in thin section with crossed nicols. Scale = 14 mm across photo.



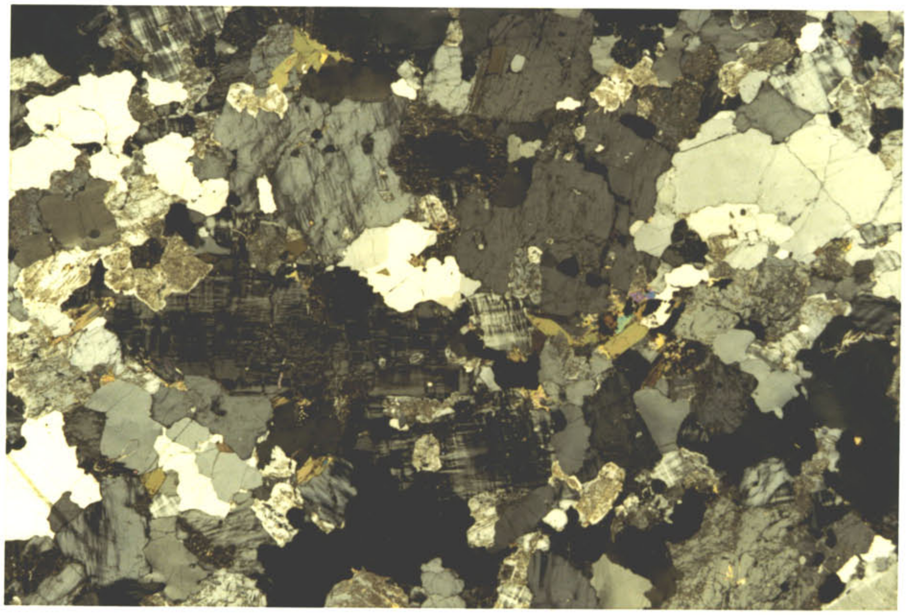
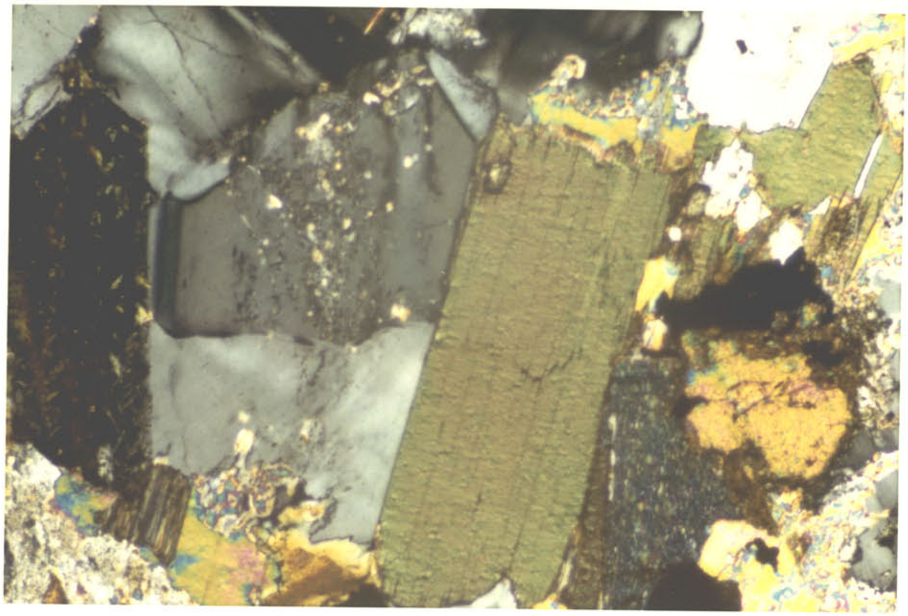


Fig. L. Thin section view with crossed nicols showing pleochroic halo surrounding zircon inclusion in biotite from Narragansett Pier granite. Also to be noted is the abundance of muscovite. Scale = 1.25 mm across photo.

Fig. M. Thin section view with one nicol showing large grain of muscovite associated with biotite in Narragansett Pier granite. Also to be noted is the magnetite concentrated along grain boundaries in biotite. Scale = 1.25 mm across photo.



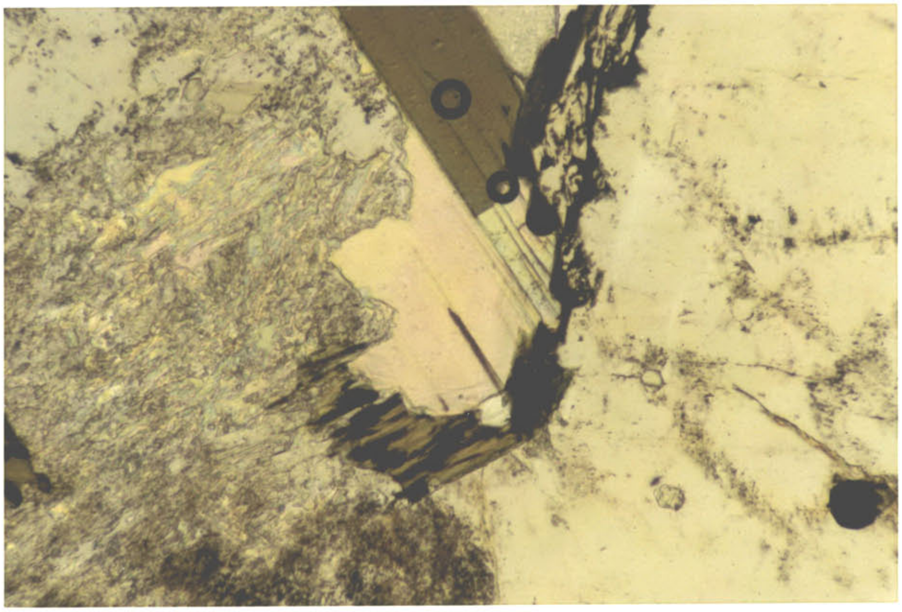
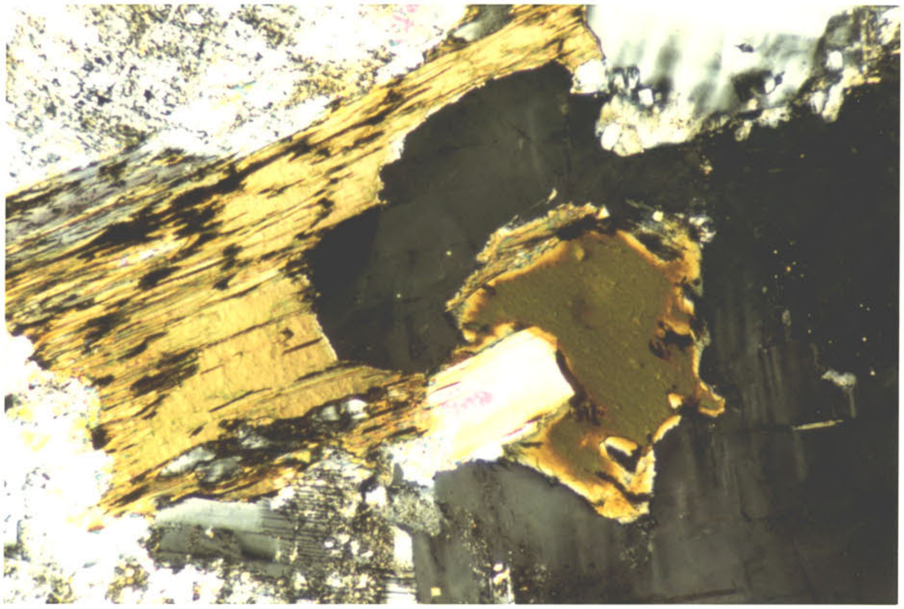


Fig. N. Thin section view with crossed nicols showing magnetite concentrated along grain boundaries in biotite from Narragansett Pier granite. Also to be noted is the associated muscovite. Scale = 1.25 mm across photo.

Fig. O. Westerly granite in thin section with crossed nicols. Scale = 14 mm across photo.



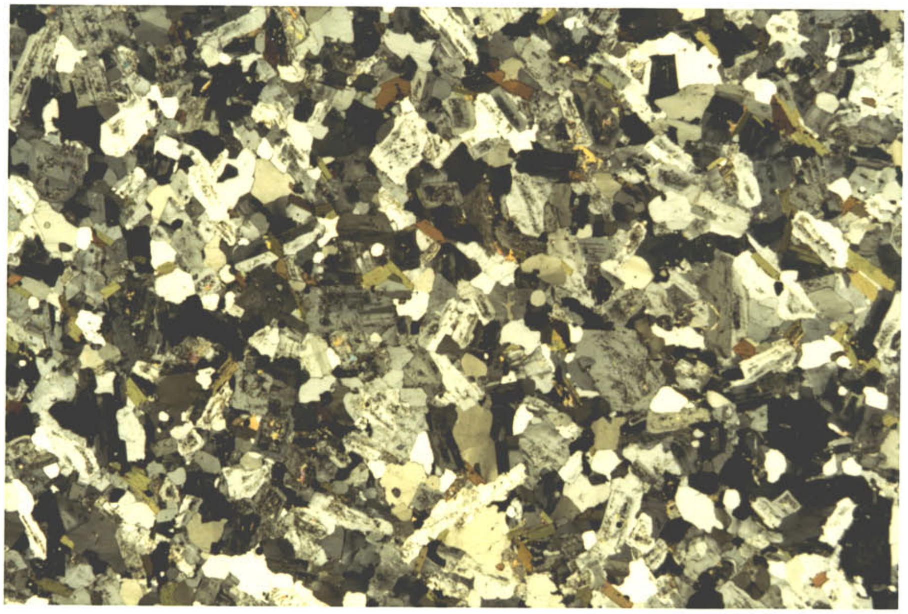
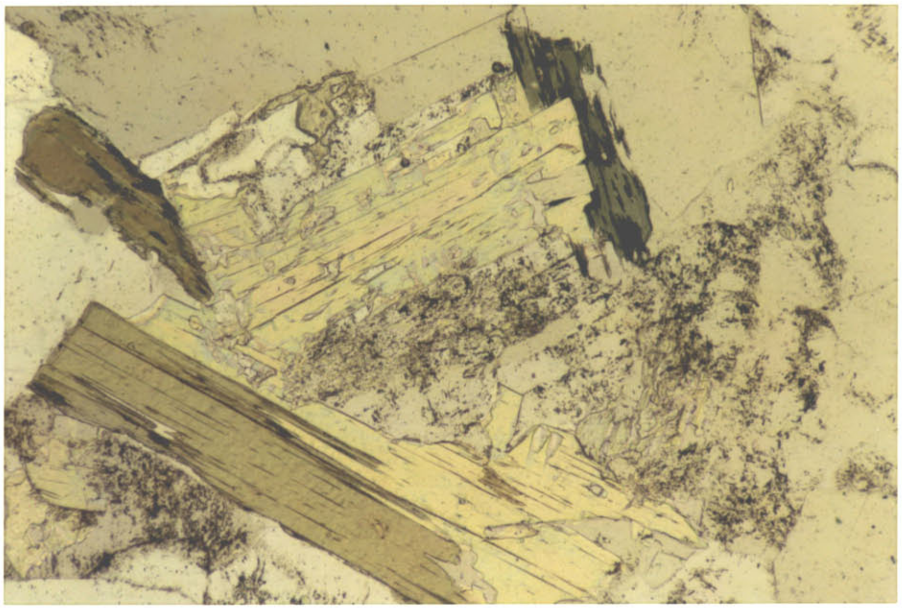


Fig. P. Thin section view with 1 nicol of large muscovite grains associated with biotite in Westerly granite. Scale = 1.25 mm across photo.

Fig. Q. Thin section view with crossed nicols showing pleochroic halo surrounding zircon included in biotite from Westerly granite. Also to be noted are irregular blebs of magnetite which may have crystallized before biotite. Scale = 1.25 mm across photo.



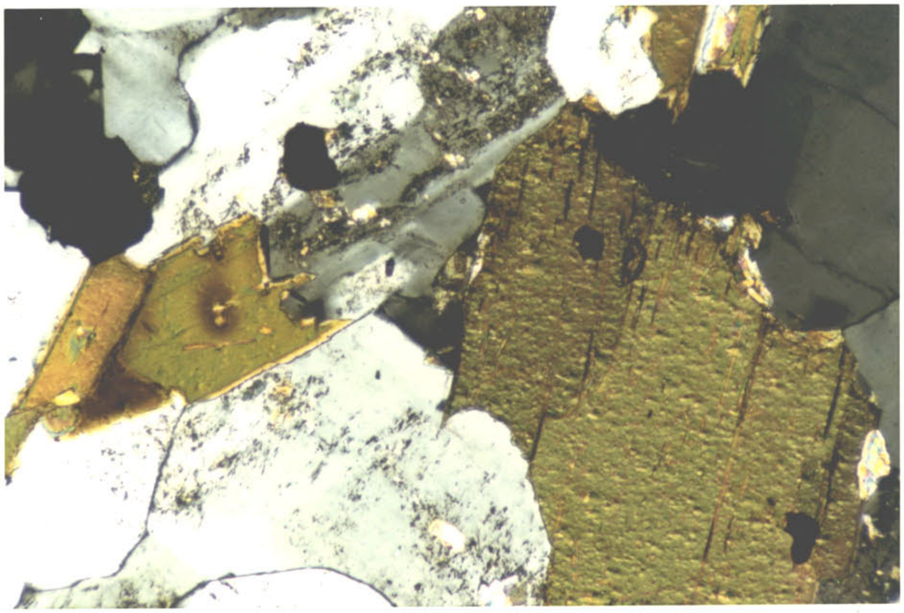


Fig. R. Thin section view with 1 nicol showing irregular blebs of magnetite not particularly associated with biotite. The magnetite appears to have crystallized out before the biotite. Scale = 1.25 mm across photo.

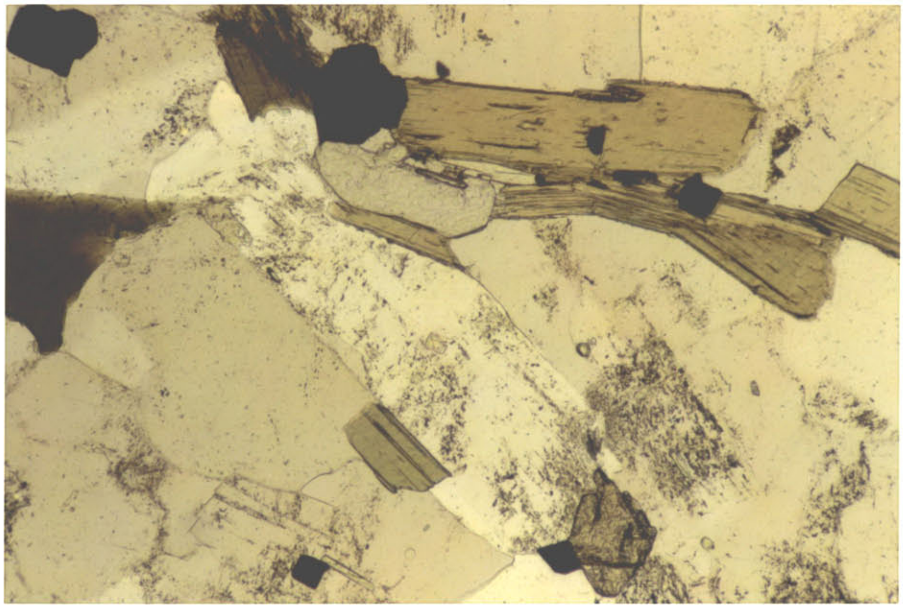
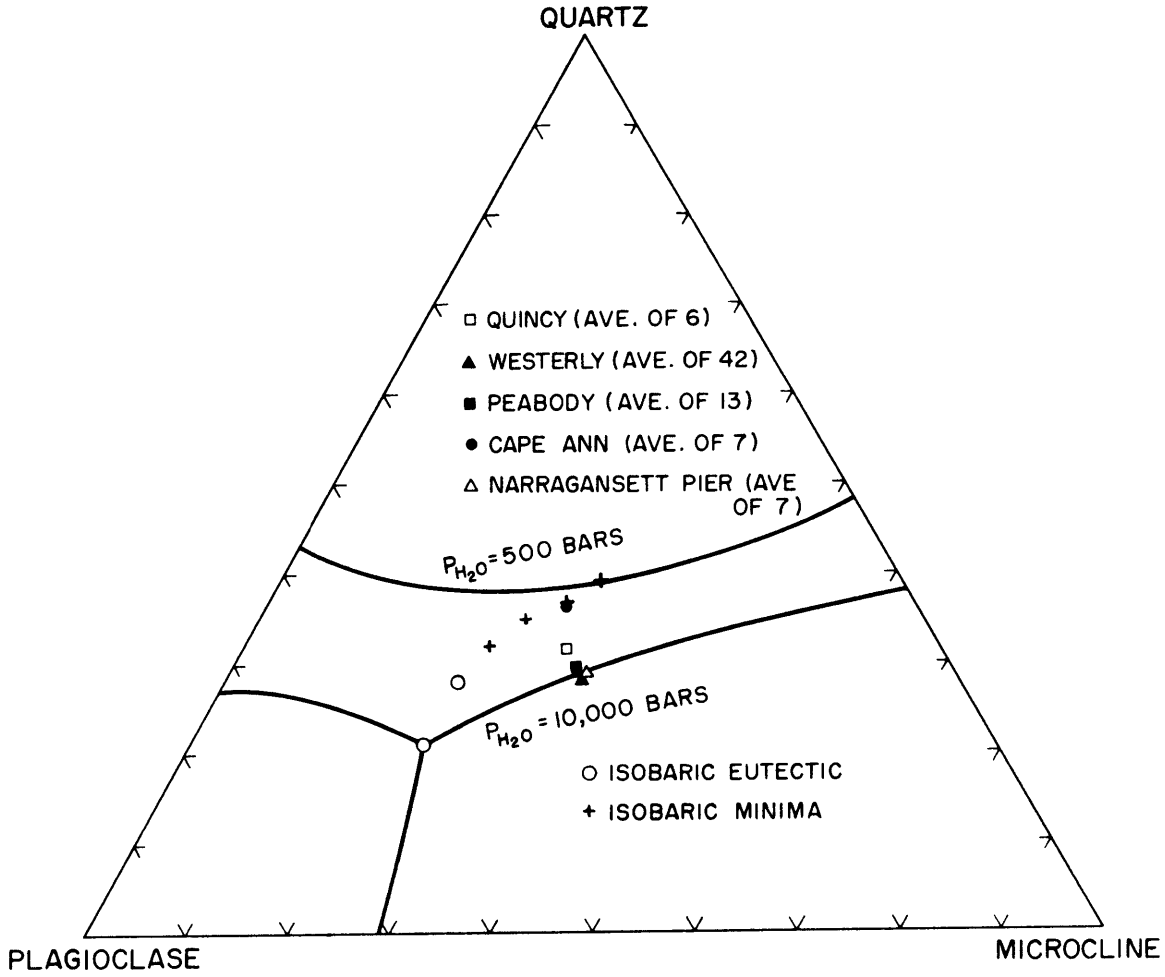


Fig. S. Equilibrium diagram for the granite system after Luth et al. (1964) showing the positions of the granites studied in this paper in relation to the isobaric minima.
References:

Narragansett Pier -- Moore (1959), Feininger (1964).
Westerly -- Whitney (1969), Chayes (1952), Dale (1938), Feininger (1964), Quinn (1968), Fairbairn (1968).
Peabody -- Whitney (1969).
Cape Ann -- Whitney (1969).
Quincy -- Warren (1913).


QUARTZ
PLAGIOCLASE
MICROCLINE
□ QUINCY (AVE. OF 6)
▲ WESTERLY (AVE. OF 42)
■ PEABODY (AVE. OF 13)
● CAPE ANN (AVE. OF 7)
△ NARRAGANSETT PIER (AVE OF 7)
P_{H_2O}=500 BARS
P_{H_2O} = 10,000 BARS
○ ISOBARIC EUTECTIC
+ ISOBARIC MINIMA

APPENDIX 2

A. General:

The technique of instrumental neutron activation analysis (I.N.A.A.) for granitic rocks is discussed by Gordon et al. (1968). Refinements of the technique with emphasis on certain effects such as geometry and etc. are discussed by Denechaud (1969).

The whole rock samples were prepared for irradiation by placing ≈ 0.5 gm of powdered sample into a 2 dram polyethylene vial. The standards were prepared in a manner which would result in similar geometries for both sample and standard. Approximately 0.2 gm of spec-pure SiO_2 was added to a 2 dram vial. First ≈ 0.03 gm of spec-pure Na_2CO_3 was added to the silica and dissolved by the addition of HNO_3, which was evaporated away in an oven. The Na_2CO_3 was added separately because it was desired to vary the amount of Na in the standards. The disolution in HNO_3 and subsequent evaporation was necessary to maintain the desired geometry. Then 0.3 ml of standard solution was pipeted onto the silica. This was enough to just wet all of the silica. The moisture was then evaporated away in an oven. In this way a relatively uniform distribution of the residue on the silica was achieved. After the vial was sealed, further mixing of the silica by shaking helped insure homogeneity. Samples of the silica and Na_2CO_3 were run along with some of the samples and all impurities were found to be negligible for all analyses except for those of quartz and magnetite. For this reason liquid standards were used in these instances.

Data pertaining to the set of whole-rock analyses presented in the main text are tabulated in tables 2-I and 2-II.

TABLE 2-I

Counting Group	Decay Time	Detector	Counting Time
I	3 hr.	LEPS	70 min.
II	5 days	LEPS	140 min.
III	12 days	26 cc.	300 min.
IV	40 days	26 cc.	300 min.

These data differ only slightly in some areas for the mineral fraction analyses and these differences are mentioned in the discussions of the individual mineral fraction runs. In general, three samples and one standard were included in each run. Experiments have shown the neutron flux to be fairly uniform for this geometry (Anderson, 1968). Samples of the spectra for count sets II, III and IV measured after 5, 12, and 40 days respectively, are presented in figs. II-A, II-B and II-C respectively. These are only sample spectra and

Table 2 - II

Elem.	Conc. in std. (ppm) ± 3.5%	Nucld.	Pk. En. (Kev)	Count Group	Fract. of Pk.*	Est.** Err. (%)	Precsn. (%)
La	154	La^{140}	329	III	1/2	5.8	1.9
Ce	267	Ce^{141}	145	III	Wh. Pk.	5.8	0.3
Sm	18.5	Sm^{153}	103	II	Wh. Pk.	5.9	5.8
Eu	2.36	Eu^{152}	1408	IV	Wh. Pk.	6.9	0.4
Tb	8.85	Tb^{160}	879	IV	Wh. Pk.	6.2	7.8
Dy	3.06	Dy^{165}	95	I	Wh. Pk.	10	6.9
Yb	1.82	Yb^{175}	283	III	Wh. Pk.	8.7	7.6
Lu	0.433	Lu^{177}	208	III	Wh. Pk.	6.6	19.2
Zr	504	Zr^{95}	757	IV	1/2	8.1	0.4
Hf	18.5	Hf^{181}	482	IV	Wh. Pk.	5.9	0.2
Ta	1.90	Ta^{182}	1222	IV	1/2	9.3	4.3
Sc	6.04	Sc^{46}	889	IV	Wh. Pk.	6.4	0.5
Th	50.6	Pa^{233}	312	III	1/2	5.9	1.4

* The use of the computer to integrate peaks was found satisfactory for all elements except Zr and Dy. Computer integrated values were used only after thorough study and comparison with hand integrated values.

** Error estimates were made following the discussion by Denechaud (1969).

Fig. 2-I Sample spectrum of Quincy granite (Q-1) 5 days after irradiation showing the 103 kev peak of 47-hour Sm^{153}. This spectrum was taken with a small (1/2 cc.), high-resolution (≈ 0.6 kev @ 100 kev) Ge(Li) detector (LEPS). The analyzer was calibrated at ≈ 20 channels/kev. The 95 kev peak of 2.35-hour Dy^{165}, counted ≈ 3 hours after irradiation, is similar to this peak, but has a slightly more erratic background. The spectrum shown here was a sample spectrum only and was not used for analysis.

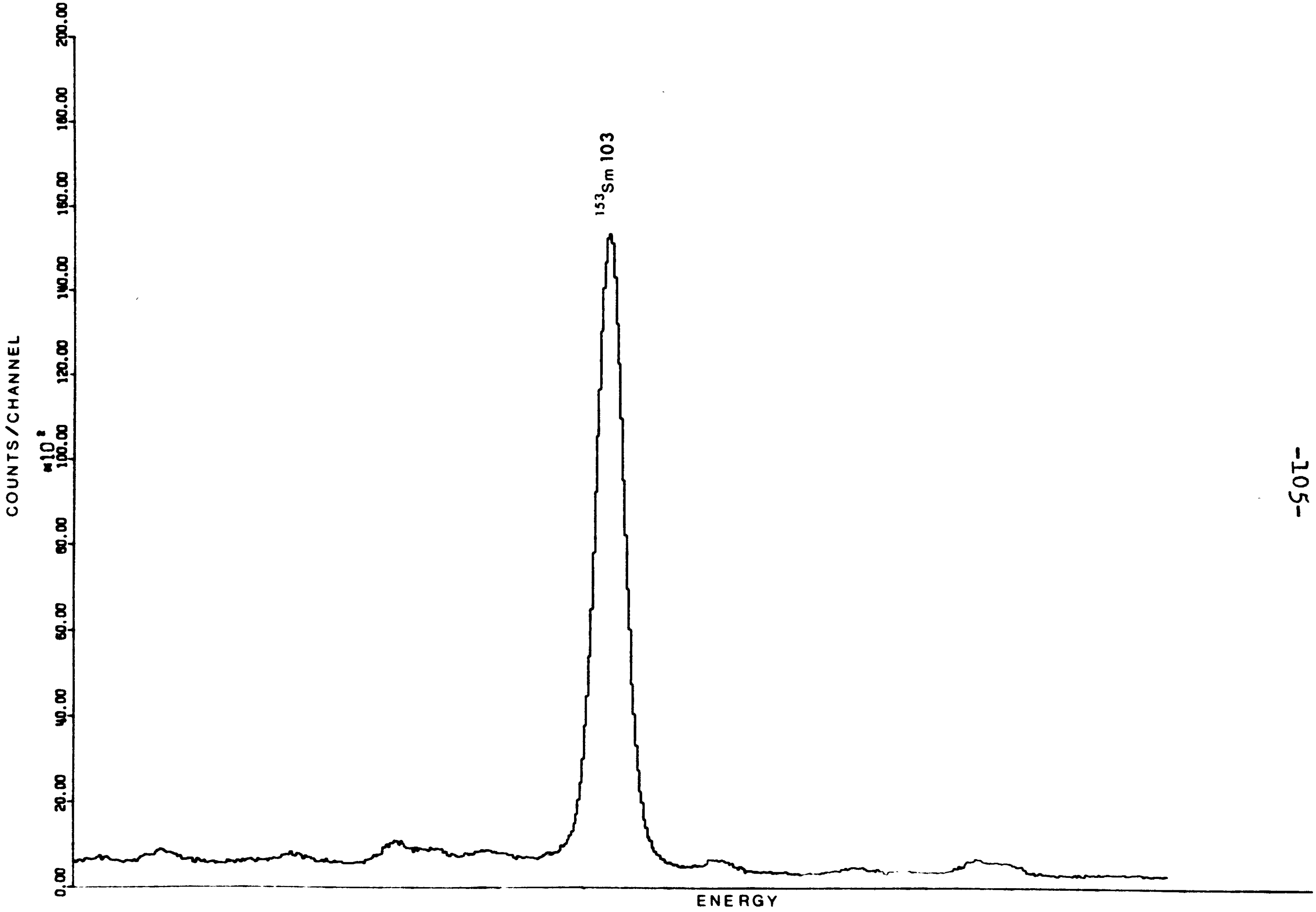
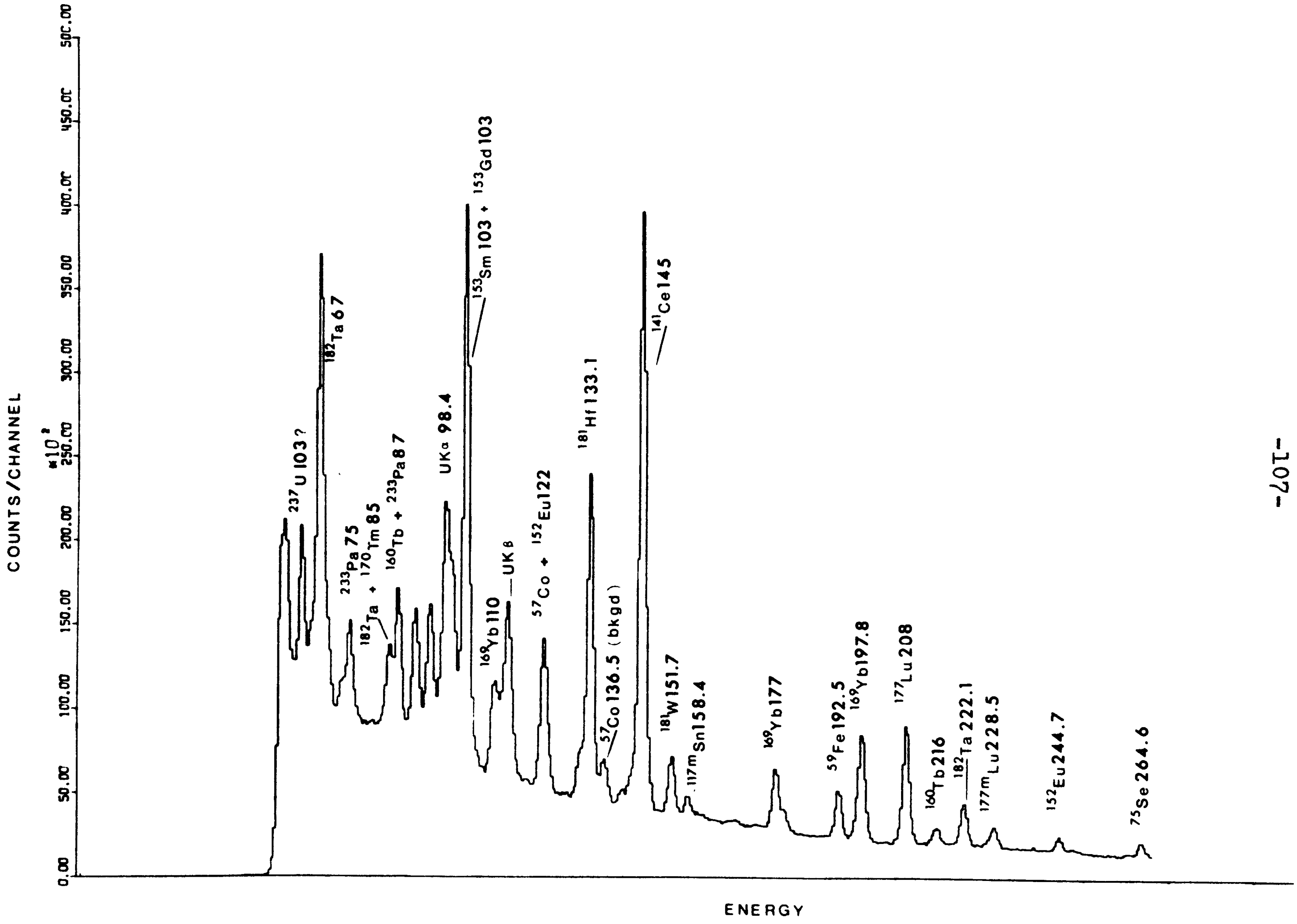
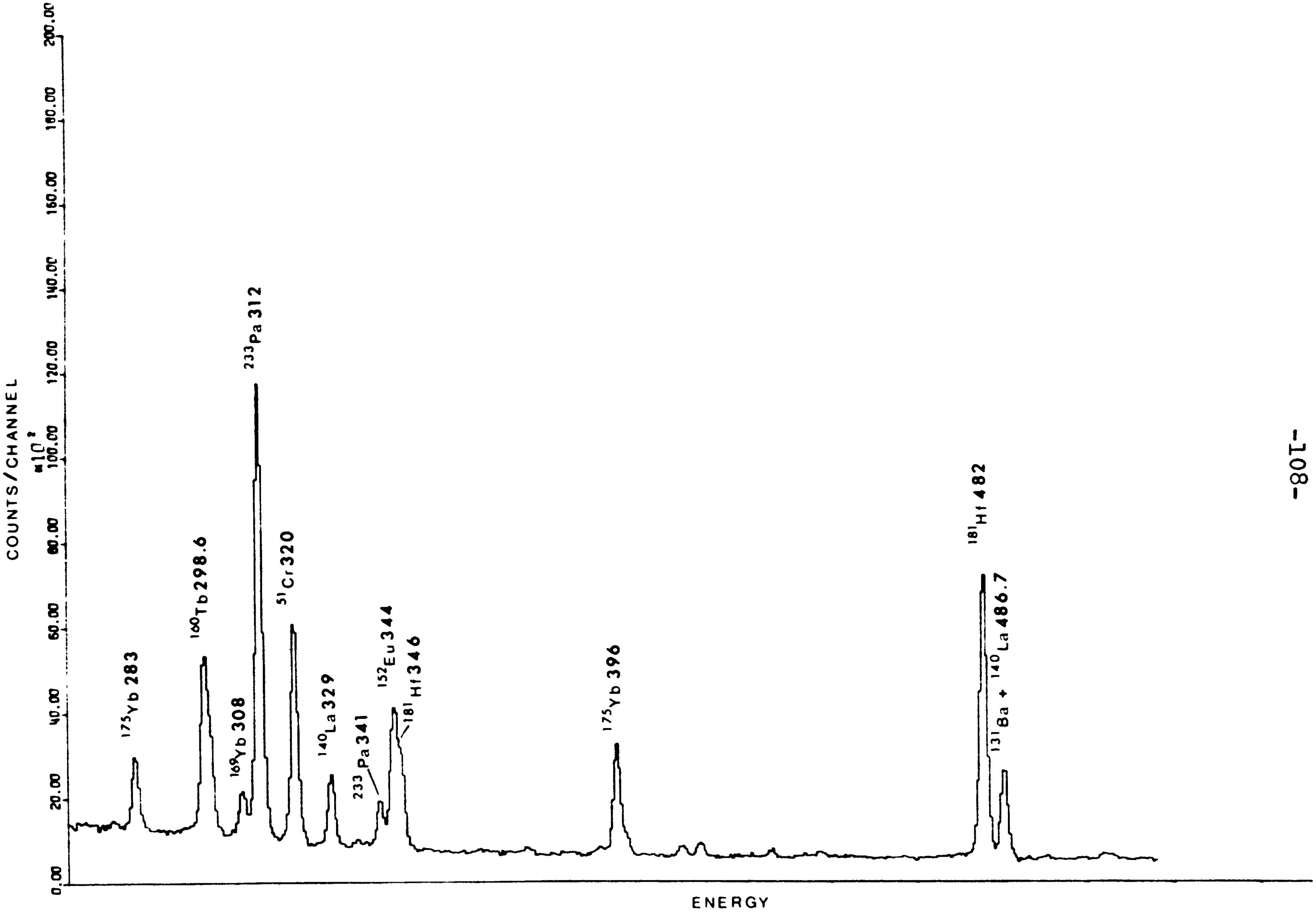
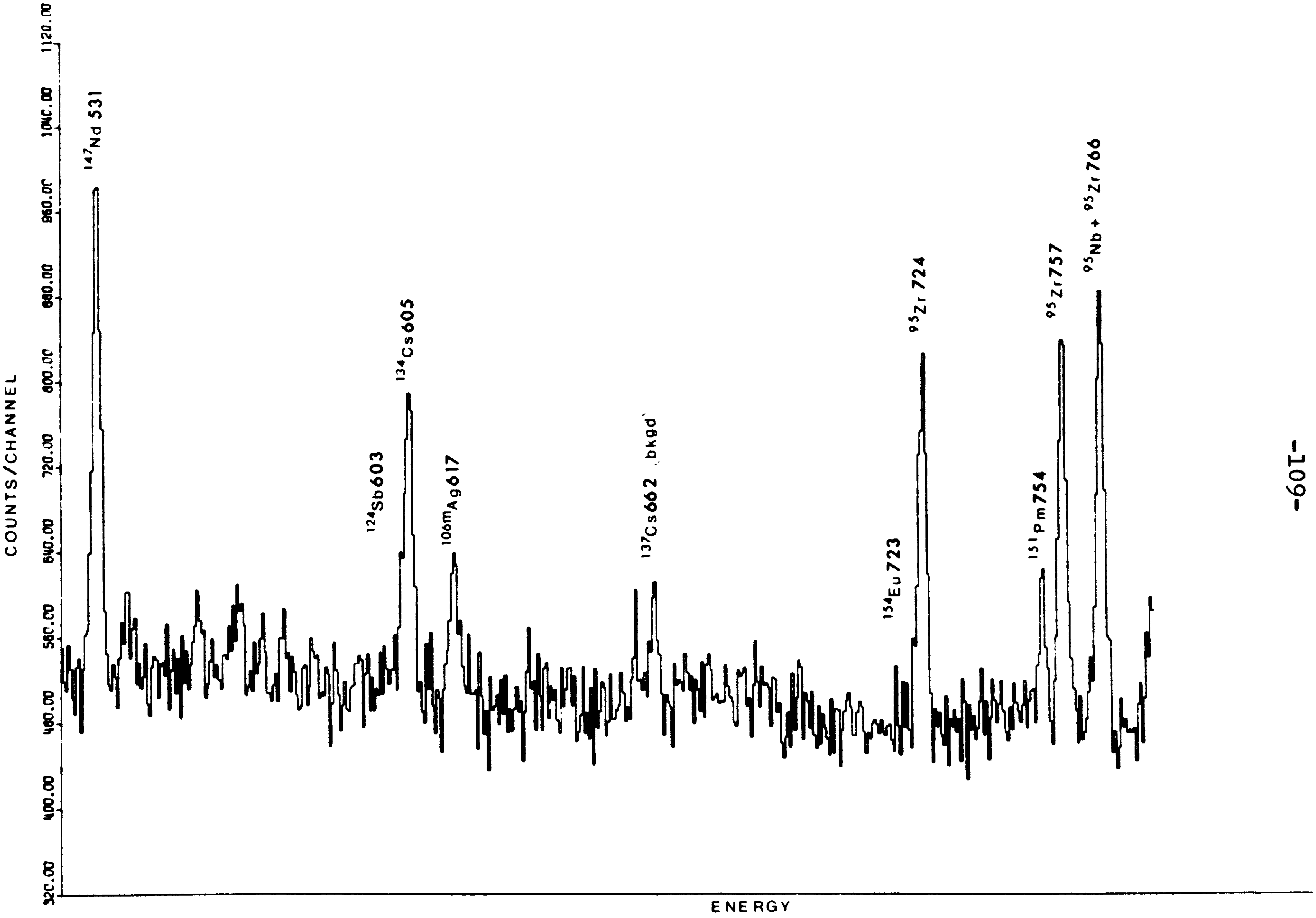
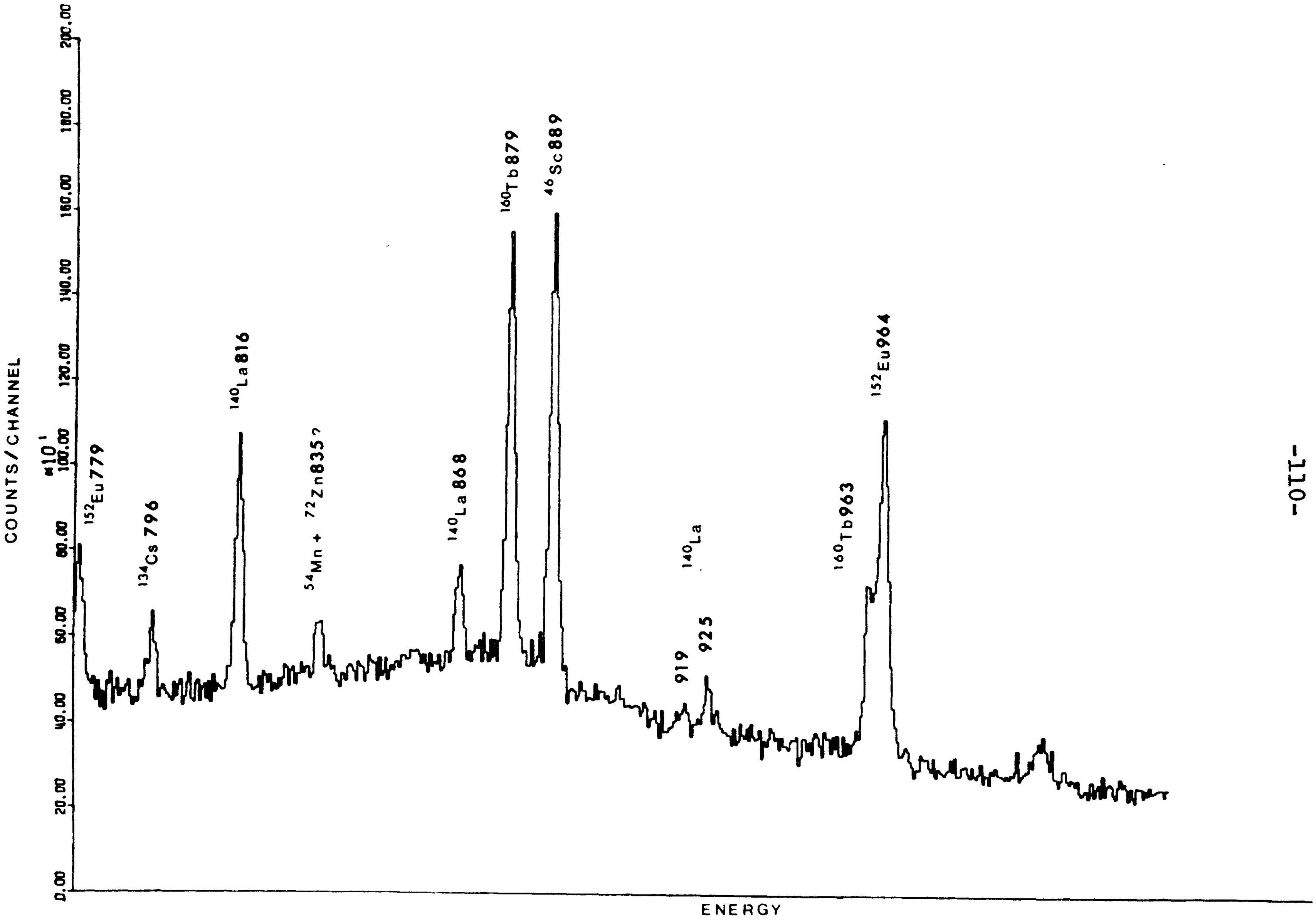

200.00
180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
COUNTS/CHANNEL
×10²
^{153}Sm 103
ENERGY

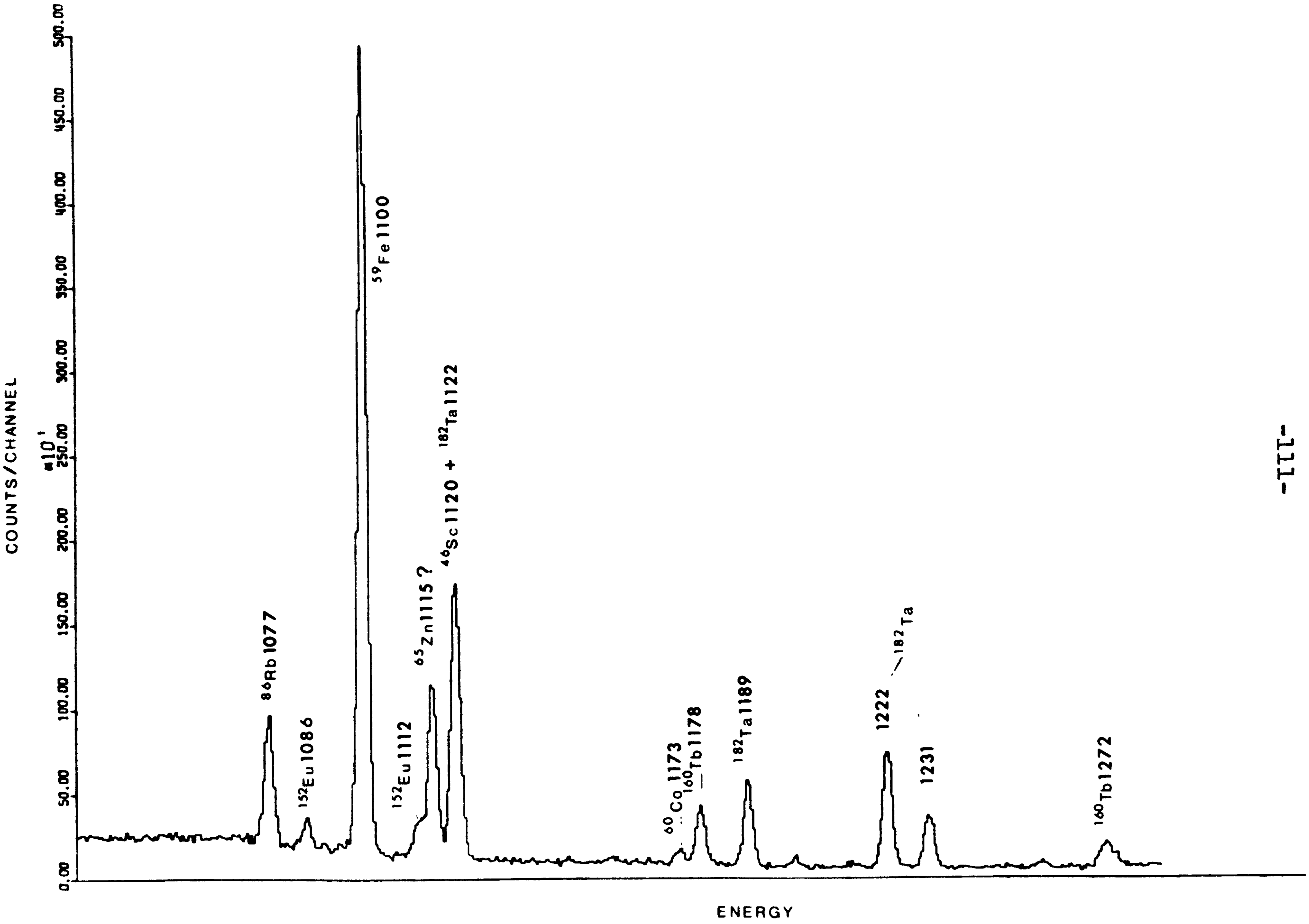
Fig. 2-II Sample spectrum of Quincy granite (Q-1) 12 days after irradiation. This spectrum was taken with a 26 cc. Ge(Li) detector (resolution ≈ 2.5 kev @ 1000 kev) with the analyzer calibrated at ≈ 2 channels/kev. This is a sample spectrum only and was not used for analysis.


COUNTS/CHANNEL
×10²
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
500.00
ENERGY
^{237}U 103 ?
^{182}Ta 67
^{233}Pa 75
^{182}Ta + ^{170}Tm 85
^{160}Tb + ^{233}Pa 87
UKα 98.4
^{153}Sm 103 + ^{153}Gd 103
^{169}Yb 110
UKβ
^{57}Co + ^{152}Eu 122
^{181}Hf 133.1
^{57}Co 136.5 (bkgd)
^{141}Ce 145
^{181}W 151.7
^{117m}Sn 158.4
^{169}Yb 177
^{59}Fe 192.5
^{169}Yb 197.8
^{177}Lu 208
^{160}Tb 216
^{182}Ta 222.1
^{177m}Lu 228.5
^{152}Eu 244.7
^{75}Se 264.6


COUNTS/CHANNEL
x10²
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
ENERGY
¹⁷⁵Yb 283
¹⁶⁰Tb 298.6
¹⁶⁹Yb 308
²³³Pa 312
⁵¹Cr 320
¹⁴⁰La 329
²³³Pa 341
¹⁵²Eu 344
¹⁸¹Hf 346
¹⁷⁵Yb 396
¹⁸¹Hf 482
¹³¹Ba + ¹⁴⁰La 486.7


COUNTS/CHANNEL
ENERGY
1120.00
1040.00
960.00
880.00
800.00
720.00
640.00
560.00
480.00
400.00
320.00
^{147}Nd 531
^{124}Sb 603
^{134}Cs 605
^{106m}Ag 617
^{137}Cs 662 (bkgd)
^{154}Eu 723
^{95}Zr 724
^{151}Pm 754
^{95}Zr 757
^{95}Nb + ^{95}Zr 766


COUNTS/CHANNEL
*10^1
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
ENERGY
^{152}Eu 779
^{134}Cs 796
^{140}La 816
^{54}Mn + ^{72}Zn 835 ?
^{140}La 868
^{160}Tb 879
^{46}Sc 889
919
^{140}La
925
^{160}Tb 963
^{152}Eu 964


COUNTS/CHANNEL
x10¹
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
500.00
ENERGY
86Rb 1077
152Eu 1086
59Fe 1100
152Eu 1112
65Zn 1115 ?
46Sc 1120 + 182Ta 1122
60Co 1173
160Tb 1178
182Ta 1189
1222
182Ta
1231
160Tb 1272

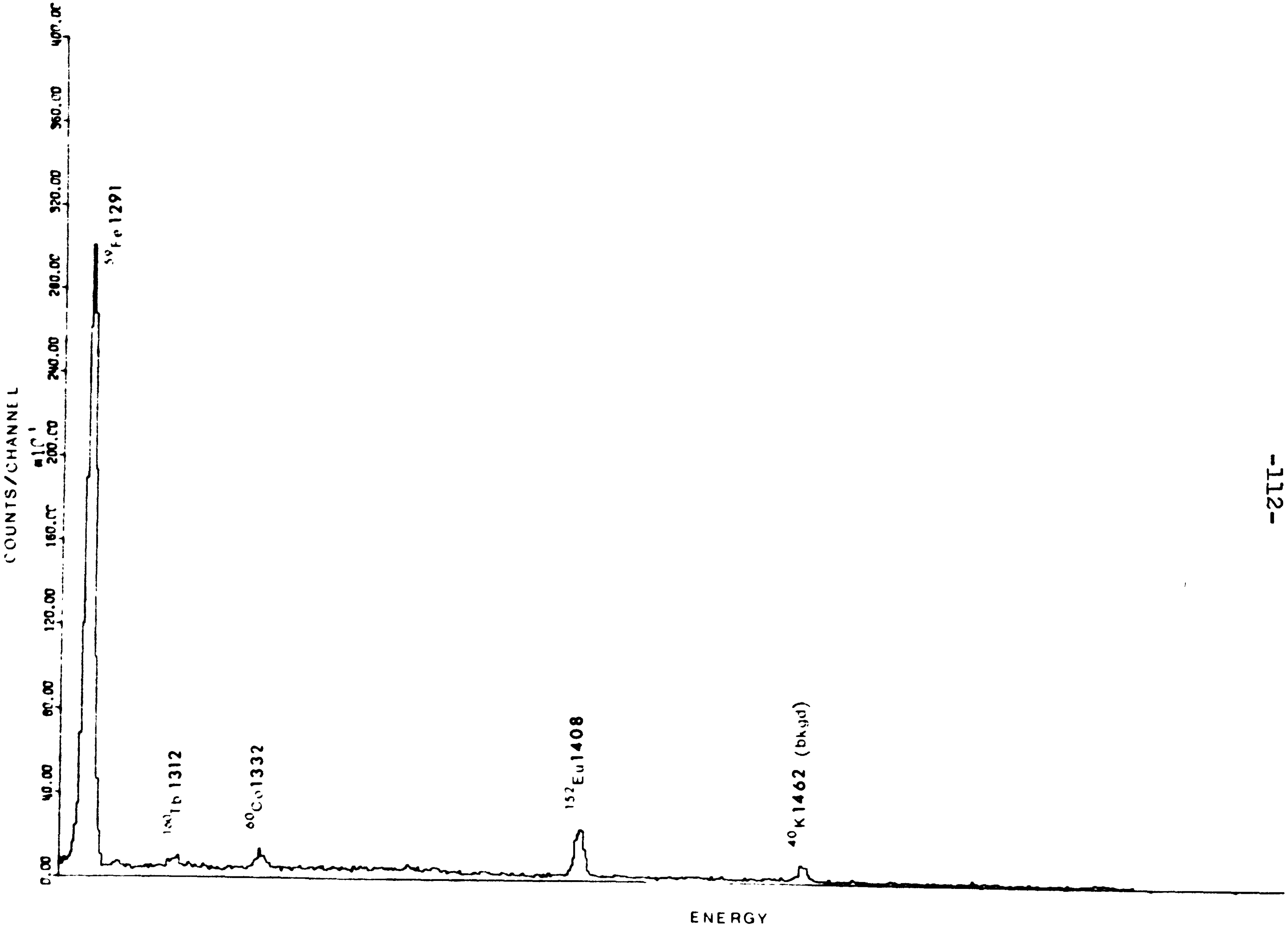
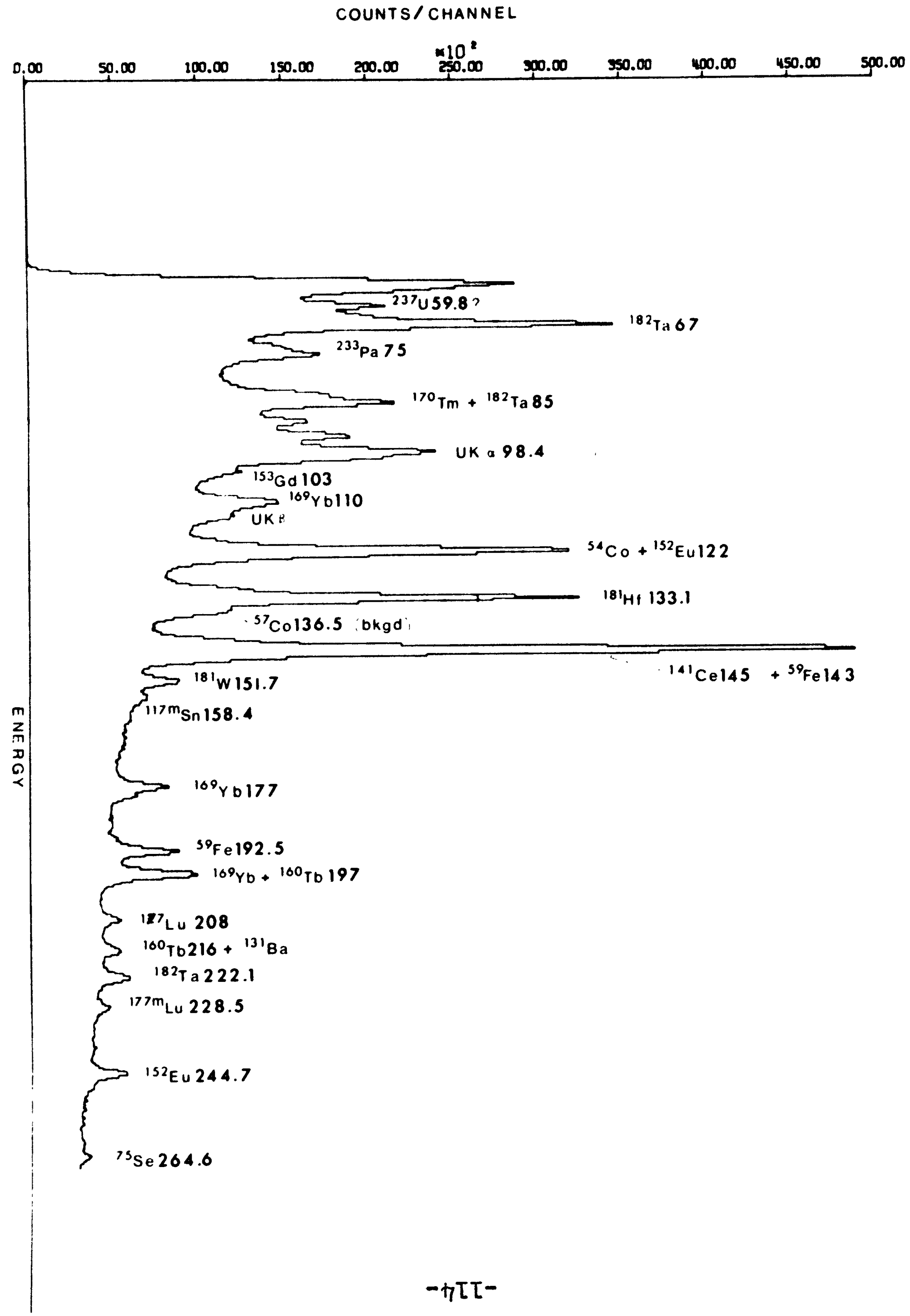
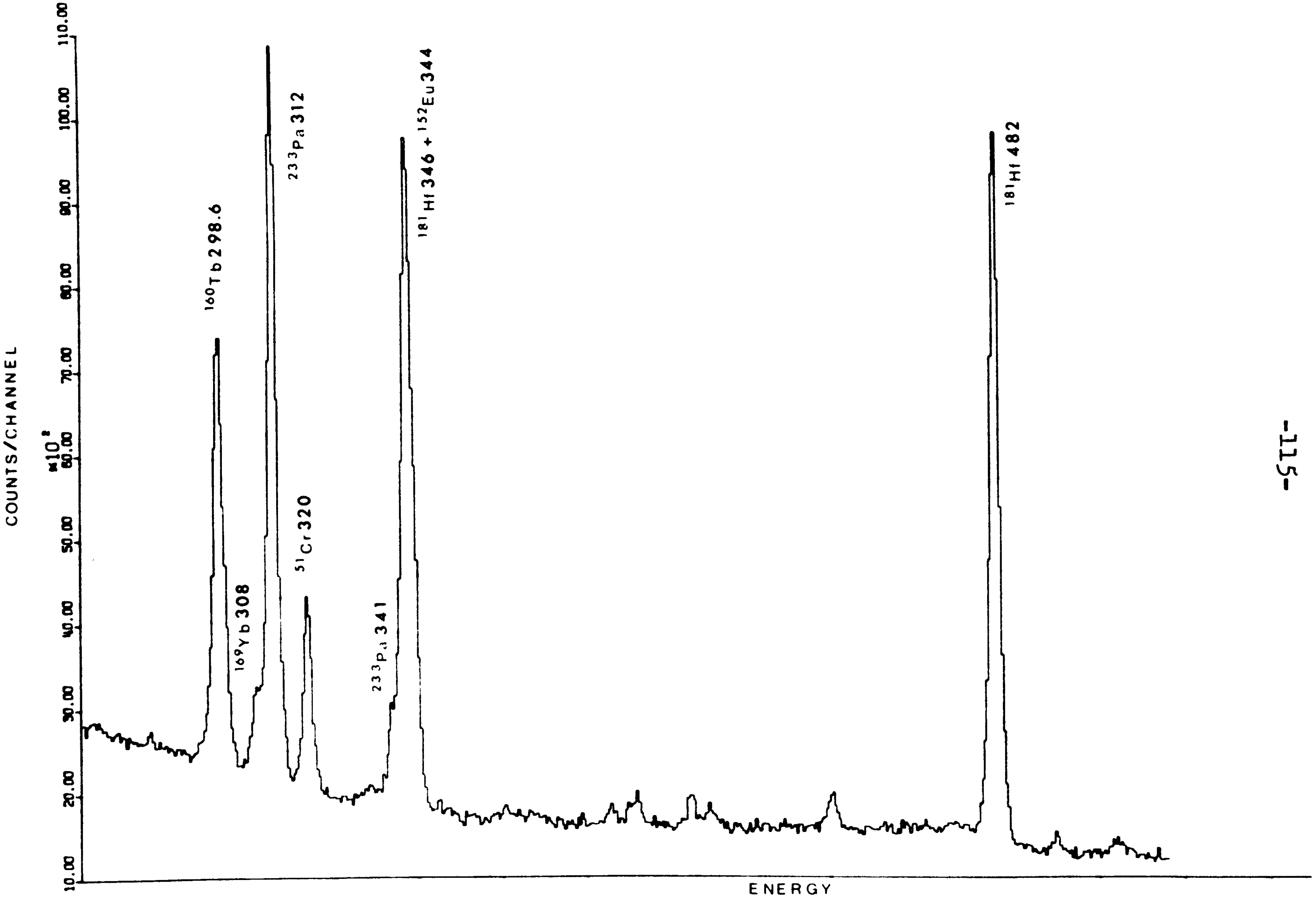
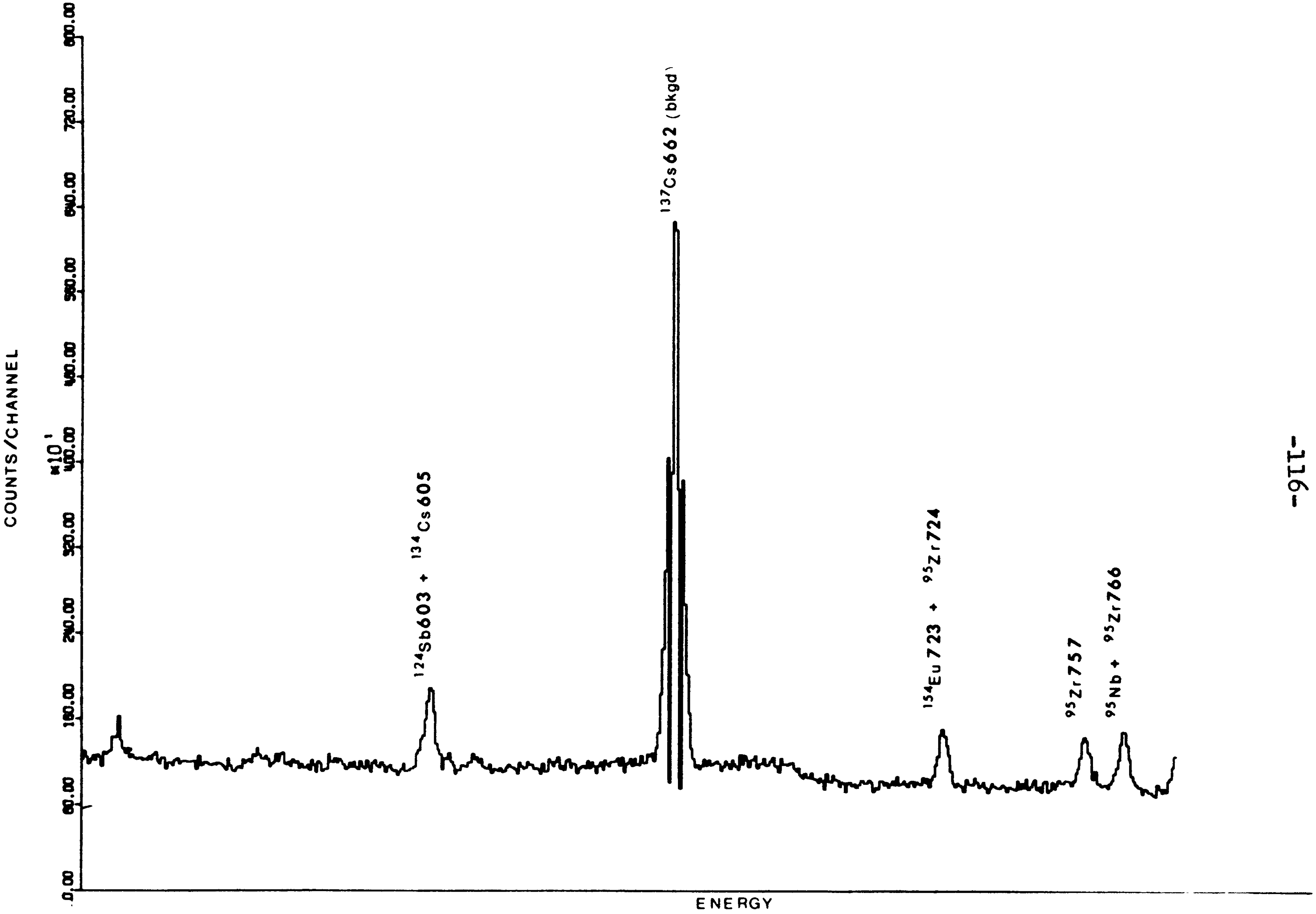
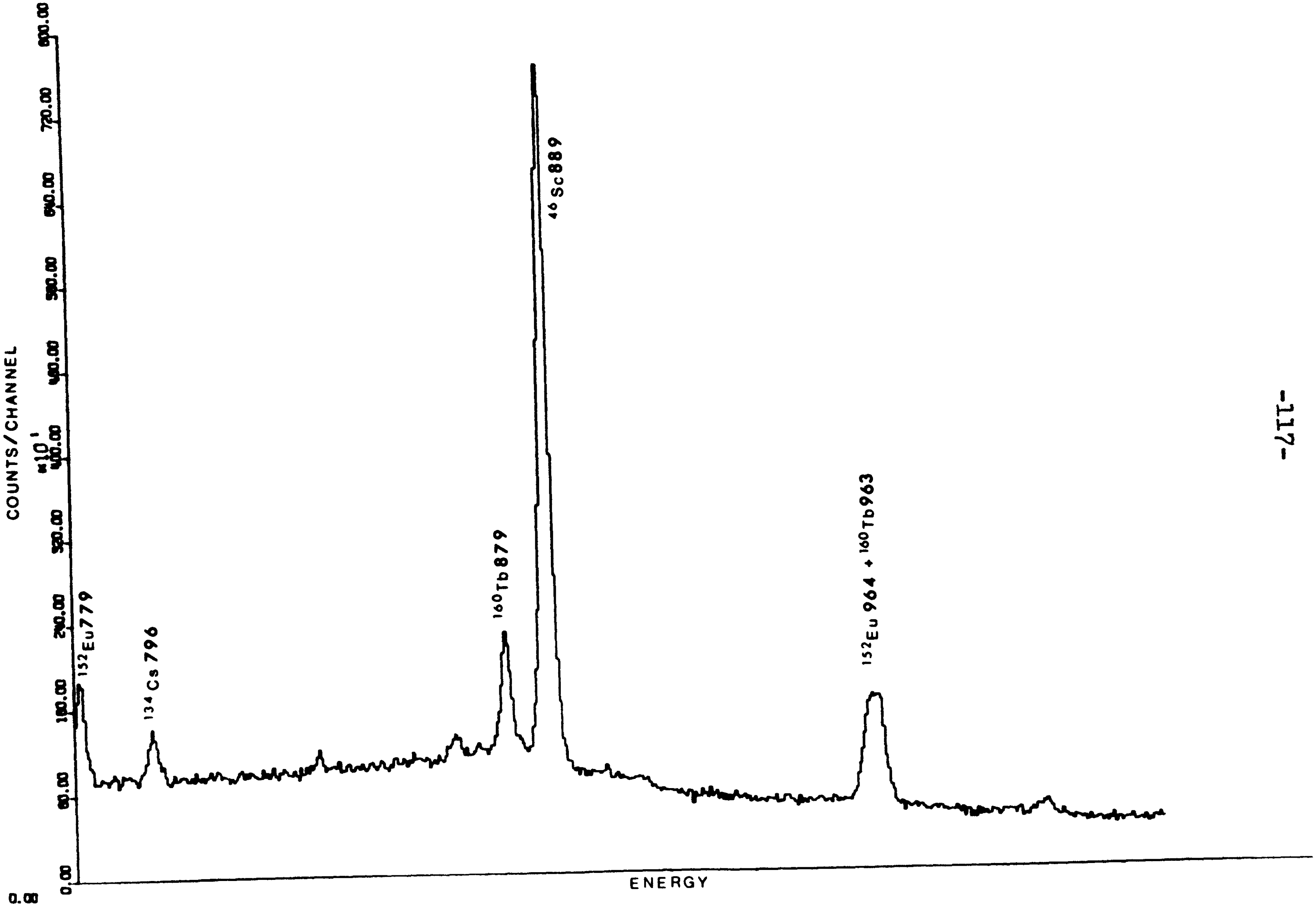

COUNTS/CHANNEL
x10^1
0.00
40.00
80.00
120.00
160.00
200.00
240.00
280.00
320.00
360.00
400.00
59Fe 1291
160Tb 1312
60Co 1332
152Eu 1408
40K 1462 (bkgd)
ENERGY

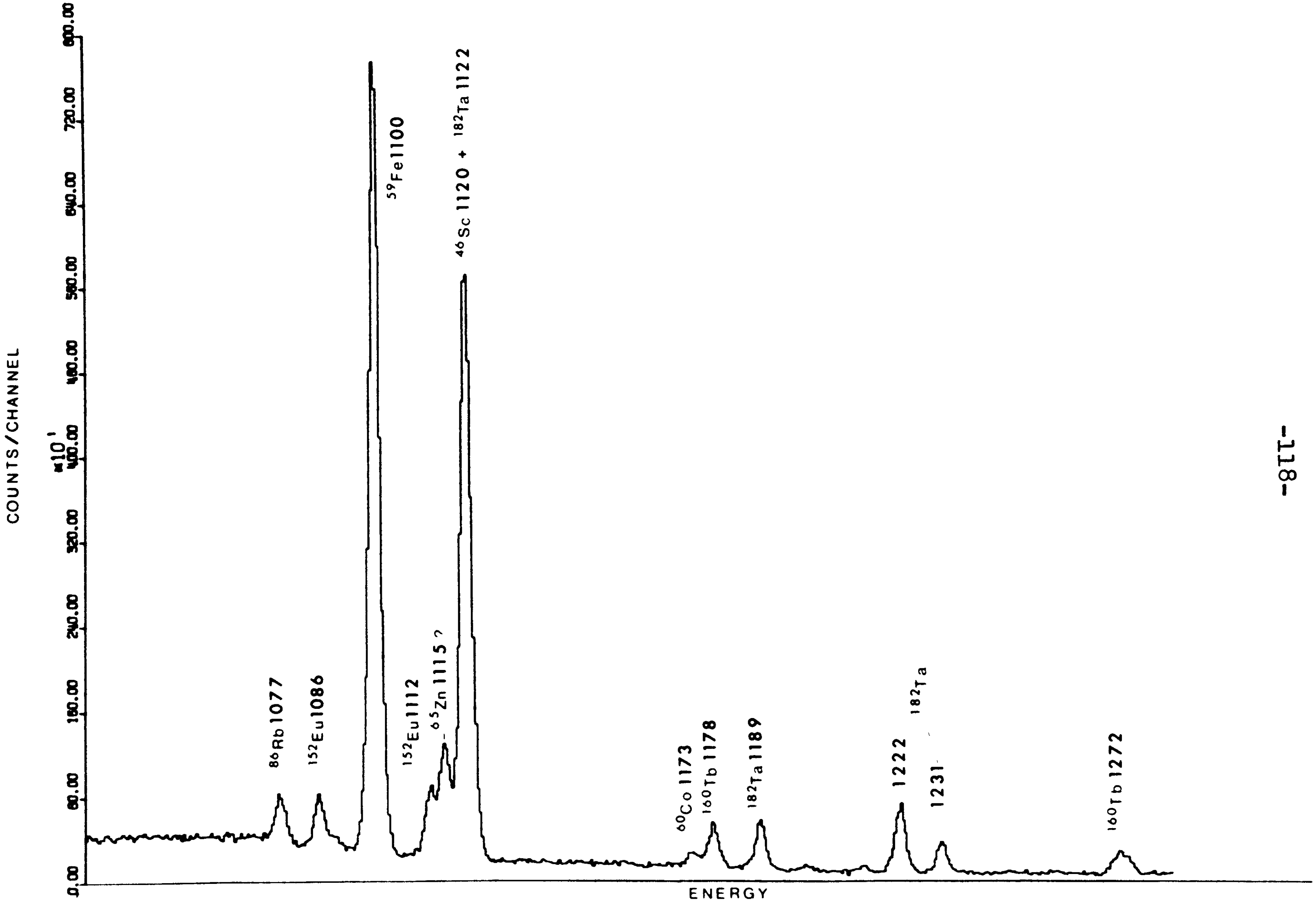
Fig. 2-III Sample spectrum of Cape Ann Granite (C-1) taken 40 days after irradiation. This spectrum was taken with a 26 cc. Ge(Li) detector (resolution ≈ 2.5 kev @ 1000 kev) with the analyzer calibrated at ≈ 2 channel/kev. This is a sample spectrum only and was not used for analysis.

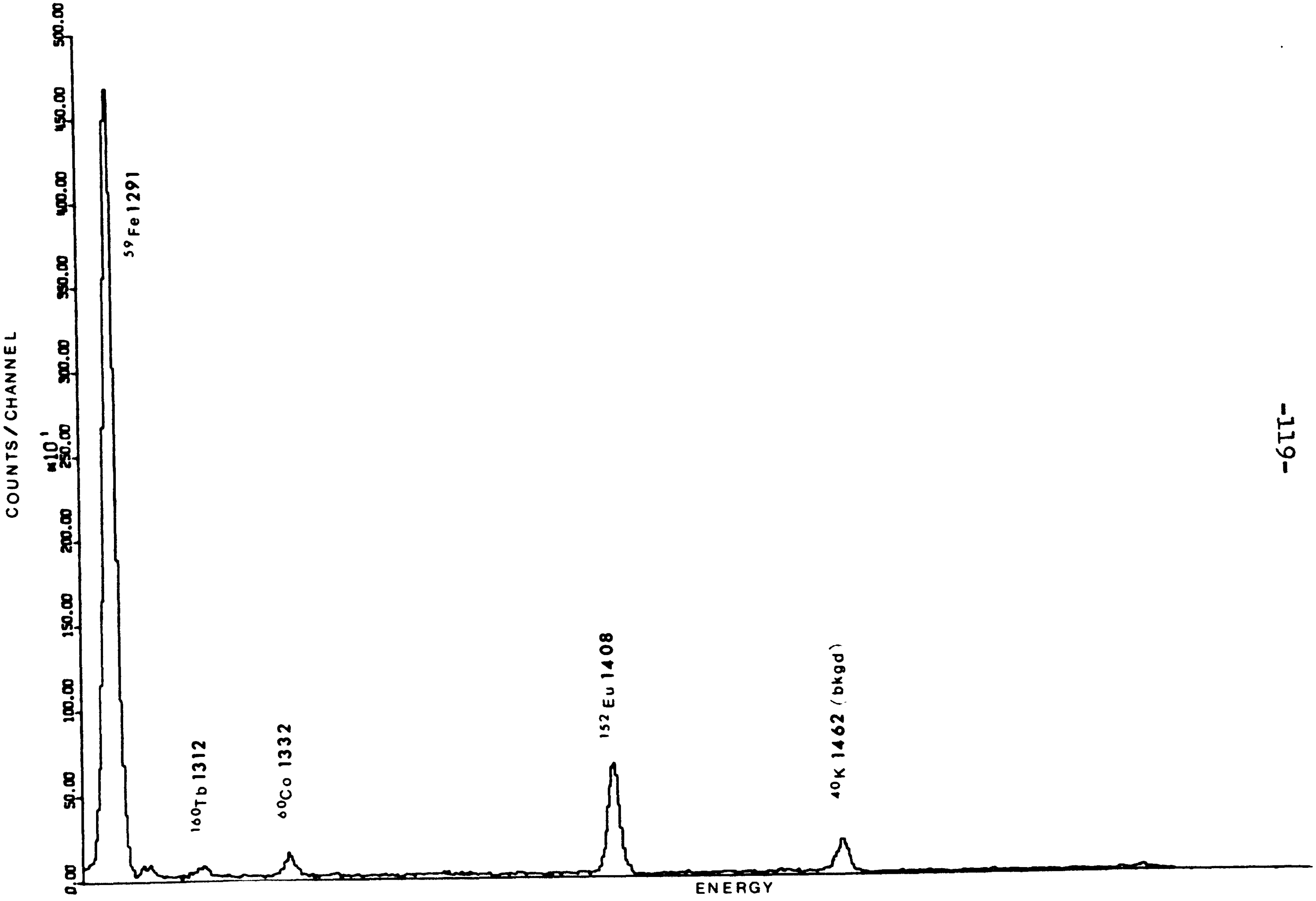

COUNTS/CHANNEL
×10²
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
500.00
ENERGY
^{237}U 59.8 ?
^{182}Ta 67
^{233}Pa 75
^{170}Tm + ^{182}Ta 85
UK α 98.4
^{153}Gd 103
^{169}Yb 110
UK β
^{54}Co + ^{152}Eu 122
^{181}Hf 133.1
^{57}Co 136.5 (bkgd)
^{141}Ce 145 + ^{59}Fe 143
^{181}W 151.7
^{117m}Sn 158.4
^{169}Yb 177
^{59}Fe 192.5
^{169}Yb + ^{160}Tb 197
^{177}Lu 208
^{160}Tb 216 + ^{131}Ba
^{182}Ta 222.1
^{177m}Lu 228.5
^{152}Eu 244.7
^{75}Se 264.6


COUNTS/CHANNEL
x10²
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
ENERGY
^{160}Tb 298.6
^{169}Yb 308
^{233}Pa 312
^{51}Cr 320
^{233}Pa 341
^{181}Hf 346 + ^{152}Eu 344
^{181}Hf 482


COUNTS/CHANNEL
x10¹
0.00
80.00
160.00
240.00
320.00
400.00
480.00
560.00
640.00
720.00
800.00
ENERGY
124Sb603 + 134Cs605
137Cs662 (bkgd)
154Eu723 + 95Zr724
95Zr757
95Nb + 95Zr766


COUNTS/CHANNEL
x10¹
800.00
720.00
640.00
560.00
480.00
400.00
320.00
240.00
160.00
80.00
0.00
0.00
ENERGY
^{152}Eu 779
^{134}Cs 796
^{160}Tb 879
^{46}Sc 889
^{152}Eu 964 + ^{160}Tb 963


COUNTS/CHANNEL
×10¹
0.00
80.00
160.00
240.00
320.00
400.00
480.00
560.00
640.00
720.00
800.00
ENERGY
86Rb 1077
152Eu 1086
59Fe 1100
152Eu 1112
65Zn 1115 ?
46Sc 1120 + 182Ta 1122
60Co 1173
160Tb 1178
182Ta 1189
1222
182Ta
1231
160Tb 1272


COUNTS / CHANNEL
×10¹
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
500.00
⁵⁹Fe 1291
¹⁶⁰Tb 1312
⁶⁰Co 1332
¹⁵²Eu 1408
⁴⁰K 1462 (bkgd)
ENERGY

were not used for analysis.

B. Details of the analyses:

Lanthanum: Of the peaks listed by Gordon et al. (1968) that are suitable for analysis, the 1596 kev peak would appear to be the most favorable; however, after comparison of several analyses the 329 kev peak gave better precision. There is no ready explanation for this. Denechaud does not mention the 1596 kev peak.

Cerium: Cerium is interesting; it yields only one prominent peak--that of 33-day Ce^{141} at 145.4 kev. The interferences are 45-day Fe^{59} at 143 kev and 4.21-day Yb^{175} at 144.8 kev. Denechaud, who separated the rare-earths chemically as a group but not individually, was concerned mainly with the interference of Yb^{175}, and therefore counted Ce late. Gordon on the other hand performed no chemistry at all upon his samples and found Fe to be the more troublesome interference, and counted it earlier.

In lieu of the fact that the samples studied here are similar to those studied by Gordon, his advice was followed. The contribution due to Yb^{175} was assumed to be negligible. In the compilation by Dams and Adams (1968) this peak is not listed among the prominent peaks of Yb^{175} and Denechaud estimates the interference to be in the range of tenths of a percent.

There is Fe in the samples initially, but Fe and W contamination was inevitable during preparation of the samples. For this reason it was necessary to check the contribution to the Ce peak by Fe for various types of samples. This was done by integrating the Fe peak at 1291.4 kev and using the relative intensities listed by Gordon to compute the intensity of the Fe peak at 142.5 kev. In all cases except for magnetite, the contribution was found to be negligible (<2%). Although the concentration of Fe in the mafic mineral fractions was greater than in the rock as a whole, the corresponding concentration of Ce was also proportionately greater. A meaningful number for Ce could not be obtained from magnetite because of the size of the Fe peak. The very best one could do was an order-of-magnitude estimate using peak heights in the case of the magnetite sample from the Narragansett Pier granite.

Samarium: In the case of the 103 kev peak of 47-hour Sm^{153} Denechaud is primarily concerned with contributions from 242-day Gd^{153}, while Gordon discussed possible contributions from UK_{α} X-Rays at 94 and 98 kev. Both of these effects are negligible if the sample is counted 5 days after irradiation.

The 103 kev peak used here for analysis can be counted on either a large or small detector. The smaller detector was chosen because of much better resolution (≈ 0.6 kev @ 100 kev vs. ≈ 2.5 kev @ 1000 kev). The biggest problem with this peak is the rough background, and it is easier to find a consistent place to measure background with the better resolved spectrum. The height/background ratio of this peak is > 10 on the small detector, and therefore if the sample is counted long enough the background effects become negligible.

Europium: Europium can be counted both early and late and thus be used as a cross check between count sets I & IV. Denechaud and Gordon discuss the various peaks available, but Denechaud makes no mention of the 1408 kev peak chosen here. These samples were counted late because of the reduced background. There are no interferences or background problems with Eu, making it probably the easiest to analyze for, and the results are excellent.

Terbium: Neither Gordon nor Denechaud used the 879 kev peak for analysis, although Gordon lists it as the most intense peak arising from decay of 72.1-day Tb^{160}. The main problem with using this peak is resolving it from the 889 kev peak of 83.9-day Sc^{46}. In this study it was found that if care was taken, these two peaks could be resolved well enough that a background measurement could be made at the valley between them. In general the resolution was better than that shown in the sample spectrum for count set IV.

The only interference is from the 873 kev line of 16-year Eu^{154} but the intensity of this peak is minimal (Dams and Adams). In this study the best results were obtained by using the 889 kev peak.

Dysprosium: The interference problems discussed by Gordon and Denechaud are overcome by using a small high resolution detector (LEPS) (Cobb, 1967). The biggest problem with the Dy analysis is the high Na content of these rocks which results in high levels of radioactivity, even after short periods of irradiation. The samples must be counted as soon as possible after irradiation, requiring precautionary handling procedures. With such highly radioactive samples dead time becomes a problem, and the best results were obtained by placing the samples far enough away from the detector that the dead time was < 20%.

High background levels result from the highly active samples, making it difficult to obtain a respectable height/background ratio. The optimum counting time which satisfies both conditions appears to be about an hour.

There is no sample spectrum showing the Dy peak, but it is similar to the Sm peak, only having a higher more irregular background. (See fig. 2-I)

Ytterbium: As discussed by Denechaud, Yb can be counted during count set III or IV and can thus be used as a cross-check between them. The 283 kev line of 4.21-day Yb^{175} counted after 12 days gave the best results in this study. The only problem with this peak is its low intensity which results in a relatively high statistical uncertainty (Denechaud).

Lutetium: Gordon expresses difficulty in obtaining values for both Lu and Yb. The 208 kev peak arising from the decay of 6.7-day Lu^{177} is a good strong line and easily resolved between the neighboring peaks discussed by Denechaud and Gordon. The poor precision obtained from the analyses is probably related to its low abundance.

Zirconium: Zirconium analyses are plagued with several problems. The 766 kev peak arising from the decay of 35.3-day Nb^{95} appears to be the best of the peaks listed by Gordon; however, the use of this peak gave inconsistent results. After comparison of several analyses, the 757 kev peak of 65-day Zr^{95} was found to give the best results. The exact reason for the inconsistency of the 766 kev peak of Nb^{95} is not known; however, another gamma ray is suspected.

Another source of error arises from the fact that mass number (A) 95 is at the peak of the fission product yield curve for fission of U^{235} (Friedlander et al., 1966). Using published values for U and Zr in G-2 (Flanagan, 1969) and cross-sections and abundances listed on the Chart of the Nuclides (Goldman and Roesser, 1966), calculations show that as much as 13.4% of the Zr^{95} and Nb^{95} produced during neutron bombardment could arise from fission of U^{235}. This value is a limiting value assuming that all of the nuclides that are produced by fission of U^{235} have more than 53 Neutrons (N). All the nuclides with $A = 95$ and $N > 54$ decay to Nb^{95} ($N = 54$). According to the above assumption, if the 766 kev peak of 35-day Nb^{95} were counted, 13.4% of the activity would result from fission of U^{235}. Unfortunately, Mo^{95} ($N = 53$) is also a fission product of U^{235}. Mo^{95} is also a stable isotope. Because of this situation, there is no convenient method to determine what proportion of the fission products with $A = 95$ were Mo^{95}. An estimate of the contribution of U fission to Zr^{95} can be made, however, by checking the abundance of Ba^{140} in the sample because essentially all of Ba^{140} would come from U^{235} fission. Fission products of mass number 140 arise simultaneously with those of mass number 95. Ba^{140} has a gamma ray at 537.3 kev (Lederer, et al., 1968) which does not have a greatly different value from the 757 kev peak of Zr^{95} when both are plotted on the 26 cc. detector efficiency curve. The percent of energy yields are 34% and 49% respectively. Under these circumstances one would expect to see comparable intensities for these two peaks, certainly within a factor of 2. This peak was only observed in one spectrum and there it was small enough to indicate that the effect could be neglected. Furthermore, if the effect were significant one would expect to see high Zr values accompany high Th values in these samples, but this is not observed. The highest value for Th in the Westerly granite correlates with the lowest value for Zr. Such arguments are not conclusive however, since high Th values could arise from a greater abundance of high Th minerals relative to Zircon as discussed in the text.

It may be concluded then that the errors in Zr analyses may be larger than those listed in table 2-II but certainly not large enough to invalidate the arguments based on Zr/Hf ratios. The fact remains that good precision is obtained and the results are in good agreement with values reported in the literature. Further exploratory work is needed before neutron activation analyses for Zr can be considered reliable, and future work should include independent checks on Zr by other techniques such as X-ray fluorescence.

It should be noted that mass number 141 is also on the peak of the fission yield curve and should be considered when using the 145 kev peak of Ce^{141} for Ce analysis. Due to the high Ce values and low U abundances the effect was negligible (< 1%) for these samples, but it should be kept in mind for future work.

Hafnium: The only interference with the 482 kev peak arising from the decay of 42.5-day Hf^{181} listed by Gordon is the 487 kev line arising from the decay of 1.67-day La^{140} and 12-day Ba^{131}. After 40 days this interference is gone completely. The only problem encountered in analyzing for Hf was the occasional appearance of a small blip on the low energy side of the peak. In such cases the background was taken on the low energy side of the blip. The source of the blip has not yet been discovered.

Tantalum: Gordon claims to have obtained the best results using the 67.75 kev and 100.10 kev lines arising from the decay of 115.1-day Ta^{182}; in this study however, the best results were obtained from the 1222 kev line. Gordon doesn't list any interferences and there do not seem to be any background problems.

Scandium: Gordon discusses the problems associated with scandium analyses. In this study the best results were obtained from the 889 kev line arising from the decay of 83.9-day Sc^{46}. The main problems with this peak are resolution from the 879-kev line of 72.1-day Tb^{160} and its position on the Compton edge of the 1120 kev line. After 40 days both peaks are small enough that they can be resolved as mentioned in the discussion of Tb. The background measurement on the high energy side is a matter of judgement, but the height/background ratio is > 10 and after counting for 5 hours the background problem is nigligible. Thorium: All of the prominent lines listed by Gordon as arising from the decay of 27-day Pa^{233} are plagued with interferences. The best results in this study were obtained from the 311.9 kev line. The main problem with this peak is that it cannot always be resolved from the 308 kev line of 32-day Yb^{169}. This of course is a situation which doesn't improve with age and therefore the sample is best counted after about 12 days, as soon as the background noise has subsided.

Background measurements are taken at the outside of both peaks, and only the center portion of the peak is used for analysis as shown in table 2-II. In this way the effect of contribution from the 308 kev line of Yb^{169} is kept to a minimum. Denechaud discusses the use of portions of peaks for analysis.

C. Comments on analyses of certain mineral fractions:

In general, estimates of the RE content of the various minerals were made and the radiation times estimated to give approximately the same count rates as the whole-rock samples.

Feldspars: The same procedure was followed for the feldspars as for the whole-rock samples, except that the second irradiation was for 1 hour rather than 1/2 hour. The abundances were in general rather low, Tb being below the limit of detection in the K-spar fraction from the Narragansett Pier. The large amounts of Na precluded obtaining any reliable numbers for Dy. Analyses for Na were based on the amount of Na_2CO_3 added separately to the standard.

Quartz and magnetite: Poor planning resulted in quartz and magnetite fractions being paired. Because of the high activity from Fe^{59} the magnetite had to be counted separately with the standard in a different position than for the quartz.

Because of the extremely low abundances expected, liquid standards were used. Smaller, highly purified samples were also required--they were collected in small polyethylene tubing which was heat sealed and positioned in the center of the 2 dram vials for counting purposes. An irradiation of 12 hours was attempted on the first set but the amount of heat generated proved to be too great and the heat seal broke. Attempts to estimate the actual loss by reirradiation and counting of Dy with another standard have yielded doubtful results; however, the relative values should be good.

The second set was irradiated for only 4 hours and thus longer counting times (12 hours) were required for the later counts. Comparison of these results with those obtained for the first set indicates that the values obtained for the Peabody quartz fraction and the Narragansett Pier magnetite fraction could be as much as an order of magnitude too high. The Dy values however were not affected and should be accurate.

The high level of activity of the magnetite samples resulting from the large Mn content makes it difficult if not impossible to obtain meaningful numbers for Dy. In fact, high background problems from lingering Fe activity plague the analyses for most of the elements, and the errors are probably greater than those shown in table 2-II for the whole-rock samples. If Ce numbers are considered critical, the 145 kev peak of Ce^{141} and the 143 kev peak of Fe^{59} could be resolved by using a smaller detector (LEPS). In future work an iron extraction procedure should be followed if magnetite values are critical. The possible high Hf values in the Peabody quartz fraction warrant further study.

<u>Mafic minerals</u>: The RE concentrations in the mafics were expected to be high but the samples were small, and therefore they were irradiated for 1/2 hour on the long irradiation. These samples were also collected in small tubes as discussed above. The lack of a Ce number for the amphibole

fraction from the Peabody granite is believed to be due to equipment malfunction.

Heavy minerals: Here again the trace element concentrations were expected to be high, but only very small samples were available. The samples were collected in small tubes as before, and irradiated for 15 minutes only on the long irradiation.

D. Sampling errors:

The importance of determining the exact nature of the inclusions in the quartz fractions came up earlier concerning the possible contamination of the quartz fraction from the Narragansett Pier granite. The inclusions are colorless when observed under the microscope. The Narragansett Pier quartz fraction is enriched in the heavy REE. Zircon is known to concentrate heavy REE. (See fig. 4) This implies that the enrichment of the Narragansett Pier quartz fraction might be due to small inclusions of zircon.

Adams et al. (1959) discuss the constancy of the Th/Zr ratio for a variety of crustal materials. It will be noted from tables 5 and 6 that the Th/Zr ratios for the heavy mineral fractions (predominantly zircon) are about an order-of-magnitude lower than those of the other mineral fractions. Therefore the lower this ratio is for various mineral fractions, the more suspicious one becomes of contamination by zircon--especially if inclusions of zircon are observed in other minerals in thin section. The Peabody granite can be taken as the limiting case. On the basis of the above argument it is concluded that the quartz is relatively free from contamination by zircon, because < 0.1% contamination would dominate the Th/Zr ratio in that fraction. In the case of the amphibole fraction, a 1% contamination by zircon would reduce the Th/Zr ratio to ≈ 42% of the value shown in table 6. The sensitivity of course decreases with increasing contamination so that a 2% contamination results in a ratio ≈ 35% of the given value. Assuming that the Th/Zr ratio should remain constant, at least within an order-of-magnitude, it is concluded that the mafic fractions are also relatively free from contamination by zircon.

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