APPALACHIAN RHYOLITES: GEOCHEMICAL DATA CONCERNING THEIR ORIGIN

by

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ABSTRACT: Rhyolites of the Mt. Rogers area (Virginia) have been analyzed for trace elements by applying instrumental neutron activation analysis. Field evidence, petrographic and chemical data indicate that the Mt. Rogers rhyolites can be divided into three units (units A, B and C). Type C rhyolites are the oldest ones and contain phenocrysts of perthite and plagioclase. Types A and B rhyolites are the youngest and contain phenocrysts of quartz and perthite. Types A and B differ in the total phenocryst content (about 30% in Type A and 10% in Type B) and in their rare earth element (REE) patterns.

There are systematic chemical trends in the sequence of Mt. Rogers rhyolites. The abundance of SiO_2 *increases in going from Type C rhyolites to Types A and B, and the abundances of CaO,* Na_2O, TiO_2 *and Fe decrease in the same way. Rocks of Types A and B are strongly depleted in Ba, Sr and Eu when compared with rock Type C. This suggests that Types A and B rhyolites were derived by a process of crystal fractionation from a magma of composition of Type C rhyolites, and that feldspars played an important role in this process.*

Major element data and phenocryst composition in conjunction with a least-squares fitting program were used to determine the fractional crystallization parameters necessary to explain rhyolites A and B as liquid derived by fractional crystallization from C. These calculations resulted in feldspar removal ranging between 20-40% in passing from Type C rhyolites to Types A and B. Using estimated partition coefficients the Eu data can be explained by a fractional crystallization of feldspar ranging between 24-39%. In most cases major and trace elements agree within 5%. The disagreement may be a result of not treating the Mg and Fe data in the computer program. Particularly difficult to explain are the absolute abundances of light and heavy REE rhyolites when sole crystallization of feldspar is considered.

Some rhyolites of the Traveler Mt. volcanic center (Maine) were also analyzed for trace elements, sodium and potassium and their abundance is compared with that of Mt. Rogers rhyolites. Also the Mt. Rogers rhyolites are compared with some New Zealand volcanic rocks (Taupo Rhyolites and Mayor Island Pantellerites). It is observed that the Traveler Mountain rhyolite and the New Zealand volcanic rocks are more like the Type C Mt. Rogers rhyolites than Types A and B. An important difference between the New Zealand volcanics and the Appalachian rhyolites is in the Na/K ratio being greater than 1 in the first ones and less than 1 in the Appalachian rhyolites. This fact may be very significant in the origin of the Mt. Rogers and Traveler Mt. rhyolites.

THESIS SUPERVISOR: Frederick A. Frey

TITLE: Assistant Professor

To my wife, Ana Rosa, and to my children Marcelo Andrés, Gonzalo Alberto, Leopoldo Patricio and Ana Carolina.

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Introduction

The aim of this work has been to determine the abundance of some major and trace elements of volcanic rock samples representative of the Mount Rogers volcanic center, Virginia, (1) in order to attempt a possible explanation of their genesis.

Also, trace element abundances were determined in volcanic rock samples representative of Traveler Mountain (2) (early Devonian age) in North Central Maine.

Finally, two rocks whose lithology is characteristic of the Pond Mountain volcanic center (southwest of Mount Rogers) and one sample of rhyolite that is stratigraphically underneath the rhyolites of the Mount Rogers center, were studied for major and trace elements.

The determination of the abundance of trace elements was carried out in this laboratory by applying the Instrumental Neutron Activation Analysis technique (see Appendix). For the rocks of Virginia determination of major elements via wet chemical techniques and some trace elements via emission spectrography were done by the United States Geological Survey (U.S.G.S., Washington. D.C.)

Dr. Rankin has made the field studies of both regions. According to Rankin (1), at Mount Rogers it is possible to distinguish three units: Wilburn rhyolite (rhyolite A), Whitetop rhyolite (rhyolite B) and quartz latite (rhyolite C).

The last one is a lava flow and, in the field, is older than the other two. Rhyolites A and B are younger and they are respectively ash flow and lava flow mixed with ash flow.

Rankin et al. (3) have determined the age of one rhyolite type A and that of a rhyolite type B. The age of type A is between 750 and 798 million years and that of type B is between 586 and 778 million years.

The three groups have similar ground mass rich in alkali-feldspar. Common accessory minerals are apatite, zircon, xenotime, monazite, sodic amphibole and magnetite. They differ in their phenocrysts: Type A and B contain phenocrysts of perthite and quartz; rhyolite C contains phenocrysts of perthite and plagioclase.

When the normative quartz, orthoclase and albite of the whole rock of these samples are plotted in the Ab-Or-Qtz diagram of Tuttle and Bowen (4), it can be seen that they are spread around the low temperature trough. The comparison of this diagram with those obtained by Lipman for six tertiary rhyolitic ash-flow sheets from southern Nevada (5). suggests there exists a possible sequence between rocks V11, V3 and V6 and V9. For this reason these four rocks have been considered as representative of their respective groups and the discussion of the possible evolution of the magma has been centered mainly on them.

Rocks V6 and V9 are very similar in major and trace elements and in the kinds of phenocrysts they have. They differ markedly from rock V11 in chemical and in phenocryst composition. Rock V11 contains more Al_2O_3, MgO, FeO, CaO, P_2O_5 and less SiO_2 and K_2O than rocks V6 and V9. The same striking difference can be seen when the minor and trace elements are considered.

There are some significant differences in chemical composition within a given group. This shows that the magma which gave origin to a given group was not homogeneous or that the samples have experienced different post-magmatic processes. This is an important point to be considered in the elaboration of a genetic model for these rocks.

In the Traveler Mountain volcanic center (2) about 80 cubic miles of rhyolite occur within a structural depression thought to represent an ancient caldera. Two members have been distinguished in this unit: the basal Pogy member and the overlying Black Cat member. The difference between them is in the amount of quartz phenocrysts. Rocks of the upper member have few or no quartz phenocrysts. Rocks from the lower member are richer in them. This suggests the last ones were somewhat more crystallized at the time of the eruption. According to Rankin, this observation is consistent with the idea that the basal Pogy member came from the cooler upper part of a magma chamber and the overlying Black Cat member came subsequently from deeper in the magma chamber

This idea is supported by the fact that rocks of the Pogy member contain lithic fragments that are absent in the Black Cat. Unfortunately, the rocks from the Traveler Mountain volcanic center analyzed in this work came only from the Black Cat member. For this reason, the discussion will be centered on the rocks of the Mount Rogers volcanic center and the data for Traveler Mountain will be used only to be compared with the respective ones for Mount Rogers rocks. A similar analysis will be made for the data for the two rocks whole lithologies corresponding to that of the Pond Mountain volcanic center and with the data for that rock sample representative of the rhyolitic layer underneath the rhyolites of the Mount Rogers volcanic center.

The following are the main problems that will be discussed in this work: a) the possibility that a magma of composition of rock V11 be the parent magma of rocks of composition V3, V6 and V9; b) the possibility that the chemical differences between rocks type B rhyolites can be attributed to a certain kind of differentiation, to the mode of eruption, the post-depositional conditions or simply those differences are not significant; c) the possible origin of rocks V8, V4, V2 and V1 whose descriptions are given later. Finally, a comparison will be made between the patterns for the Mount Rogers samples and those for the Traveler Mountain rhyolites, Taupo rhyolites of New Zealand (23) and Mayor Island pantellerites of New Zealand.

Results

The rock samples studied in this work are described below. The first number preceding each sample from Virginia is that given to them by Dr. Rankin; the second one is the corresponding number used by the author. The samples from Traveler Mountain are identified by the letter M preceding a number and the samples from Virginia are identified with the letter V. The modal analysis was made on the basis of 1000 point count.

WS3-68-1 = V6 (type A) is an ash flow. In thin section it consists of 91.8% of ground mass (mainly alkali feldspar and quartz), 3% phenocrysts of perthite, 2.7% quartz phenocrysts and 2.3% opaques. Accessory minerals are: apatite, zircon, xenotime, epidote, riebeckite and monazite.

RWS-3-2 = V2 (type A) is an ash flow. In thin section it consists of 66.4% of ground mass (mainly alkali-feldsapr and quartz), 26.3% of perthite phenocrysts, 6.6% of quartz phenocrysts. The main accessory minerals are apatite, mafic and zircon.

RTC 2-17 = V3 (type A). In thin section it presents 69.3% of ground mass (mainly alkali feldspar and quartz); 22.4% of perthite phenocrysts; 6.6% of quartz phenocrysts; 0.9% opaques. The main accessory minerals are apatite, zircon, mafic and monazite.

RWS-1-56 = V1 (type B) consists almost entirely of a ground mass of alkali feldspar and quartz. Some crystals of mafic and alkali amphibole are observed, but no phenocrysts.

TSI-5 = V4 (type B) consists of 91% of groundmass; 4.9% of perthite phenocrysts; 3.5% of quartz phenocrysts; 0.1% of opaques and 0.5% of others.

WSH69-25A = V8 (type C rhyolite) consists of 75.8% of groundmass (mainly alkali feldspar and plagioclase); 8.7% of perthite phenocrysts; 13.1% of plagioclase phenocrysts; 0.9% opaque and 1.5% of other (apatite, sphene, epidote, sericite and albite).

RPN4-13 = V11 (type C) consists of 81% of ground mass (mainly alkali feldspar and plagioclase); 4% of perthite phenocrysts; 7.5% of plagioclase phenocrysts; 0.7% of opaques and 6.8% of other (apatite, epidote, chlorite, sericite, albite vesicles, fluorite xenotime).

The composition of plagioclase phenocrysts in type C rhyolites is approximately $Ab_{92}An_8$. This composition was determined by applying the Carlsbad albite twins method. The composition of perthite in these samples is approximately $Ab_{40}Or_{60}$. This composition was determined by counting albite and orthoclase in different perthite phenocrysts.

It was not possible to get a thin section of sample WS4-69-26 = V9 (type B). For this reason its description is not given.

MWC-69-37 = V7 and RPNI-8 = V10 are coarsely porphyritic rhyolites. The first one contains appoximately 58% of groundmass; 31% phenocrysts of perthite; 6% phenocrysts of quartz; 4% of opaques and 1% of others. Sample V10 contains 46% of groundmass; 35% phenocrysts of perthite; 16% phenocrysts of quartz; less than 1% phenocrysts of plagioclase and 2% of others. The lithology of these rock samples is characteristic of Pond Mountain volcanic center which is southwest of the Mount Rogers volcanic center.

RPN4-21 = V5 is a porphyritic rhyolite containing about 66% of groundmass; 18% phenocrysts of perthite; 8% phenocrysts of quartz; 1% phenocrysts of plagioclase; 6% of albite vesicles and 2% of others. This sample is representative of a rhyolitic layer that is stratigraphically underneath the rhyolites of the Mount Rogers volcanic center and currently not assigned to any center (Rankin, personal comunication).

The samples from Traveler Mountain analyzed in this work are, in general, very similar. They contain approximately 90% of a very compact fine groundmass, 7.5% phenocrysts of plagioclase whose composition is about $Ab_{53}An_{47}$ (although some are zoned); 2% phenocrysts of augite; less than 1% is magnetite. Some samples contain phenocrysts of quartz, but its abundance is always less than 1%. There also may be present phenocrysts of biotite and horblende. In general, the phenocrysts and groundmass are altered (mafics to chlorite and calcite; feldspars to sericite and calcite). Finally, it is possible to observe some sedimentary fragments.

Analysis of G-2.- In order to check if the standard solution used for the determination of trace elements was correct, a run was made with the geological standard G-2. The results obtained are shown in the first column of the Table I. As a way of comparison, this table also contains the results for G-2 obtained by others workers. The number that follows the ± sign in the first column of this table represents the " standard error of the mean ". This number was calculated in the following way:

a) A number "n" of determinations for each elements was made. Generally the value of "n" was 4, but in those cases, such as Ta, in which more than one peak was used for its determination, the value of "n" was greater than 4.

b) The values "x_i" obtained in those "n" determinations were added and then divided by "n" in order to get an average value $\bar{x}$.

c) The deviation of each determination from the average, ie ($x_i-\bar{x}$), was calculated and then squared. These values were added, ie $\Sigma (x_i-\bar{x})^2$ was obtained. This sum was divided by (n-1) and the squared root of the ratio was calculated. This correspond to the standard deviation of the mean, "s",ie:

$$s = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{n-1}}$$

d) The standard error of the mean, "e", which is a measure of the precision of the measurements, was calculated by dividing the standard deviation by the square root of the number of determinations "n", ie:

$$e = \frac{s}{\sqrt{n}}$$

Explanation of tables II to VI.- Table II shows the results of the chemical analysis for major elements on reduced water free basis. Table III shows the results of the chemical analysis for mayor elements when water is taken into account and with no correction for iron oxidation states. Chemical analysis for major elements were made only on samples from Virginia. Table IV displays the results of chemical analysis for minor and trace elements. In this case, all the results, except those for Na and K, are given in ppm. The results for Na and K are given in percentages.

The next step in the treatment of the data was the calculation of the norms. The results based on the composition of reduced, water free rock are displayed in Table V. (The results for oxidized, water free rock do not differ significally from those displayed in Table V. For example, the weight percentages of Ab, Or and Qtz for the reduced, water free sample V6 are respectively 31.42%, 29.58% and 38.99%, while for the oxidized, water free sample V6 they are respectively 32.97%, 29.31% and 37.72%). The norms were calculated according to the CIPW method outlined by Niggli.

The normative Ab, Or and Qtz for samples of Virginia were expressed in weight per cent and plotted in the Ab-Or-Qtz diagram To do this, the normative Ab, Or and Qtz, which are expressed in " equivalent per cent " were first transformed to " gram " by multiplying the normative amount of Ab by the factor 52.44 gm/equiv, that of Or by 55.67 gm/equiv and the normative amount of Qtz by 60.08 gm/equiv. These convertion factors were determined by dividing the molecular weight of each substance by the number of cations present in their respective molecules. The amount of each substance expressed in gm. was then recalculated to 100 in order to express it in weight per cent. These values were plotted in the triangular diagram Ab-Or-Qtz to see if it was possible to observe some crystallization trend between then (Figure 1).

The rare earth element (REE) data, which are one of the more useful indices of fractionation (6) were normalized against their respective abundance in chondrites (Figures 2,3 and 4), since it has been suggested that the average rare earth pattern for the whole earth matches the chondritic pattern (7).

Finally, Table VI shows some critical element ratios which are also very useful indices of fractionation (6).

Table I

Trace Elements in G-2

	This Work	1	2	3	4	5	6
La	94±2	93±7	93±6	78	87	95	81
Ce	173±3	163±5	177±5	110	175	185	144
Nd	55±3	48±2	51±2	67	42	51	-
Sm	7.9±0.3	7.2±0.1	7.3±0.1	7.0	6.7	7.8	7.3
Eu	1.48±0.02	1.52±0.02	1.53±0.02	1.3	1.50	1.60	1.37
Gd	3.7±0.1	3.5±0.1	3.9±0.2	3	6.2	6.5	-
Dy	-	2.5±0.1	-	5.2	2.0	2.1	2.1
Yb	0.74±0.02	0.62±0.02	0.81±0.03	0.9	0.65	0.72	0.8
Lu	0.10±0.05	0.12±0.01	0.13±0.01	0.13	0.13	-	0.18
Rb	193±5	191±3	177±5	-	-	-	129
Ba	2000±80	-	-	-	-	-	-
Co	4.3±0.3	-	-	-	-	-	-
Sc	3.3±0.2	-	-	-	3.5	-	-
Th	23.9±0.5	-	-	-	25.9	-	-
Ta	0.97±0.06	-	-	-	1.0	-	-
Cs	-	-	-	-	-	-	-
Na	3.15	-	-	-	-	-	3.08%
K	3.97	4.66±0.05	-	-	-	-	4.0%
Hf		-	-	-	7.8	-	-

Table I continued

	7	8	9	10	11	12
La	84	76	142	85±2	81±1	82 - 130
Ce	167	175	180	168.5	144±4	131 - 2400
Nd	-	-	-	-	-	-
Sm	9.1	10	-	7.4	8.7±0.15	7.3 - 9.4
Eu	1.6	-	-	1.29±0.01	1.37±0.05	-
Gd	-	-	-	-	-	-
Dy	-	-	-	2.3±0.3	-	-
Yb	21	-	-	0.56±0.05	0.8±0.2	-
Lu	-	-	-	0.10±0.02	0.18±0.08	-
Rb	185	108	513	-	129±4	150 - 550
Ba	-	-	-	-	1800±70	1500 - 2000
Co	-	-	-	-	4.3±0.2	3 - 6.2
Sc	-	-	-	3.12±0.02	3.5±0.2	3 - 6
Th	-	-	-	24.5±1.4	25.9±0.5	24.9 ± 1.4
Ta	-	-	-	0.80±0.04	1.0±0.1	-
Cs	-	-	-	-	1.4±0.3	-
Na	-	-	-	-	2.95±0.05 %	2.89 - 3.07 %
K	3.9%	3.3%	3.9%	-	2.0±0.5%	3.69
Hf	-	-	-	8.26±0.02	7.8±0.5	8.4 ± 0.2

1&2 Rey et al. Anal.Chim.Acta 51 (1970) 163

3 Morrison, cited by Rey et al.

4&5 Higuchi, cited by Rey et al.

6,7,8 & 9 Others cited by Rey et al.

10 Buma, M.Sc.Thesis MIT (1970)

11 Gordon et al. GCA 32 (1968) 369.

12 Range of the values obtained by other authors cited by Gordon et al.

Table II

Results of the Chemical Analysis for Major Elements in Dry Rock Samples from Virginia

		SiO_2	Al_2O_3	FeO	MgO	C_2O	Na_2O	K_2O	TiO_2	P_2O_5	MnO
	V6	76.55	11.73	2.41	0.06	0.57	3.71	4.72	0.22	0.02	0.01
A	V2	76.66	12.14	2.29	0.16	0.66	3.84	3.94	0.24	0.02	0.05
	V3	74.79	12.58	2.82	0.30	0.63	3.96	4.57	0.28	-	0.06
	V4	78.47	11.34	2.43	-	0.19	4.56	2.84	0.13	-	0.04
B	V1	77.14	11.44	2.14	0.17	0.03	2.91	6.02	0.12	0.01	0.03
	V9	77.13	11.62	2.53	0.05	0.52	3.23	4.75	0.17	-	-
	V8	70.53	13.48	4.60	0.19	0.99	3.04	6.28	0.63	0.20	0.05
C	V11	68.87	13.96	5.30	1.11	1.01	4.15	4.65	0.68	0.19	0.08
*	V7	76.41	11.52	2.81	0.08	0.56	3.54	4.85	0.21	0.02	-
	V10	73.46	13.17	2.31	0.22	1.22	2.53	6.59	0.36	0.07	0.06
	V5	72.70	13.24	3.70	0.15	1.05	2.91	5.72	0.39	0.08	0.05

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Table III

Results of Chemical Analysis for Major Elements of Rock Samples from Virginia when Water is Taken into Account

		SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O
A	V6	76.25	11.68	1.67	0.90	0.06	0.57	3.70	4.70
	V2	75.80	12.00	1.40	1.00	0.16	0.65	3.80	3.90
	V3	73.70	12.40	2.60	0.44	0.30	0.62	3.90	4.50
B	V4	75.70	11.20	2.40	0.24	-	0.19	4.50	2.80
	V1	76.90	11.40	2.10	0.24	0.17	0.03	3.90	6.00
	V9	76.30	11.50	2.20	0.52	0.05	0.51	3.20	4.70
C	V8	69.60	13.30	3.60	1.30	0.19	0.98	3.00	6.20
	V11	68.10	13.80	4.80	0.42	1.10	1.00	4.10	4.60
*	V7	75.60	11.40	2.60	0.44	0.08	0.55	3.50	4.80
	V10	72.50	13.00	2.40	0.12	0.22	1.20	2.50	6.50
	V5	71.94	13.10	3.09	0.88	0.15	1.04	2.88	5.66

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Table III continued

		H_2O^+	TiO_2	P_2O_5	MnO	CO_2	F	S
A	V6	0.16	0.22	0.02	0.01	0.02	0.30	0.01
	V2	0.56	0.24	0.02	0.05	0.18	-	-
	V3	0.42	0.28	-	0.06	0.12	-	-
B	V4	0.25	0.13	-	0.04	-	-	-
	V1	0.35	0.12	0.01	0.03	-	-	-
	V9	0.62	0.17	-	-	0.05	0.12	-
C	V8	0.62	0.62	0.20	0.05	0.05	0.21	-
	V11	0.66	0.67	0.19	0.08	-	-	-
*	V7	0.60	0.21	0.02	-	-	0.16	-
	V10	0.47	0.36	0.07	0.06	0.66	-	-
	V5	0.11	0.39	0.08	0.05	0.06	0.08	-

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Table IV

Results of Chemical Analysis for Minor and Trace Elements of Rock Samples from Virginia and Maine

		La	Ce	Nd	Sm	Eu	Gd	Dy
	M1	54.77	117.87	56.18	11.21	1.82	12.76	16.53
	M3	57.64	114.77	55.78	14.02	1.84	12.69	-
	M5	53.29	126.42	62.60	12.12	2.07	12.43	-
	M6	42.11	95.59	48.86	12.46	1.95	10.28	-
	M8	65.31	129.46	64.25	15.26	2.15	14.20	15.25
	M10	58.68	112.99	57.44	13.91	1.90	12.28	16.36
	M14	57.42	112.78	62.93	14.41	1.32	12.33	-
A	V6	66.31	159.25	83.15	25.16	0.24	25.78	-
	V2	115.27	254.15	134.41	31.59	0.37	23.73	20.16
	V3	151.49	296.91	168.96	34.73	0.54	23.35	21.70
B	V4	50.38	111.13	51.47	13.01	0.15	15.38	-
	V1	36.51	88.86	59.21	21.58	0.20	18.26	27.35
	V9	61.97	166.99	89.46	28.85	0.32	27.86	-
C	V8	94.97	210.86	97.12	18.77	3.49	16.48	-
	V11	76.12	147.93	69.88	14.36	2.77	11.66	-
*	V7	230.32	563.08	215.86	43.10	0.63	35.41	-
	V10	103.26	192.36	81.30	15.74	1.60	13.19	-
	V5	115.59	228.18	108.01	20.90	2.58	19.01	-

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Table IV Continued

		Yb	Lu	Th	Ta	Ba	Ba**	Sr**	Hf
	M1	7.48	-	15.13	1.30	595.82			12.84
	M3	6.83	1.17	14.37	1.28	618.63			12.10
	M5	6.35	1.09	12.66	1.51	615.83			15.08
	M6	6.71	1.11	13.12	1.31	595.29			14.23
	M8	7.81	1.16	14.99	2.70	562.16			14.44
	M10	7.89	1.09	14.22	2.35	581.85			15.02
	M14	7.42	1.23	12.61	1.25	163.17			12.99
A	V6	18.45	2.35	21.61	7.60	Nd	40	20	33.99
	V2	9.02	1.48	13.16	3.37	Nd	48	20	20.37
	V3	9.46	1.53	26.24	3.04	Nd	84	28	22.65
B	V4	16.29	2.78	22.45	6.28	Nd	22	10	30.35
	V1	14.16	2.29	17.86	5.28	Nd	68	14	19.21
	V9	19.93	3.11	27.28	5.13	Nd	88	26	36.13
C	V8	7.76	1.29	8.66	1.46	2243.73	1800	160	20.95
	V11	6.11	1.07	6.54	1.68	1081.15	900	98	17.53
*	V7	10.38	1.74	18.18	2.80	Nd	64	18	23.13
*	V10	5.74	0.95	15.44	1.93	894.71	840	84	13.31
	V5	8.85	1.52	10.63	2.33	1382.44	1000	100	23.53

* Pond Center

** Determined Spectrographically

Table IV continued

		Rb	Cs	Sc	Co	Na	K
	M1	202.16	5.36	-	1.32	2.11	5.00
	M3	181.56	2.98	29.23	2.16	-	-
	M5	189.26	4.79	28.38	2.27	-	-
	M6	182.36	7.40	29.69	2.71	-	-
	M8	202.58	12.97	33.50	2.26	1.77	6.06
	M10	180.38	18.14	33.27	2.00	2.73	5.66
	M14	Nd	Nd	26.10	1.59	-	-
A	V6	274.31	Nd	0.30	0.37	-	-
	V2	122.87	14.41	0.55	0.78	2.93	5.00
	V3	119.48	0.68	0.90	0.22	3.11	4.40
B	V4	126.14	2.74	0.21	Nd	-	-
	V1	171.75	0.79	0.12	Nd	1.84	5.66
	V9	260.23	Nd	0.59	Nd	-	-
C	V8	218.11	Nd	9.72	3.57	-	-
	V11	112.28	Nd	7.83	3.41	-	-
*	V7	137.43	Nd	0.59	Nd	-	-
*	V10	167.88	1.53	2.68	0.80	-	-
	V5	127.74	1.57	5.02	0.90	-	-

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*Pond Center

Table V

Norm Compositions for Rock Samples from Virginia
Based on Compositions of Dry Rocks

	A			B		
	V6	V2	V3	V4	V1	V9
Qtz	34.05	35.85	30.30	38.74	35.17	36.96
Cor	-	0.40	-	0.43	0.10	0.22
Or	27.88	23.31	26.99	16.75	35.57	28.07
Ab	31.43	32.52	33.49	38.56	24.62	27.37
An	1.39	3.13	3.08	0.95	0.08	2.56
Wo	0.55	-	0.02	-	-	-
En	0.15	0.40	0.76	-	0.42	0.13
Fs	4.08	3.89	4.82	4.32	3.78	4.36
Il	0.42	0.46	0.54	0.25	0.23	0.33
Ap	0.05	0.05	-	-	0.02	-

Table V continued

	C		Pond Center		
	V8	V11	V7	V10	V5
Qtz	23.54	19.68	34.12	29.17	28.79
Cor	0.36	0.72	-	-	0.54
Or	37.13	27.49	28.67	38.92	33.80
Ab	27.72	35.09	29.93	21.44	24.63
An	3.60	3.76	1.23	5.12	4.69
Wo	-	-	0.58	0.19	-
En	0.48	2.77	0.20	0.56	0.38
Fs	7.50	8.76	4.81	3.75	6.24
Il	1.19	1.29	0.40	0.69	0.75
Ap	0.48	0.46	0.05	0.17	0.19

Table VI

Some Critical Element Ratios Useful as Indices of Fractionation

	A			B		
	V6	V2	V3	V4	V1	V9
Ba/Sr	2.00	2.40	3.00	2.20	4.90	3.40
Ba/Rb	0.15	0.39	0.70	0.17	0.40	0.34
K/Rb	143	266	318	187	291	152
La/Sm	2.64	3.65	4.36	3.87	1.69	2.15
Eu/Eu*	0.03	0.04	0.06	0.03	0.03	0.04
Sm/Yb	1.36	3.50	3.67	0.80	1.52	1.45
La/Yb	2.18	7.75	9.71	1.87	1.56	1.88

	C		Pond Center		
	V8	V11	V7	V10	V5
Ba/Sr	11.30	9.20	3.56	10	10
Ba/Rb	8.25	8.04	0.47	5.00	7.83
K/Rb	239	345	293	326	372
La/Sm	5.06	5.30	5.34	6.56	5.53
Eu/Eu*	0.62	0.69	0.05	0.35	0.43
Sm/Yb	2.42	2.35	4.15	2.74	2.36
La/Yb	7.42	7.55	22.19	17.99	13.06

Discussion

A. Differentiation trends in Mt. Rogers rhyolites.

It has already been mentioned that Mt. Rogers volcanic center contains three rock units. Rankin (personal communication) has classified the rocks analyzed in this work as follows: V2, V3 and V6 are type A rhyolites; rocks V1, V4 and V9 are type B rhyolites and rocks V8 and V9 are type C rhyolites. The latter ones are the oldest and zircon age studies (3) have demonstrated that type B rhyolites are the youngest.

Rankin classified rock V6 as a rhyolite A because it had a somewhat higher percentage of phenocrysts than a typical rhyolite B and because it contained a sodic amphibole in the groundmass. The only other occurrences of solid amphibole are in rhyolite A. The major and trace element chemistry of rocks sample V6 looks more like that of rock sample V9 (rhyolite B) than any of the other rock samples of rhyolite A. Rankin also pointed out that the contact between rhyolite A and rhyolite B is gradational in terms of the percentage of phenocrysts and rock V6 is from a large float block on the side of a ridge down slope from the contact line. All these facts suggest that rock V6 may be a link between a typical rholite A and a typical rhyolite B. Petrologically rock V6 has characteristics of a rhyolite A, but chemically it looks more like a rhyolite B. As a simplification and because this discussion is based more on the chemical trends observed in the three rock units, rock V6 will be considered as a rhyolite B.

The plot of the composition of samples of this volcanic center on the Ab-Or-Qtz diagram shows that although they are spread, they are quite close to the low temperature trough. The most spread are samples of rhyolite B.

The spread could result for several reasons: errors in experimental work, samples were not fresh and they were not formed under conditions of crystal-liquid equilibrium. One fact is interesting to point out: Table VII shows that the Na/K ratio of type B rocks decreases in passing from V4 to V6 and V1. Table VII also shows that this fact is not only due to a depletion in the absolute abundance of sodium, but also to an increment in the absolute abundance of K.

The enrichment in K and the depletion in Na suggest that while sodium has been removed, potassium has been added. Probably the loss of sodium is due to ground water leaching and some excess of K_2O is possibly due to an ion exchange process - K_2O substituting for some of the leached sodium. Similar trends were found by Noble (8) and Lipman (9) in some natural hydrated glasses of southern Nevada.

Table VII shows that the leaching process affected exclusively the sodium abundance. SiO_2 which is also very susceptible to loss bt leaching was not affected. Also it is

TABLE VII. Some trends in type B rhyolites.

	Na_2O/K_2O	Na_2O	K_2O	SiO_2	Al_2O_3	FeO	La	Eu	Yb	Ba	Sr
V1	0.48	2.91	6.02	77.14	11.44	2.14	36.31	2.90	14.16	68	14
V9	0.68	3.23	4.75	77.13	11.62	2.53	61.97	4.64	19.93	88	26
V6	0.79	3.71	4.72	76.55	11.73	2.41	66.31	3.48	18.45	40	20
V4	1.61	4.56	2.84	78.47	11.34	2.43	80.38	2.17	16.29	22	10

seen that whatever the process or processes responsible for the Na/K ratio in type B rocks, these processes are not responsible for the absolute amount of trace elements since there is not correlation between the Na/K ratio trends and the trends observed in trace elements.

Another fact that must be mentioned is that if the difference in Na/K ratio are due to differences in Na/K ratio in the magmatic liquid, then one expects that the feldspar phenocrysts compositions are different. If the phenocrysts are all the same composition, then the Na/K ratio changes are due to a process that occurred after the phenocrysts precipitated. Unfortunately, there is currently not enough evidence available to solve this problem.

Luth et al. (10) found that when the composition of 507 granitic rocks and 97 aplites they studied were plotted on the Ab-Or-Qtz diagram a trend resulted which is represented in Fig. 1 by the line GG' for granites and the line AA' for aplites. Similar trends were observed by Lipman in six tertiary rhyolitic ash-flow sheets from southern Nevada.

It can be observed in Figure 1 that rock V3 of unit A, rocks V6 and V9 of unit B and rock V11 of unit C are the closest in their respective groups to the trends observed by the mentioned authors. On this basis these four rocks have been chosen as representative of their respective groups in order to look for a simple model that might be useful as a first approximation to the true phenomena that accompanied the evoluation of the magma that gave origin to these rocks.

The main differences between rock sample V11 and rock sample V6 and V9 are: rock V11 contains a higher amount of Al, Fe, Mg, Ca, Na, Ti, P, Mn, Ba, Sc, Co, Sr, and Eu than rocks V6 and V9, but rock V11 is depleted with respect to rocks V6 and V9 in K, Th, Ta, Hf, Rb, Cr, Sm, Gd, Yb, and Lu. However these three rock samples have similar amounts of La, Ce and Nd. The situation of rock samples V3 in general is intermediate between that of rock V11 and that of rocks V6 and V9 except for the fact that rock V3 is notably enriched in light REE (Fig. 5).

Critical element ratios also indicate the differences between rock V11 and the other three: the Ba/Rb ratio which is a very sensitive petrogenetic ratio is much greater in rock V11 than in rocks V3, V6 and V9. Similar results occur with the K/Rb ratio and the Ba/Sr ratio (Table VI).

The rare earth pattern for these four rock samples, normalized against chondrites are shown in Figure 5. It is observed that although rocks V11, V6 and V9 are similar in La, Ce and Nd, rocks V11 differs markedly from the other two in the relative abundance of Sm, Eu and the heavy REE. It is also observed that rock V3 is extremely rich in light REE but in Eu and heavy REE presents an intermediate position between rock V11 and Rocks V6 and V9. Rocks V3, V6 and V9 are strongly depleted in Eu with respect to rock V11. The

Eu/Eu* ratio (Eu* is the abundance interpolated from chondrite normalized Sm and Gd abundances and represents the ideal value that Eu would have if there would be no depletion) which gives an idea of the magnitude of this depletion, is equal to 0.69 for rock V11, 0.06 for rock V3, 0.03 for rock V6 and 0.04 for rock V9.

Figure 6 shows a plot of Rb, Ba and Sr versus the Eu/Eu* ratio. For Rb there exists a light negative correlation, but Ba and Sr exhibit a strong positive correlation when passing from type A and B rocks to C rocks.

The low Ba/Rb ratios, low K/Rb ratios and low Eu/Eu* ratios for rocks V3-V6 and V9, together with the general trends observed in Fig. 6, are consistent with those expected during a crystal fractionation (12). Thus, going from rock sample V11 to samples V3, V6 and V9 the abundance of Rb increases (slowly from V11 to V3 and quickly from V3 to V6 and V9) and the abundance of Ba, Sr and Eu decreases. This is due to the preferential entry of Ba^{++} and Sr^{++} into K^{+} feldspar sites. The similar behavior of Eu indicates that it is probably present as Eu^{+2} whose size is 1.22 Å, a value intermediate between that for Ba^{++} (1.35 Å) and that for Sr (1.18 Å). Rb (1.48 Å) is concentrated in the residual liquid due to its relative exclusion from K^{+} sites (12).

If one considers the behavior of the major elements, it is possible to observe that as one goes from rock V11 to rocks V3, V6 and V9 there is a general trend of increasing and decreasing, but there is some mix-up between rocks V6 and V9 (they are very similar in major and trace elements). SiO_2 increases but Al_2O_3, CaO, MgO, FeO, MnO and TiO become depleted. These trends together with those observed in the trace elements could be explained by assuming that rocks V3, V6 and V9 were derived by a process of crystal fractionation from a magma of composition of rock V11. Since rocks V6 and V9 are very similar and both belong to the same unit, from now on as a matter of simplification, only rocks V11, V3 and V6 will be considered which is essentially rhyolite C, rhyolite A and rhyolite B. Having in mind that rock V11 has phenocrysts of perthite and plagioclase and that rocks V3 and V6 have perthite and quartz, it could be assumed that the main factors in this process of fractional crystallization have been alkali feldspar and plagioclase. Fe and Mg will not be taken into account because no phenocrysts of Fe, Mg minerals except for some magnetite are observed. It is necessary to point out that a definitive Mg, Fe trend is observed. As a simplified model these trends will not be taken into account, but to really explain these rocks by fractional crystallization some Mg, Fe bearing minerals must be precipitated out because Mg goes from significant amounts in rhyolite V11 to practially zero in rhyolite 6 and Fe became depleted by a factor of 2 on passing from rock V11 to V6. A fractional crystallization model requires removal of a mafic (Fe, Mg) phase to explain the Fe-Mg trends.

A computer program (see Appendix I for details) developed by Doherty and Wright (13), was applied to determine quantitatively through the major elements composition the amount of phenocryst that it is necessary to subtract from a magma of composition of rock V11 in order to get a magma of composition of rock V3 and V6. The results show that given the composition of rocks V11, V3 and V9 and given the composition of the perthite and plagioclase phenocrysts in these rocks the maximum amount of phenocryst that it is possible to subtract from a magma of composition V11 in order to generate a magma of composition of rock V3 is 21% (14% perthite phenocrysts and 7% of plagioclase phenocrysts). To pass from a magma of composition of rock V3 to a magma of composition of rock V6 a further subtraction of 9% of feldspar phenocrysts is necessary.

It now would be interesting to see if the results given by trace elements such as Eu, Sr, and Ba agree with those given by the major elements.

By applying the expression:

$$\frac{Eu(V3)}{Eu(V11)} = (1-x)^{\lambda Eu-1} \qquad (I)$$

given by Haskin et al. (14) [where: Eu(V3) and Eu(V11) are respectively the Eu abundances in rocks V3 and V11; x is the fraction of the original magma that it is necessary to crystallize as feldspar phenocrysts to obtain the composition of the derivative rock and λEu is the bulk distribution coefficient for Eu] it is possible to calculate the fraction of original magma that has to crystallize as feldspar in order to explain the Eu anomaly exhibited by rock V3 when it compared to rock V11 (Figure 7). This calculation is easy to carry out when the distribution coefficient of Eu in the feldspars are known. Because only the whole rock composition was analyzed, data for the mentioned distribution of coefficients were not obtained. To fill this gap, data for the distribution coefficients of Eu in plagioclase and K-feldspar were taken from the literature (15a, 15b, 16, 17). These data were plotted versus the anorthite composition of the feldspars of the rocks (Figure 8). Then these data were extrapolated to $Ab_{100}An_0$. Something entirely similar was done for Sr and Ba (Figures 9 and 10). It can be observed in Figure 8 that if the composition of the feldspar is Ab_{92}-An_8 the distribution coefficient for Eu ranges between the values of 0.8 and 7. Now, if the maximum value of this range, 7, is used as the bulk distribution coefficient in the Equation I, the value for x obtained times 100, i.e., 24% represents the minimum amount of feldspar that it is possible to crystallize to explain the Eu depletion observed in Figure 7 . Therefore, the value for the percentage of feldspar that has to crystallize in order to pass from a magma of composition of rock V11 to a magma of composition of rock V3 calculated through the major elements composition agrees within 3% with that obtained through the Eu abundances in rocks V11 and V3 if the value for the bulk Eu distribution coefficient is 7. The next necessary step is to check this value by separating and analyzing the feldspar phenocrysts in the Mt. Rogers rocks.

Similar expressions to that represented by the Equation I were used in the cases of Sr and Ba. When the value 3.87 was used for the bulk distribution coefficient of Sr (see Figure 9) and the value 6.12 was used for the bulk distribution coefficient of Ba (see Figure 10) the values obtained for "x times 100" are respectively 35% and 38%. Similarly to the case of Eu these values represent respectively the minimum amount of feldspar that is necessary to subtract from rock V11 in order to explain the Sr and Ba abundances in the derivative rock V3. It is probable that the differences between the results given by major elements and Eu and those given by Sr and Ba are due to uncertainties in the determination of these last two elements. Work is now being done to check the values of Ba and Sr.

The crystallization of feldspar could explain therefore the major element composition (except Fe and Mg) of rock V3 assuming that this rock sample is derived from a magma of composition of rock V11. This feldspar crystallization could also account for the Eu depletion, but it can not explain within a reasonable percentage of error the abundance of heavy and light REE observed in rock V3. However, if one applies an expression similar to equation (I) for the La(V3)/La(V11) ratio or for the Yb(V3)/Yb(V11) ratio and uses for "x" any value within a 5% error of the value obtained for "x" from the Eu(V3)/Eu(V11) ratio, the values for the bulk distribution coefficients of La and Yb become negative. This suggests that some additional process is also responsible for the abundances of heavy and light REE in rock V3. By applying the expression

$$\frac{(\mathrm{La/Yb})_{V3}}{(\mathrm{La/Yb})_{V11}} = \frac{1 - (\ 1-x\ )^{\lambda \mathrm{La}}}{1 - (\ 1-x\ )^{\lambda \mathrm{Yb}}} \qquad \text{(II)}$$

similar to that given by Haskin et al. (14), one can observe that feldspar removal can explain the La/Yb ratio in V3 if the bulk distribution coefficient for La is 0.10 and for Yb is 0.08.

The feldspar crystallization can explain the major element composition (except Fe and Mg) and the Eu depletion in rock V6 when it is considered as derived from a magma of composition of rock V3. But the feldspar removal can not explain either the absolute abundance of light and heavy REE nor the La/Yb ratio

(if the distribution coefficient for La is 0.10 and for Yb is 0.08). Rock V6 is extremely depleted in light REE when compared with rock V3. If rock V6 is derived from a magma of composition of rock V3, what was the cause of this extreme depletion?. Was the crystallization of a mineral that has great affinity for light REE (monazite, for example) responsible for this depletion?. Monazite is observed in rock V6, but for the moment, there is not enough data to answer this question. On the other hand, rock V6 is extremely enriched in heavy REE in comparison with rock V3. The feldspar crystallization alone can not explain this fact.

From what has been said so far, the following can be concluded: a fractional crystallization model can explain the composition of rock V3 as derived from a magma of composition of rock V11. It can also explain the composition of rock V6 as derived from a magma of composition of rock V3. Feldspar crystallization played an important role in this process of crystal fractionation, but the feldspar removal alone can not explain the absolute abundances of both heavy and light REE nor the La/Yb ratio in rock V6.

B.- Details of Lanthanide Abundances and Fractionation Trends

In order to clarify the variations of REE in all rocks analyzed, their patterns were compared with that of rock V11.

The results are shown in Figure 11. Two major patterns can be observed: that displayed by rocks V8, V3 and V2, and that displayed by rocks V9, V6, V4 and V1. To see more clearly these two patterns, the ratio La/Yb for each rock was calculated. This ratio gives an idea of the slopes of the curves exhibited in Figure 11 and the values are shown in the following table:

TABLE VIII

La/Yb ratio of types A,B and C rhyolites when are normalized against V11

	V8(C)	V3(A)	V2(A)	V9(B)	V6(B)	V4(B)	V1(B)
La/Yb	0.98	1.28	1.02	0.29	0.25	0.25	0.21

In the first group the La/Yb ratio is about unity, ie, the pattern for REE, excepting Eu, is almost flat, but for the second group it is about 0.25, ie, this group is depleted in light REE, but enriched in heavy REE with respect to the first group. On this basis, the REE composition of rocks V2 and V3 were normalized against the REE composition of rock V8 (Figure 12). These patterns together with the pattern shown in Figure 4 (normalization of rocks V8 and V11 against chondritic composition) suggest that type C rhyolites were derived from the same original magma. Rocks V3 and V2 could derive from a magma of composition of rock V8 by feldspar subtraction and rocks V1, V4, V6 and V9 could derive from a magma of composition of rock V11 by a similar process. Table IX shows the approximate amounts of feldspar that it is necessary to subtract from the possible parent rock in order to obtain the derivative rock. The first column in this table, PR, corresponds to the parent rock; the second, DR, contains the derivative rock; the third column, M, shows the amount of feldspar that must be subtracted from the parent rock when the major element composition and the computer program are used; the fourth column, E, shows the amount of feldspar that must be subtracted from the parent rock when the Eu abundances and a distribution coefficient for Eu equal to 7 are used in the calculations.

In this table is observed: a) for only three transitions (V8 to V3, V6 to V9 and V11 to V10) do the data given by the major element compositions differ from those deduced from the Eu abundances by more than 5%, and in all cases both kinds of results agree within 10%. b) The results for the transition V6 to V9 imply that trace and major elements data lead to inconsistent results. c) It is possible that rocks V10 and V7, which because of their lithology are considered to belong to the Pond volcanic center, may be genetically related through a feldspar fractionation. d) The genetic relationship between rocks of Pond center and Mt. Rogers volcanic center is not clear, at

TABLE IX

Approximate amount of feldspar that it is necessary to subtract from the possible parent rock in order to obtain the derivative rock. The calculations are based in the major elements composition and in the Eu abundances.

PR	DR	M	E
V8	V3	20.4%	27.0%
V3	V2	8.8%	6.1%
V11	V1	31.2%	35.5%
V11	V4	39.0%	38.0%
V11	V6	30.0%	33.0%
V6	V9	8.0%	≃ 0.0%
V11	V3	21.2%	23.8%
V11	V10	15.6%	8.7%
V10	V7	10.0%	15.0%
V3	V6	9.0%	13.0%

least when one looks for a relationship through type C rhyolites. e) Rock V3 is in a very special position. It looks like a bridge between rock V8 and V2, and also it looks like a bridge within the trend V11-V6-V9. f) In going from a magma of composition of rock V11 to any of the type B rhyolites, the feldspar crystallization can explain the abundance of major elements (except Fe and Mg), the Eu depletion (assuming a bulk distribution coefficient equal to 7 for Eu) and the La/Yb ratio (assuming a bulk distribution coefficient of 0.10 for La and equal to 0.08 for Yb), but there are some problems in explaining the absolute abundances of REE, either the light, or the heavy, or both. g) A feldspar crystal fractionation can also account for the major element composition (except Fe and Mg), Eu depletion and La/Yb ratio of type A rhyolites when they are considered derivatives of a magma of composition of rock V8. But, anyway, rock V3 fits much better with a magma of composition of rock V11 as a parent than with a magma of composition of rock V8. On the other hand, rock V2 fits much better with a parent magma of composition of rock V8. The feldspar subtraction can account for the abundances of major elements (except Fe and Mg), Eu depletion, absolute abundance of heavy REE and La/Yb ratio of rock V2 when it is considered as a derivative rock of a magma of composition of rock V8. But a feldspar removal alone can not explain the absolute abundances of light REE in rock V2 when it is considered as derivative of a magma of composition of rock V8.

In the first part of this discussion it was mentioned that type B rhyolites are spread and one cause of this spread could be a selective leaching of Na plus an ion-exchange process that could explain the K increasing in going from rock V4 to V6, V9 and V1. Now, it would be interesting to compare the absolute REE abundances of these rocks between them. Figure 14 shows the REE abundance of rocks V4, V9 and V1 normalized against the REE abundance of rock V6. It can be observed that rocks V6 and V9 are the most similar ones (this fact was already noticed in part A of this discussion), rock V4 is the most dissimilar and V1 is in between.

Finally, it is necessary to mention that with the data available it is difficult to attempt an explanation for the origin of type C rhyolites. Unfortunately no rocks of the zone beneath the Mt. Rogers rhyolites were analyzed. Rankin (personal communication) says that most of the rhyolites overlie basalt, but he is not certain that the basalt is directly related to this center.

What has been said so far in this discussion represents a simple model for a process that surely was much more complicated and probably involved other factors such as contamination with the walls of the magma chamber, mixing of magmas, volatile transfer, leaching, etc. This work must be considered as a first approach to the true genesis of these rocks.

C.- Estimate of Oxygen and Water fugacities.

Figure 14 shows the Eu^{+3} distribution coefficient versus the composition of the feldspar. The values for Eu^{+3} were obtained by averaging the distribution coefficients for Sm and Gd. The general distribution of the points is flat. This indicates that the distribution coefficient of Eu^{+3} practically is independent of the composition of the feldspar. This situation is not observed for the distribution coefficient of Eu total. In this case, the general distribution of the points steadily increases as the Ab content of the feldspar increases. This implies that the distribution coefficient for Eu^{+2} increases with the Ab content of the feldspar. In other words, the more albitic the feldspar the greater is its affinity for Eu^{+2}. This can be considered from another point of view: if it is assumed that the water is the sole contributor to the total vapor pressure and the effect of other volatile constituents undoubtedly present in magma are not taken into account (5), the reaction

$$2\ H_2 + O_2 = 2\ H_2O$$

would be practically the only reaction that would regulate the oxygen fugacity as the system crystallizes. This reaction allows one to calculate how the oxygen fugacity varies with the temperature (18). From the data of Bowen it can be seen how the plagioclase felspar composition varies with the temperature (19). Figure 8 shows how the Eu distribution coefficient varies with the composition of plagioclase feldspar. From these considerations it is easy to calculate how the Eu distribution coefficient varies with the oxygen fugacity. These data are shown in the following table

TABLE X

Relationship between temperature feldspar composition, oxygen fugacity and Eu distribution coefficient

temp. (celcius)	Plag. comp.	ln f_{O_2}	Eu distr. coef. (range)
1557	Ab_0An_{100}	-18.6	
1467	$Ab_{16}An_{84}$	-20.8	0.5 - 0.1
1377	$Ab_{33}An_{67}$	-22.3	1.2 - 0.2
1299	$Ab_{50}An_{50}$	-24.2	2.3 - 0.4
1207	$Ab_{67}An_{33}$	-26.5	3.7 - 0.6
1177	$Ab_{75}An_{25}$	-27.7	4.7 - 0.7
1122	$Ab_{100}An_0$	-28.3	8.8 - 1.4

In this table one can observe that as the temperature decreases the plagioclase becomes more and more albitic; the oxygen fugacity diminishes making the conditions more and more reducing. This situation would be responsible for the reduction of Eu^{+3} to Eu^{+2} which enters more easily in the feldspar. This fact explains the increase with Ab component in the Eu distribution coefficient values.

It would be interesting to point out here another fact. According to Lipmann (5) the plot of the bulk-rock composition of a rock series presumed related to a single line of liquid descent can be used to establish a differentiation trend. Depending on the initial composition of the series, the trend may indicate a water pressure either by intersecting the line of isobaric minimum or by bending to follow an isobaric line toward the minimum. This approach yields a water pressure for the time of differentiation rather for the time of phenocryst crystallization. This statement, which has been corroborated by Ewart (20), allows one to say that the rocks under study were subjected to a water pressure of about 500 bars at the time of differentiation.

D.- Comparison of Mt. Rogers rhyolites with other Rhyolites.

Finally, it would be interesting to make a short comparison of Mt. Rogers rhyolites with other rhyolitic type rock already analyzed. Figure 4 shows a plot of the average REE pattern

(normalized to chondrites) for the rocks from Traveler Mt. (Figure 15 shows the REE pattern range, normalized to chondrites, for the Traveler Mt. rhyolites studied in this work). These rocks were analyzed only for REE and some other minor and trace elements. The REE pattern of these rocks is most similar to that exhibited by type C rhyolites than those exhibited by types A and B rhyolites. The Traveler Mt. rhyolites are depleted, with respect to rhyolites C, in light REE and in Eu, but they present similar abundances of heavy REE. The Na/K ratio (determined by INAA) in Traveler Mt. rhyolites is less than unity, a fact that is also observed in Mt. Rogers rhyolites. The Ba abundances (also determined by INAA) in Taveler Mt. rhyolites is closer to that of rhyolites C than to those of type A and B rhyolites, but they are depleted by a factor of 2 or 3 with respect to type C rhyolites (Table IV). Traveler Mt. and Mt. Rogers rhyolites are in general similar in Th, Ta, Hf and Rb abundances, but the Traveler Mt. rhyolites are enriched in Cs and Sc. The Co abundance in Traveler Mt. rhyolites is closer to that of type C than to those exhibit by types A and B.

Figure 4 also shows the average REE pattern (normalized to chondrites) of the New Zealand Taupo rhyolites. These rhyolites are believed to have originated by partial melting of eugeosynclinal sediments of overall andesitic composition (21). Rhyolites C and Taupo rhyolites present similar slope in their REE patterns, but the total REE abundance in the latter is smaller than in type C rhyolites. Both are similar in the magnitude of the Eu depletion. The Na/K ratio in Taupo rhyolites is greater than unity, a fact that is not observed in type C rhyolites. Ewart et al. say that the overall dominance of Na_2O over K_2O is one of the most significant feature of the eugeosynclinal sediments of andesitic-dacitic composition. Since this is not observed in type C rhyolites one doubts the possibility that they were derived from partial melting of crustal sediments. Type C rhyolites and Taupo rhyolites are similar in Rb, Ba, Sr, and Th contents, but type C rhyolites are depleted with respect to Taupo rhyolites in SiO_2 and Al_2O_3. Actually, for their SiO_2 and Al_2O_3 content Taupo rhyolites looks more like type A and B rhyolites than type C.

Figure 4 also shows a graph of the average REE pattern (normalized to chondrites) for the Mayor Island (New Zealand) Pantellerites (22). In general, the pattern of Pantellerites and those for type C rhyolites are very similar excepting for Eu. Mayor Island Pantellerites are very depleted in Eu. These rocks are also extraordinary depleted in Ba and Sr, but they are enriched in Rb. The silica and alumina content of Mayor Island Pantellerites is closer to that of type A and B rhyolites than to that of type C, ie, they are enriched in silica and alumina with respect to C rhyolites. Similarly to the Taupo rhyolites, Mayor Island Pantellerites exhibit a Na/K ratio greater than unity, an aspect that is entirely dissimilar to what is observed in Mt. Rogers and Traveler Mt. rhyolites.

Summary and conclusions

In Mt Rogers volcanic center it is possible to distinguish three rocks units. The main difference between these units is in the amount and type of phenocrysts they have: units A and B contain phenocrysts of perthite and quartz. Unit A contains about 30% of phenocrysts and unit B contains only between 0 to 10%. On the other hand unit C, which is the oldest one and the least abundant in volume contains about 20% of phenocrysts of perthite and plagioclase. No quartz phenocrysts are observed in the rocks of this unit.

When the normative Ab, Or and Qtz of these rocks are plotted in the Ab-Or-Qtz diagram it is observed that they are spread around the low temperature trough. One possible explanation of this fact is that they were formed under conditions of non crystal-liquid equilibrium. Another possible explanation that could be valid for explaining the spread in type B rhyolites is a selective leaching of Na accompanied by an ion-exchange process that would cause an increase in the abundance of K. Samples V11, V3, V6 and V9 are the closest to the crystal-liquid equilibrium evolution trend. There exists a sequence between them with rock V11 as the most primitive rock. Accepting an error of about 5% in the computation of the data it is possible to derive rocks V3, V6 and V9 from a magma of composition of rock V11 by a process of crystal fractionation. Feldspars are the most important minerals in this process.

The REE pattern for rocks V3, V6 and V9 are dominated by a large Eu depletion relative to rock V11. This characteristic is strongly indicative of the important role of feldspar crystallization and subtraction in the production of the Mt.Rogers rhyolitic magmas.

The values for the percentages of feldspar phenocrysts that are necessary to subtract from a given type of magma to get the next magma in the series calculated through the major elements composition agree with those calculated using the Eu abundances within 5% in most of the cases and within 10% in all of the cases.

No phenocryst separation and analysis was done in this work, so theoretical values were used for the bulk Eu distribution coefficient. The best bulk Eu distribution coefficient was 7. This value is being checked now experimentally.

Rocks V3, V6 and V9 are also dominated by a strong depletion of Sr and Ba, which is additional evidence of the important role of feldspar in this process of crystal fractionation. The enrichment in Rb as one goes from rock V11 to rocks V3, V6 and V9 is not as spectacular. Also rocks V3, V6 and V9 are depleted in Sc and Co when they are compare with rock V11.

Although conventional crystal fractionation of feldspar can account for the abundance of most elements in the youngest rocks, when they are considered as derivatives of rock V11, it seems possible that some additional process may be required to account for the extraordinary enrichment in light REE in rock V3 when it is compare with rock V11 and the extraordinary depletion in the same elements when rocks V6 and V9 are compare with rock V3.

Further work is required to explain the origin of type C rhyolites.

When the REE pattern of the Mt. Rogers volcanic center rhyolites are compared with those of Traveler Mt. rhyolites (Maine, USA), Taupo rhyolites (New Zealand) and Mayor Island pantellerites (New Zealand) it is observed that the latter are more like type C rhyolites than types A and B. The Taupo rhyolites are greatly depleted in REE when they are compare with type C rhyolites. It is also observed that the Eu depletion increases in the following order: Taupo rhyolites, Mt. Rogers type C rhyolites, Traveler Mt rhyolites, Mayor Island pantellerites and Mt. Rogers type A and B rhyolites. It is also observed that the slope of the REE pattern is generally similar in all the volcanic rocks mentioned excepting type A and B rhyolites. If the Eu depletion is a measure of the degree of fractionation, the Mt rogers rhyolites (type C) would be more fractionated than the Taupo rhyolites but less fractionated than the Traveler Mt. rhyolites, Mayor Island pantellerites and type A and B rhyolites.

In general, the minor and trace element abundances of Traveler Mt. rhyolites, Taupo rhyolites and Mayor Island pantellerites look much more like those of rhyolites type C than those of types A and B. Maybe the most significant difference between the pair Taupo rhyolites-Mayor Island pantellerites and the pair Mt. Rogers rhyolites-Traveler Mt. rhyolites is in the Na/K ratio. This ratio is greater than unity for the New Zealand volcanicsrocks but less than unity in the US rhyolites. Does this fact keep some relation with the origin of the Mt. Rogers and Traveler Mt. rhyolites ?. Further work must be done to answer this question.

Rocks V7 and V10 do not seem to be genetically related with the Mt. Rogers rhyolites, but it is possible to derive rock V7 from rock V10 by a process of feldspar crystal fractionation. The REE pattern for these rocks (Figure 16) are characterized by a similar trend in the slope and for an Eu depletion when they are normalized to the chondritic composition. The Eu depletion of rock V7 is large when is compare to chondrites.

The major element chemistry of rock V5 does not suggest any genetic relation of this rock with the Mt. Rogers rhyolites and with rock V7 and V10. The REE pattern of rock V5 (Figure 16), when compare with the chondrites pattern, is characterized by an Eu depletion similar to that of rock V10. In general, rocks V10, V5 and overall V7 are very rich in light REE . Rock V7 has the highest total REE content of the rhyolites of Virginia. The REE pattern of rock V7 together with its low abundance in Ba and Sr suggests that it has been strongly affected by a process of feldspar crystal fractionation.

APPENDIX I

Determination of Fractional Crystallization Parameters by using Major Element data and the Least Square Fitting Program

Appendix I

Determination of Fractional Crystallization Parameters by using Major Element data and the Least Square Fitting Program.

Calculation of the amount of feldspar that it was necessary to subtract from the parent rock in order to obtain the derivative rock was carried out by applying a computer program elaborated by Patrick C. Doherty and Thomas L. Wright, found in the " Computer Contribution Number 7 of the U.S. Geological Survey "

" This program uses a least square subroutine to fit the chemical composition of a rock by calculating the proportions of two or more analyzed minerals that make up the rock. The program has an option which permits any minerals to be combined as a positive or as a negative quantity; hence, mineral reactions may be calculated and balanced ".

This program may be used in different kinds of petrological calculations (13), (23). One of them is the use given in this work, ie, to calculate a mineral assemblage or assemblages that relate two magma types (represented by rock analysis) lying along a single liquid line of descent. The scheme of this application is:

$$\text{Rock(parent)} - \sum_{i=2}^{n} x_i y_i \qquad = \qquad \text{Rock(differentiate)}$$

where x_i is the proportion of the mineral i in the rock and y_i is the composition of the mineral i.

A simple example will illustrate how the computer program was used in this work. One of the problems studied was the possibility that rock V9 would derive from a magma of the composition of the rock V6 by crystallization of feldspar. To solve this problem one has to know the chemical composition of the parent and derived rock and also one has to know the chemical composition of the feldspar. The chemical composition of rocks V6 and V9 used were those in Table II. The chemical composition of the feldspar was calculated in the following way: it was assumed that the feldspar which participated in this transition had the composition $An_{51.5}\ Or_{42.4}\ An_{6.1}$ given by Carmichael (24). This assumption was made because it was not possible to get a thin section of the rock sample V9. Then was calculated the chemical compositions of pure Ab, Or and An. These are shown in the following table:

TABLE XI

Chemical composition of pure Or, Ab and An

	SiO_2	Al_2O_3	CaO	Na_2O	K_2O
Or	64.7%	18.4%	-	-	16.9%
Ab	68.7%	19.5%	-	11.8%	-
An	43.2%	36.7%	20.1%	-	-

Finally, the contribution of Or, Ab and An to the chemical composition of the feldspar was found by multiplying the percentage of each mineral in the feldspar by the chemical composition of the pure mineral and dividing by 10000. For example, the abundance of Or in the feldspar is 42.4%. Therefore the contribution of Or to the SiO_2 of the feldspar is equal to 42.4 times the percentage of SiO_2 in pure Or, ie 64.7, and dividing by 10000. In this manner the following table was obtained:

TABLE XII

Contribution of each of the components found in the feldspar to the chemical composition of the feldspar.

	SiO_2	Al_2O_3	CaO	Na_2O	K_2O
Or (42.4%)	27.43%	7.80%	-	-	7.17%
Ab (51.5%)	35.38%	10.04%	-	6.08%	-
An (6.1%)	2.64%	2.24%	1.23%	-	-
Chem. comp. of feldspar	65.45%	20.08%	1.23%	6.08%	7.17%

The addition of the individual contribution gives the chemical composition of the feldspar (Table XII).

Once the chemical composition of the parent rock, derivative rock and of the minerals that participate in the crystallization is known, one is ready to punch the input cards. Detailed explanation of the rules that must be followed in this process are in the cited booklet by Doherty and Wright. The format used to punch the mineral/rock card correspond to the " Type M mineral/rock card ". An illustration of the output data is presented in the following pages. A detailed explanation of the meaning of the data contained in the output is also given in the mentioned booklet by Doherty and Wright. One thing it is necessary to comment . In order to get the best fit between the experimental composition of the derivative rock and the composition of the derivative rock calculated through the computer program various combinations of weight factors were asigned to the oxides. This process is tedious and expensive and does not guarantee finding the best possible fit unless all possibilities are tried. The set of weights choosen was that which gave for most of the oxides an error about 5% or less in the difference between the actual composition and the calculated composition. The following table gives an illustration of these trials. The first column in this table shows the different oxides used in the calculation. The second column gives the weight factor assigned to them. The third column shows the percentage of error in the difference between the experimental composition and the composition calculated by using those weight factors in the computer program. Finally, with each set of oxides is also shown the percentage of feldspar phenocrysts that is necessary to subtract from the parent magma to obtain the derivative magma when those weights are used.

TABLE XIII

(See text for explanation)

I (oxides)	II (weight factor)	III (error)	% Phenocryst
SiO_2	3.00	0.35	
Al_2O_3	20.00	0.92	
CaO	10.00	5.56	2.56%
Na_2O	15.00	12.91	
K_2O	5.00	2.04	
SiO_2	3.00	0.09	
Al_2O_3	10.00	2.59	
CaO	15.00	1.85	4.95%
Na_2O	20.00	11.11	
K_2O	15.00	3.27	
SiO_2	10.00	0.49	
Al_2O_3	1.00	4.27	
CaO	10.00	0.00	7.14%
Na_2O	10.00	9.31	
K_2O	10.00	5.00	

TABLE XIII (Continuation)

I (oxides)	II (weight factor)	III (error)	% Phenocrysts
SiO_2	3.00	0.52	7.28%
Al_2O_3	1.00	4.44	
CaO	10.00	0.00	
Na_2O	10.00	9.31	
K_2O	10.00	4.50	
SiO_2	1.00	0.62	0.98%
Al_2O_3	1.00	0.17	
CaO	6.00	7.40	
Na_2O	15.00	13.81	
K_2O	90.00	1.23	
SiO_2	2.00	1.16	10.45%
Al_2O_3	1.00	6.95	
CaO	6.00	5.56	
Na_2O	15.00	6.61	
K_2O	10.00	6.34	
SiO_2	1.00	0.76	8.48%
Al_2O_3	1.00	5.36	
CaO	6.00	1.85	
Na_2O	15.00	8.41	
K_2O	15.00	5.17	

TABLE XIII (Continuation)

I (oxides)	II (weight factor)	III (error)	% Phenocrysts
SiO_2	1.40	0.08	
Al_2O_3	1.70	2.59	
CaO	2.20	1.85	4.90%
Na_2O	4.00	11.11	
K_2O	4.00	3.27	

Similar procedures to that applied to the transition V6 to V9 were also applied in all the transitions studied in this work.

Explanation of the OUTPUT (Pages 65-68).- Printed output for each problem includes a tabulation of the input data showing problem title (6-9 = transition of rock V6 to V9), constraints flags (2 means that the solution value is not constrained), parent rock (6), mineral identification (AF-ONL means alkali feldspar only), derivative rock (rock) and weights before normalization. The first column includes the oxides used in the calculation; the second column shows the percentages of these oxides in the parent rock; the third column shows the percentages of these oxides in the alkali feldspar; the fourth column shows the percentages of these oxides in the derivative rock and the fifth column shows the weights assigned to each oxide. Below the input tabulation are listed the rocks or minerals requiring normalization.

The second page of the problem output is similar in form to the input tabulation. Here, oxide percentages are shown after normalization and constraint flags are not reprinted. Solution values are printed in the row labeled "SOLUTION", calculated right-hand sides are shown in the column labeled "CALC" and the residuals are given in the column labeled "DIFF." The row labeled "SENSITIV" Gives an approximation to the partial derivative of the sum of squares of residuals with respect to the solution variable at the minimum point. These numbers are one measure of the sensitivity of the objective function to small changes in the solution values (13).

When error ranging is required, then the solution for each constituent mineral is incremented and decremented until one of the individual residuals has changed by 0.1 but not more than 0.12. The incremented and decremented solutions are printed for each constituent mineral. These results are intended to give some insight into the sensitivity of each solution value (13).

```
INPUT DATA...
                                        6-9

           6        AE-ONI     ROCK WEIGHT
            2        2

  SIO2   76.55   65.45   77.13    2.00

  AL2O3  11.73   20.08   11.62    1.00

  CAO     0.57    1.23    0.52    6.00

  NA2O    3.71    6.08    3.23   15.00

  K2O     4.72    7.17    4.75   15.00


6        HAS BEEN NORMALIZED TO 100 BECAUSE THE INPUT VALUES DID NOT TOTAL TO 100
 ROCK HAS BEEN NORMALIZED TO 100 BECAUSE THE INPUT VALUES DID NOT TOTAL TO 100
```

```
SOLUTION...
                                 6-9

           O        AF-2NL    ROCK  WEIGHT   CALC.   DIFF.

  SIO2    78.79     65.45    79.32    2.00   79.83   -0.51

  AL2O3   12.06     20.08    11.95    1.00   11.38    0.58

  CAO      0.59      1.23     0.54    6.00    0.54    0.01

  NA2O     3.82      6.08     3.33   15.00    3.63   -0.29

  K2O      4.86      7.17     4.89   15.00    4.66    0.24

SOLUTION108.55     -8.54

SENSITIV  1.31      0.02
```

```
RANGING ON 6      ...
                             6-9

          O       AF-DML   ROCK WEIGHT  CALC.  DIFF.

SIO2    78.70    65.45   79.32   2.00  79.71 -0.387

AL2O3   12.06    20.08   11.95   1.00  11.45  0.507

CAO      0.59     1.23    0.54   6.00   0.54 -0.002

NA2O     3.82     6.09    3.33  15.00   3.64 -0.318

K2O      4.86     7.17    4.89  15.00   4.68  0.210

SOLUTION107.69   -7.68


RANGING ON 6      ...
                             6-9

          O       AF-DML   ROCK WEIGHT  CALC.  DIFF.

SIO2    78.70    65.45   79.32   2.00  79.94 -0.622

AL2O3   12.06    20.08   11.95   1.00  11.31  0.643

CAO      0.59     1.23    0.54   6.00   0.53  0.009

NA2O     3.82     6.08    3.33  15.00   3.61 -0.280

K2O      4.86     7.17    4.89  15.00   4.64  0.250

SOLUTION109.39   -9.38
```

```
RANGING ON AF-ONL...
                                      6-9

              G       AF-ONL    ROCK WEIGHT   CALC.   DIFF.

   SIO2     78.70     65.45    79.32    2.00   79.72  -0.409

   AL2O3    12.06     20.08    11.95    1.00   11.44   0.514

   CAO       0.59      1.23     0.54    6.00    0.54  -0.001

   NA2O      3.82      6.08     3.33   15.00    3.64  -0.316

   K2O       4.86      7.17     4.89   15.00    4.68   0.213

 SOLUTION107.78    -7.77


RANGING ON AF-ONL...
                                      6-9

              G       AF-ONL    ROCK WEIGHT   CALC.   DIFF.

   SIO2     76.70     65.45    79.32    2.00   79.93  -0.613

   AL2O3    12.06     20.08    11.95    1.00   11.32   0.638

   CAO       0.59      1.23     0.54    6.00    0.53   0.009

   NA2O      3.82      6.08     3.33   15.00    3.61  -0.281

   K2O       4.86      7.17     4.89   15.00    4.64   0.248

 SOLUTION109.32    -9.31
```

APPENDIX II

ANALYTICAL PROCEDURE: Instrumental Neutron Activation Analysis by using Ge (Li) detectors.

Analytical Procedure

Introduction

The determination of the abundances of the elements studied was carried out by Instrumental Neutron Activation Analysis. The Neutron Activation Analysis technique, its importance and its applications, has been discussed in different works and papers (1, 2, 3, 4). The Instrumental Neutron Activation Analysis and its applications to the study of igneous rocks has been discussed by Gordon et al. (5). This technique allows the exact and precise determination of some 25 to 30 elements to the ppm. level.

Radioactivation Analysis is any process of nuclear bombardment which enables a particular element in a sample to be determined by its induced radioactivity. When neutrons are used as the bombarding particles, the method is generally called neutron activation analysis (2).

The interaction between a neutron and a target nucleus depends upon the energy of the neutron and the nature of the target nucleus. The nuclear reaction proceeds in two steps, both being separated by an interval of time of about 10^{-16} sec. During the first step, neutron and target nucleus form a compound nucleus. This is highly energetic, since it contains the kinetic energy of the incident neutron plus its binding energy which is about 7 MeV. This high energy content makes the compound nucleus unstable and in a second step it starts decaying by emission of one or more particles or by emission of gamma radiation. The kind of radiation emitted by this compound nucleus depends in great part on the energy of the incident neutron. The greater the incident neutron energy the greater the probability that the emitted radiation is a particle instead of a gamma ray. Therefore if one's interest is centered in a (n,γ) process, the sample must be irradiated with slow neutrons.

The intensity of the gamma radiation emitted by the compound nucleus is proportional to the amount of element present in the sample, irrespective of its state of chemical combination since the process is entirely nuclear in nature.

The activity which has been induced in a given isotope at the end of an irradiation time, ti, is given by the following relation:

$$A_o = \phi \cdot \sigma \cdot \Theta \cdot N_o \cdot M^{-1} \times w[1-\exp(-\lambda ti)] \qquad \text{(I)}$$

ϕ = neutron flux at which the sample has been subjected. This quantity is expressed in [neutrons $\times$ cm^{-2} $\times$ sec^{-1}].

σ = cross sections of the given isotopes expressed in barns.

Θ = isotopic abundance of the isotope that is activated.

N_o = Avogadro's Number.

M = Atomic weight of the element.

w = amount of the element in the sample irradiated.

λ = radioactive decay constant of the isotope formed during the irradiation time = $0.693/t_{\frac{1}{2}}$.

ti = irradiation time.

The product of $[\phi \cdot \sigma \cdot \Theta \cdot N_o \cdot M^{-1}]$ for a given ϕ and a given isotope is generally tabulated under the name of "saturation activity". So, the expression (I) can be written simply as:

$$A_o = SA \cdot w \cdot [1-\exp(-\lambda ti)] \qquad \text{(II)}$$

A given radioactive nuclei emits a gamma ray or a set of gamma rays whose energies are characteristic of that particular nuclei and thus it is possible to distinguish one isotope from another. Sometimes the gamma rays emitted by different radionuclides are so similar in energy that they cannot be adequately resolved in the gamma ray spectra. When this happens, it is necessary to isolate the radionuclei by using chemical methods such as precipitation, solvent extraction, ion exchange separation etc. The application of Instrumental Neutron Activation Analysis with high-resolution lithium-drifted germanium detectors gives very good resolution for gamma ray energies, reducing the need for wet chemistry after irradiation. This means that the neutron irradiation is followed by counting without any chemical separation and it is possible to determine by this method at least 30 elements (6) in rocks.

The activity, Ac, after a time t_c after the irradiation is given by the following relation also derived from the relationship for the radioactive decay process:

$$A_c = A_o[\exp(-\lambda tc)] = SA\cdot w[1-\exp(-\lambda ti)] \cdot [\exp(-\lambda tc)] \qquad \text{(III)}$$

If equation II is remembered it is possible to see that, at least theoretically, neutron activation analysis is an absolute technique, since it is possible to calculate w if all the other quantities are known. In practice, complications arise from uncertainties connected with the irradiation process, such as variation in the flux during the irradiation time, changes in the energy distribution of the bombarding neutrons, etc. For this reason neutron activation analysis is carried out in a comparative way: a standard containing a known amount of the nuclide to be determined is irradiated together with the unknown. Since all the terms in equation III, but w and Ac are the same for the sample and for the standard, the unknown amount of nuclide can readily be calculated from the relative activities (or some other quantity that is proportional to the activities such as the relative intensities) at a common time t_c.

The relative character of the neutron activation analysis also requires that sample and standard be counted in the same position relative to the radiation detector, so the fraction of the emitted radiation which is detected is the same for sample and standard. Since it is not possible to count the radiation from one sample and standard at the same time, it is necessary to correct the counts to the same time. Later on in this chapter this point will be discussed again.

Experimental

The present work was carried out through the following steps:

1. Preparation of samples and standard for irradiation.
2. Irradiation.
3. Gamma ray spectrometry.
4. Determination of elemental concentrations.

1. Preparation of samples and standard for irradiation.

This step can be subdivided into the following steps.

1.1 Preparation of stock solutions. Before starting with this substep one has to have in mind the following three factors: First, Instrumental Neutron Activation Analysis is a comparative method and the best results are obtained when the amount of the element of interest in the standard is approximately equal to the amount of the same element in the amount of sample to be irradiated. This means that it is necessary to have an idea of the abundance of that element in the rock to be studied. In this work it was assumed that the abundance of the elements of interest in the rhyolites from Main and Virginia was approximately equal to the abundances of the same elements in the Taupo rhyolites of New Zealand (7).

Second it is necessary to know what the concentration of the standard solution will be for the element of interest. The procedure to determine this is: into one of the polyethylene vials used for irradiation was put about 0.5 gr of rock sample. In another vial of the same dimensions silica (specpure) was added to reach the same height that the rock sample attained in its respective vial. Then, a minimum volume of water necessary to wet the silica was added. The same volume of standard solution must have the element of interest in about the same amount as is found in the 0.5 gr of rock sample. With this in hand one knows the concentration that the standard solution must have in a given element.

Silica is used as the carrier because it is a low cross section material and is the dominant oxide in rocks. This reduces one of the principal errors that can be produced during the irradiation, the self shielding or lack of uniformity of the flux within the sample. This error is proportional to the cross section that a given material offers to incident neutrons. On the other hand the requirement that the height of the silica in the vial must be equal to the height of the sample in its respective vial, assuming both vials are equal, is due to geometric reasons mentioned before.

Third, before starting the preparation of the stock solutions it is necessary to determine the volume of the standard solution to be prepared. It is advisable that this volume be greater (in ml.) than 10xthe number of elements that the standard solution is going to contain. The reason for this will be discussed next.

Now one is ready to start the preparation of the different stock solutions. The concentration of each of the stock solutions must be such that 10 ml. contains the amount of element necessary to prepare the volume of standard solution in the required concentration for that element. The reason for this is simple: the error one makes when pipetting 10 ml. of solution is less than the error one makes when pipetting 5 ml. or less. With this reasoning one might think: why not pipette 15 ml. or more instead of 10 ml.? The error one can make pipetting 10 ml. is already small enough that it is not justifiable to pipette a volume greater than 10 ml.

The method used to prepare the stock solutions was the following:

A. The stock solutions of REE were prepared from their respective oxides of high purity (99.99%). Since some of the REE can form non-stoichiometric oxides, ultimate standardization was by titration.

The necessary amount of REE oxide was weighed to five places and then transferred to a teflon beaker. The oxide was dissolved with 1:1 vycor distilled HNO_3 and the solution was evaporated almost to dryness. The solution was then diluted in a volumetric flask, to 250 ml. with deionized water and transferred to a clean, dry, polyethylene bottle.

B. To obtain a stock solution of Th, the necessary amount of this element was weighed and transfered to a Teflon Beaker. About 10 ml. of HCl concentrate was added and the result is a black precipitate of $ThCl_4$? This is treated with about 10 ml. of HNO_3 and the formation of a green residue is noticed. With a further addition of one drop of HF appears a white precipitate. The addition of 10 ml. of H_2O and heating makes the solution completely clear. Then the procedure continues as before: evaporation to almost dryness, dilution to 250 ml. and transferring to a clean,dry,polyethylene bottle.

C. The stock solutions of Hf and T_2 were prepared by dissolving the necessary amount of Hf and Ta in HF. This solution was evaporated almost to dryness, diluted to 250 ml. with deionized H_2O and then transferred to a polyethylene bottle.

D. The stock solutions of Cs and Rb were prepared from Cs and Rb acetate respectively 99.9% pure. These acetates are very hygrosopic, therefore it is necessary to subject them to successive heating to 110°C and cooling to reach constant weight. Then the substances were transferred to a teflon beaker to be subjected to the same treatment given to the REE oxides.

E. The stock solution of Fe was prepared from Fe wire standard. Iron was not determined because the samples were contaminated with Fe during their preparation. The Fe wire was treated with very dilute HNO_3 in order that the only possible reaction be that of electronic interchange between H and Fe. It is difficult to accomplish this. The absolute standardization of Fe was by Atomic Absorption.

F. Stock solutions of Ba and Mg were not prepared because the abundance of these elements in rhyolites is high and one must use a lot of reagent. The necessary amount of Ba (as $BaCO_3$) and Mg to prepare the standard solution were weighted accurately, then treated with an adequate amount of HNO_3 in order to get a solution of Ba^{++} and Mg^{++} nitrate and this solution was transferred directly to the volumetric flask containing standard solution.

G. Also, Na and K stock solutions were not prepared. In this case the necessary amount of Na and K that must be contained in the standard to be irradiated was weighted accuarately as Na_2CO_3 and K_2CO_3 respectively and transferred directly to an irradiation vial. The subsequent procedure will be mentioned later on in the paragraph related to the preparation of vials to be irradiated (8).

1.2 <u>Standardization of stock solutions</u>.

In most of the cases the definite determination of the concentration of the stock solution was done by back titration of copper standard solution against EDTA. The method applied were those described by Welcher (9). Reagent grade copper foil was carefully weighed to five places, dissolved in 1:1 vycor distilled HNO_3 and diluted with distilled water to a convenient volume. This solution was transferred to a clean, dry polyethylene bottle and was used as the copper standard solution. An EDTA solution was prepared and standardized with respect to the copper solution. After that most of the stock solution was standardized with respect to the copper solution by titration.

An illustration of the procedure used to standardize the stock solution of REE is described: to a 50 ml erlenmeyer flask was introduced a small amount (10-20 ml.) of water. The pH value was adjusted to 4 with a concentrated solution of acetic acid and NaOH. The success of the titration depends on proper adjustment of pH. Then a given amount of stock solution is added. As one has an idea of the concentration of the stock solution the amount of it used in the process must be such that EDTA reacts mainly with the element of interest and only the excess of EDTA reacts with Cu^{++}. An excess of EDTA is added together with two or three drops of PAN indicator. The solution is heated to facilitate the reaction of EDTA with the element of interest. The normal concentration of the stock solution is calculated by applying the following relation:

$$N_{ss} = \frac{NEDTA \times VEDTA - NCu^{++} \times VCu^{++}}{V_{ss}}$$

where ss means stock solution.

The normal concentration expressed in $[\mathrm{eq}\ \mathrm{l}^{-1}]$ is later expressed in $[\mu\mathrm{gr} \times \mathrm{ml}^{-1}]$ by applying the following relation:

$$C[\mu\mathrm{gr} \times \mathrm{ml}^{-1}] = \frac{\mathrm{At.w.}}{\mathrm{valence}}[\mathrm{gr}\ \mathrm{eq}^{-1}] \times N[\mathrm{eq} \times \mathrm{l}^{-1}] \times 10^{-3}$$
$$[\mathrm{l} \times \mathrm{ml}^{-1}] \times 10^{6}[\mu\mathrm{gm} \times \mathrm{ml}^{-1}]$$
$$C[\mu\mathrm{gr} \times \mathrm{ml}^{-1}] = \frac{\mathrm{At.w.}}{\mathrm{valence}} \times N \times 10^{3} \qquad \text{(V)}$$

As EDTA always reacts with REE, Th, Hf, etc. in the ratio 1:1 the value of the valence is the unity and therefore for these cases one has:

$$C[\mu\mathrm{gr} \times \mathrm{ml}^{-1}] = \text{atomic weight} \times N \times 10^{3} \qquad \text{(VI)}$$

1.3 Preparation of standard solution or flux monitor.

This procedure is very simple. It consists in taking from the stock solution the volume containing the necessary amount of the element of interest to prepare the standard solution and adding this volume into the volumetric flask in which the standard solution is being prepared. After all the elements to be analyzed are in the volumetric flask in the required amount, the final volume of the standard solution is completed with deionized water.

Even when the process itself is simple it is advisable to follow the following order when adding the different elements: First, introduce all those solutions containing F^-. Second, introduce the solution of Ba^{++}. After this the formation of a white precipitate of BaF_2 occurs. This is soluable in HNO_3. Third, introduce those solutions containing NO_3^-.

1.4 Preparation of vials to be irradiated.

Into three vials of polyethylene were put approximately 0.5 gr of powdered rock sample. Assuming that the diameters of the vials are equal, it is important that the height of the sample be equal in all three. It must be remembered that the NAA is a comparatice method of analysis and for this reason, the geometry is an important factor. Then the amount of sample in each vial was weighed accurately.

Into a fourth vial was put silica (specpure) to reach the same height as the samples have in their respective vials (in order to keep the same geometry). Then the necessary amount of Na and K, as Na_2CO_3 and K_2CO_3 respectively, is placed on the silica. The carbonates are transformed into nitrates by the careful addition of dilute HNO_3. Once the reaction is through, the vial is placed under the infrared lamp to evaporate the water present. This process must be carried out carefully. Placing the lamp too close to the vial can cause excessive heating which splashes the material and can cause deformations of the capsule which affects the geometry in subsequent counting.

In all the processes carried out in this step, one has to avoid any kind of contamination of the samples and of the reagents used.

2. Irradiation

The four vials were sealed, placed in a sample carrier ("rabbit") and subjected to a flux of 2×10^{13} neutrons x cm^{-2} x sec^{-1} in the core of the M.I.T. nuclear reactor. Following the irradiations the rabbit was delivered from the reactor within a few seconds via a pneumatic tube. After short irradiations (2 minutes) the samples were allowed to "cool" two hours before observation of species with half lives from 2.32 h (Dy) to 15 H (Na). After long irradiation (1 h) the samples were allowed to "cool" 5 days before observation of species with half lives from a few days to many years.

3. Gamma Ray Spectrometry

Before counting, each vial was placed unopened in another special vial that fits in the holder in front of the detector.

Gamma ray spectra of each sample were taken several times after irradiation in order to study each of the elements of interest according to their respective half lives. Following the experiences of Gordon et al (5) and Buma (8) the schedule of counting is given in table I. This table also contains the isotopic abundance of the isotope used in the determination of the abundance of its respective element, the irradiation time, the isotope produced during the irradiation, the cross section of the target expressed in barn (10^{-24}cm), the photopeak used in the determination and the detector used.

A block diagram of the counting equipment is shown in figure 1 (10). Two different Ge(Li) detectors were used: one of effective volume of 13 cm^3 and the other of effective volume of 0.5 cm^3. The first one has greater efficiency than the small one and was used for observing high energy gamma rays. The FWHM (full width at half maximum) of the photopeak produced by 661.6 KeV gamma rays from ^{137}Cs was about 2.5 KeV. The small detector, LEPS, (low energy photon spectrometer, FWHM approximately 0.4 KeV at 14.4 KeV (10)), has better resolution than the 13 cc and is most effective for photons from about 10 to 150 KeV. It was used up to 400 KeV.

Pulses from the detector were passed through preamplifiers and linear amplifiers which include a base-line restorer to maintain better resolution of the pulses at high count rates. The amplifier pulses were fed to a 4096-channel analog to digital converter (Packard) and the digital information was stored in a 4096-word core memory (Packard) (10). The information from the analyzer memory was printed and it took about two minutes to empty the full memory. The output information is a tape that exhibits the number of the channel and the number of counts in that channel.

Radioactive nuclides were identified on basis of energies and intensities of the peaks. Most species emit several gamma rays, so the intensity pattern of the several gamma rays can be used as a help for identification. Energy calibration is determined from a calibration curve for each detector. These calibration curves were obtained by making use of the standards given in table II. This table also includes the detector used to get the curves, the energy of the gamma rays emitted from the different standards and the channel where these gamma rays produced peaks. The last column includes the coarse gain used in the calibration.

The calibration curve is nothing other than an energy vs. channel curve. This is indispensable in the identification of the species. In these curves it was assumed that the variation of the energy with the channel number is linear over small energy regions.

In order to maintain constant geometry, samples and standard were placed in the same position for counting.

4. Determination of elemental abundances

In order to determine the abundance of the elements of interest, the data given by the instrument were treated following the method proposed by Denechaud (11). In this method, instead of comparing the total area under a given peak in the sample and standard (this area is proportional to the activity induced during the irradiation in the particular isotope) only a fraction of the peak is analyzed. This fraction generally corresponds to one FWHM. This method tends to minimize the statistical counting error and the error in the placement of the baseline. The fundamentals of the method are discussed by the mentioned author. Therefore I will describe only briefly the mechanics of the method.

The data output is graphed on a three-cycle semilog paper. The axis of the ordinates represents the number of counts per channel, and the axis of the abscissas the channel number.

The number of counts in each channel of a given peak includes those that are associated with gamma rays of the isotope of interest and those which are associated with higher energy gamma rays (via Compton interactions). Therefore it is necessary to subtract from the total number of counts in each channel those counts in that channel at the base of the peak. It is very important to trace the baseline as exactly as possible. The first step in this task is to find the peak channel, x_o, which is generally the channel with the highest number of counts, but in those cases where the peak is not smooth. x_o is taken as the channel which corresponds to the maximum of a smooth curve drawn throught the data. When everything works properly, x_o is the same for each sample (i.e., no gain shifts).

Smooth curves are then penciled in through the data points at the beginning and end of the peaks. Tentative baselines are drawn in such a way that they start at the last channel before the peak and are tangent to the curve just past the peak. These tentative baselines are then compared between the four samples and the definitive base line is drawn from the best value for the last channel before the peak and the best point of tangency to the curve just past the peak.

The half maximum of the peak under study is calculated in the standard. This is given by the following relation:

$$HM = \frac{B + B'}{2}$$

B is the number of counts corresponding to x_o.

B' is the number of counts under the baseline at x_o.

B' is read from the graph.

Once HM has been calculated, one determines the number of channels in the peak which have a number of counts equal or greater than HM. This number is W. The area under the peak in the range of W and above the baseline is the area that is compared between sample and standard. W must be equal for samples and standard and correspond to those channels in the peak with the largest individual counts.

To calculate the peak areas (5) it is necessary to determine the median channel in the range W. From the graph, the number of counts under the baseline at the median channel is read. This number is designated as Y. Then the product $Z = W \cdot Y$ is determined. This number represents the area under the baseline in the range of W. Then the sum of the gross counts in the range W is calculated. This number, that is designated as V, represents the area under the peak in the range W. Therefore the net peak area of interest, S is equal to the difference V-Z.

Samples and standard are counted at different times (always the standard was counted first). Therefore if one wants to compare the net area of the sample with that of the standard, one has to correct to a common counting time by applying the decay law through the following relation:

$$Sc = S \times \exp(\lambda t) \qquad \text{(VII)}$$

Sc is the are the peak would have if the sample would have been counted at the same time as the standard. Sc is the corrected area.

S is the area of the peak calculated from the data provided by the instrument and from the graph.

λ is the decay constant for the given isotope. This is equal to $0.693/t_{\frac{1}{2}}$ where $t_{\frac{1}{2}}$ is the half life of the isotope.

t is the time which has passed between the counting of the sample and that of the standard.

Note: if t is expressed in minutes, λ must be expressed in inverse minutes.

t of equation VII is calculated through the following relation:

$$t = [B_i + X_i] - [B_o + X_o] \tag{VIII}$$

B_o is the time at which the counting of the standard started (provided the standard was counted first).

B_i is the time at which the counting of the sample started.

It is advisable to use the 24 hour time of day method to determine the values for B_o and B_i. For instance, suppose that the counting of the standard began at 10 PM of July 27 and that of the sample at 7 AM of July 28. In this case B_o = 22 hours and B_i = 24 + 7 = 31 hours.

The values for X_i and X_o are calculated in a different way according to the half life of the isotope of interest. If the half life of this is much greater than the counting period X_i represents the midpoint of the counting period of the sample and X_o represents that of the standard. They are calculated according to these relations:

$$X_i = 0.5(CP + CP \times DT_i) \tag{XI}$$
$$X_o = 0.5(CP + CP \times DT_o)$$

CP is the counting period set by the operator.

DT_o and DT_i are the dead times when the counting of standard and sample start respectively.

If the half life of the radioactive isotope being determined is of the same order of the counting period (Dy, for example, if it is counted for one hour), X_o and X_i of the expression VIII are calculated through the following relation given by Kerstin Löw (12).

$$X_o = 0.5[CT - \frac{1}{\lambda_o} \ln (\frac{1-DTo}{1-DT_o e^{-\lambda t}})]$$

$$X_i = 0.5[CT - \frac{1}{\lambda_i} \ln (\frac{1-DTi}{1-DT_i e^{-\lambda t}})]$$

Once one has the corrected value for the areas of samples (provided the standard was counted first) the final step is to determine the abundance of the element under study and express it in ppm. This can be done easily by applying the following relation:

$$C_E(\text{ppm}) = \frac{S_E\text{sample}/\text{Sstd} \times L_E}{\text{As}.}$$

E	stands for the element of interest.
C_E	is the concentration of the element of interest, expressed in ppm, in the rock under study.
S_E	is the corrected area for the element in the sample.
Sstd	is the net peak area of the std.
As	is the amount (expressed in grams) of the rock irradiated.

L_E is the amount of element V in the standard.

L_E can be calculated from the following relation:

$$L_E = \frac{CEss \times Vssupst.s}{Vtst.sp} \times VstE.$$

$C_E ss$ is the concentration of the stock solution in element E.

Vssupst.s is the volume of stock solution used to prepare the standard solution.

Vst.sE volume of standard solution put in the vial to be irradiated.

Vtst.sp is the total volume of the standard solution prepared.

At this point one has finally reached the aim of the analytical procedure, i.e., to determine the trace element abundance in a given rock sample.

Table I

Elem.	Target	Θ%	Irr. Time	Prod. Nucl.
Dy	164	28.2	2 min.	(2.32h) 156Dy
Na	23	100	2 min.	(15h) 24Na
K	41	6.8	2 min.	(12.4h) 42K
Sm	152	26.6	1 hr.	(47h) 153Sm
La	139	99.9	1 hr.	(40.22h) 140La
Yb	168	0.14	1 hr.	(32d) 169Yb
Ta	182	99.99	1 hr.	(115.1d) 182Ta
Nd	146	17.1	1 hr.	(11.1d) 147Nd
Th	232	100	1 hr.	(22m) 233Th→(27d)233Pa
Gd	152	0.2	1 hr.	(242d) 153Gd
Eu	151	47.8	1 hr.	(12y) 152Eu
Ba	130	0.1	1 hr.	(12d) 131Ba
Hf		32.8	1 hr.	(42.5d) 181Hf
Ce	140	88.5	1 hr.	(33d) 141Ce
Lu	176	2.6	1 hr.	(617d) 177Lu
Rb	85	72.15	1 hr.	(18.66d) 86Rb
Cs	133	100	1 hr.	(2.05y) 134Cs
Sc	45	100	1 hr.	(83.9d) 46Sc
Co	59	100	1 hr.	(5.267) 60Co

Table I continued

Elem.	σ(barns)	Photo Peak Used (KeV)	Relative Interest (%)	Decay Time	Detector
Dy	2700	94.7	4	3 hr	LEPS
Na	0.53	1369	100	1 d	13 cc
K	1.2	1524	18	1 d	13 cc
Sm	210	103.2	28	5 ds	LEPS
La	8.9	328.77	24	5 ds	LEPS
Yb	11000	63.6	54	14 ds	LEPS
Ta	21	68,100 & 1222	394	30 ds	13 cc & LEPS
Nd	2	91.1	28	14 ds	LEPS
Th	7.4	94.7	8.8	14 ds	LEPS
Gd		97.4	31	14 ds	LEPS
Eu	5900	121.9	37	14 ds	LEPS
Ba	8.8	123.78	29	14 ds	LEPS
Hf	10	133	40	14 ds	LEPS
Ce	0.6	145.5	48	14 ds	LEPS
Lu	2100	208	6.1	14 ds	LEPS
Rb	1	1077	8.8	14 ds	13 cc
Cs	31	605	98	30 ds	13 cc
Sc	23	889	100	30 ds	13 cc
Co	37	1332	100	30 ds	13 cc

Table II

Detector	Standard	E(keV)	(Rel. Int)	Ch.	C.G.
LEPS	^{241}Am	13.90	(2.75)	152	20
		17.75	(49.5)	187	20
		20.80	(12.8)	215	20
		26.36	(7.5)	266	20
		59.57	(100)	569	20
	^{152}Eu	121.9		1141	20
		244.7		2276	20
		344.4		3203	20
13 cc	^{137}Cs	661.6		1323	50
	^{152}Eu	121.8		262	50
		244.7		503	50
		344		698	50
		444.2		895	50
		965		1921	50
		1087		2165	50
		1113		2215	50
		1408		2804	50
	^{54}Mn	843.8		1666	50
	^{139}Ce	165.8		349	50

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Figure 1. Normative Ab, Or and Qtz (expressed in weight percent) of Virginia's samples plotted in the system Ab-Or-Qtz.

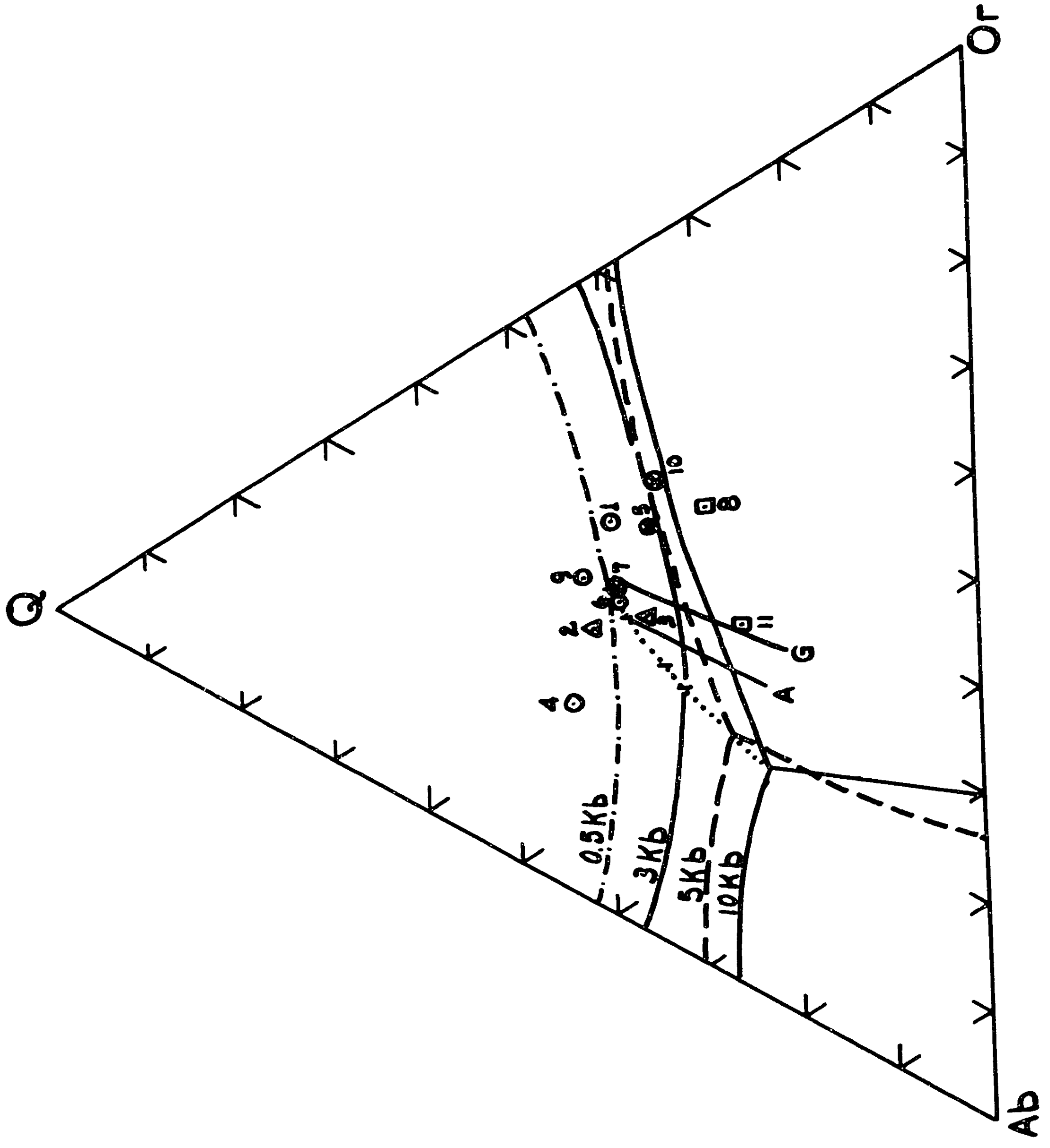

Q
Or
Ab
0.5Kb
3Kb
5Kb
10Kb
G
A
1
2
3
4
5
6
7
8
9
10
11

Figure 2. REE abundance pattern for samples V2, V3 and V6 normalized element by element to chondrite.

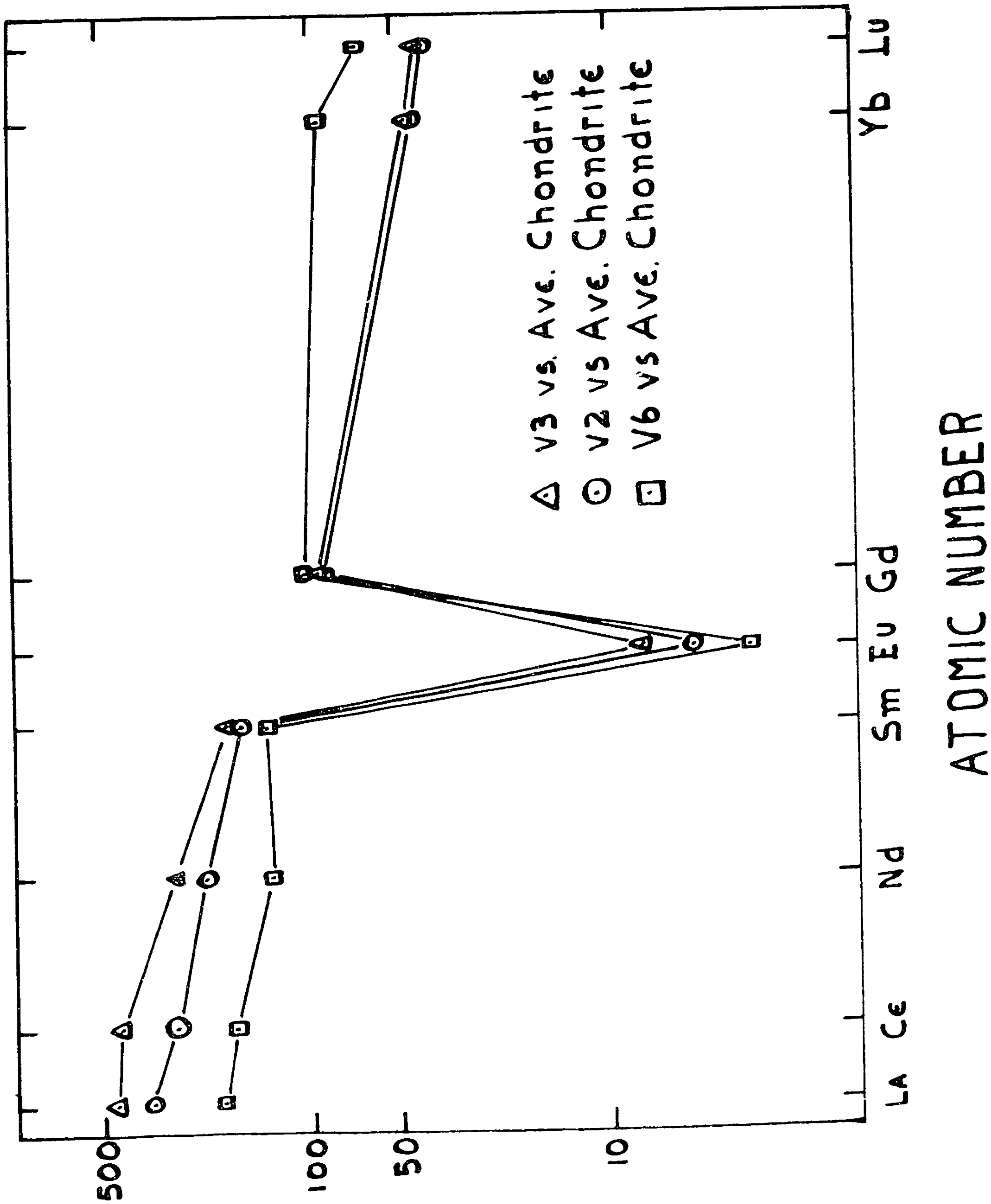

500
100
50
10
LA
Ce
Nd
Sm
Eu
Gd
Yb
Lu
ATOMIC NUMBER
△ V3 vs. Ave. Chondrite
⊙ V2 vs Ave. Chondrite
⊡ V6 vs Ave. Chondrite

Figure 3. REE abundance pattern for samples V1, V4 and V9 normalized element by element to chondrites.

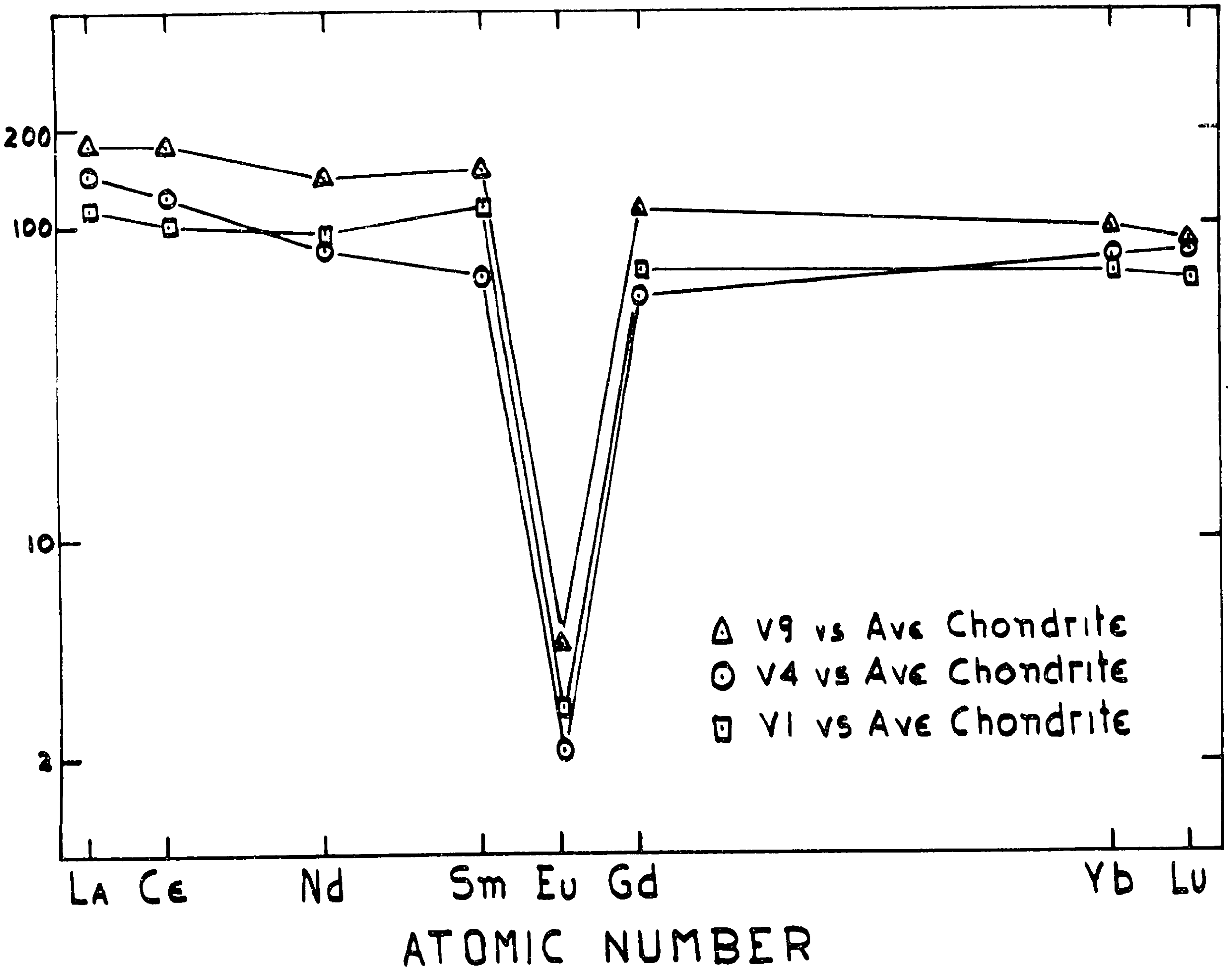
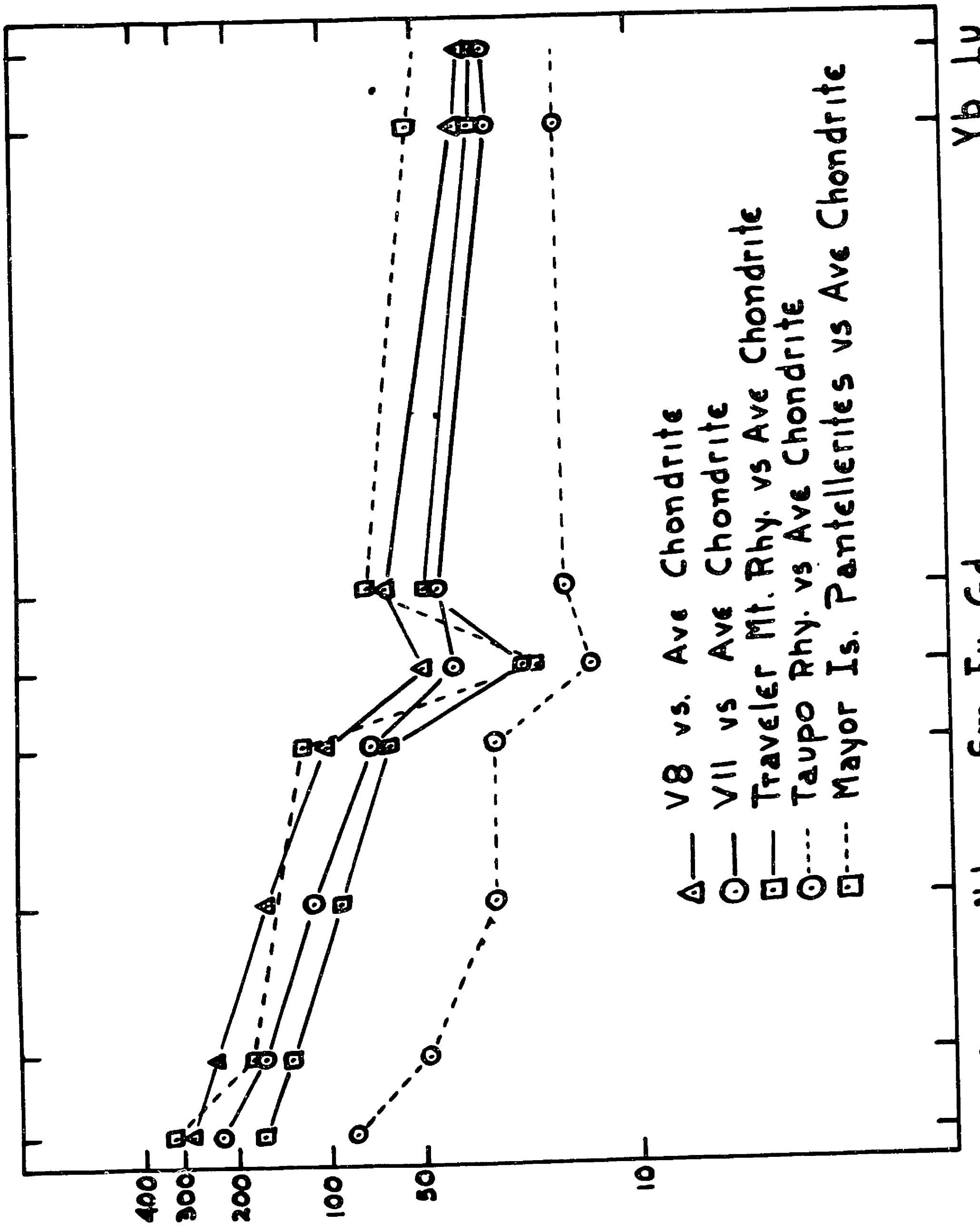

200
100
10
2
La
Ce
Nd
Sm
Eu
Gd
Yb
Lu
ATOMIC NUMBER
△ V9 vs Ave Chondrite
⊙ V4 vs Ave Chondrite
▣ V1 vs Ave Chondrite

Figure 4. REE abundance pattern for samples V8 and V9 of Mt. Rogers, for the average Traveler Mt. rhyolite, for the average Tanpo rhyolites and for the average Mayor Island pantellerites, normalized element by element to chondrites.



400
300
200
100
50
10
LA
Ce
Nd
Sm
Eu
Gd
Yb
Lu
ATOMIC NUMBER
V8 vs. Ave Chondrite
V11 vs Ave Chondrite
Traveler Mt. Rhy. vs Ave Chondrite
Taupo Rhy. vs Ave Chondrite
Mayor Is. Pantellerites vs Ave Chondrite

Figure 5. REE abundance pattern for samples V3, V6, V9 and V11 normalized element by element to chondrites.

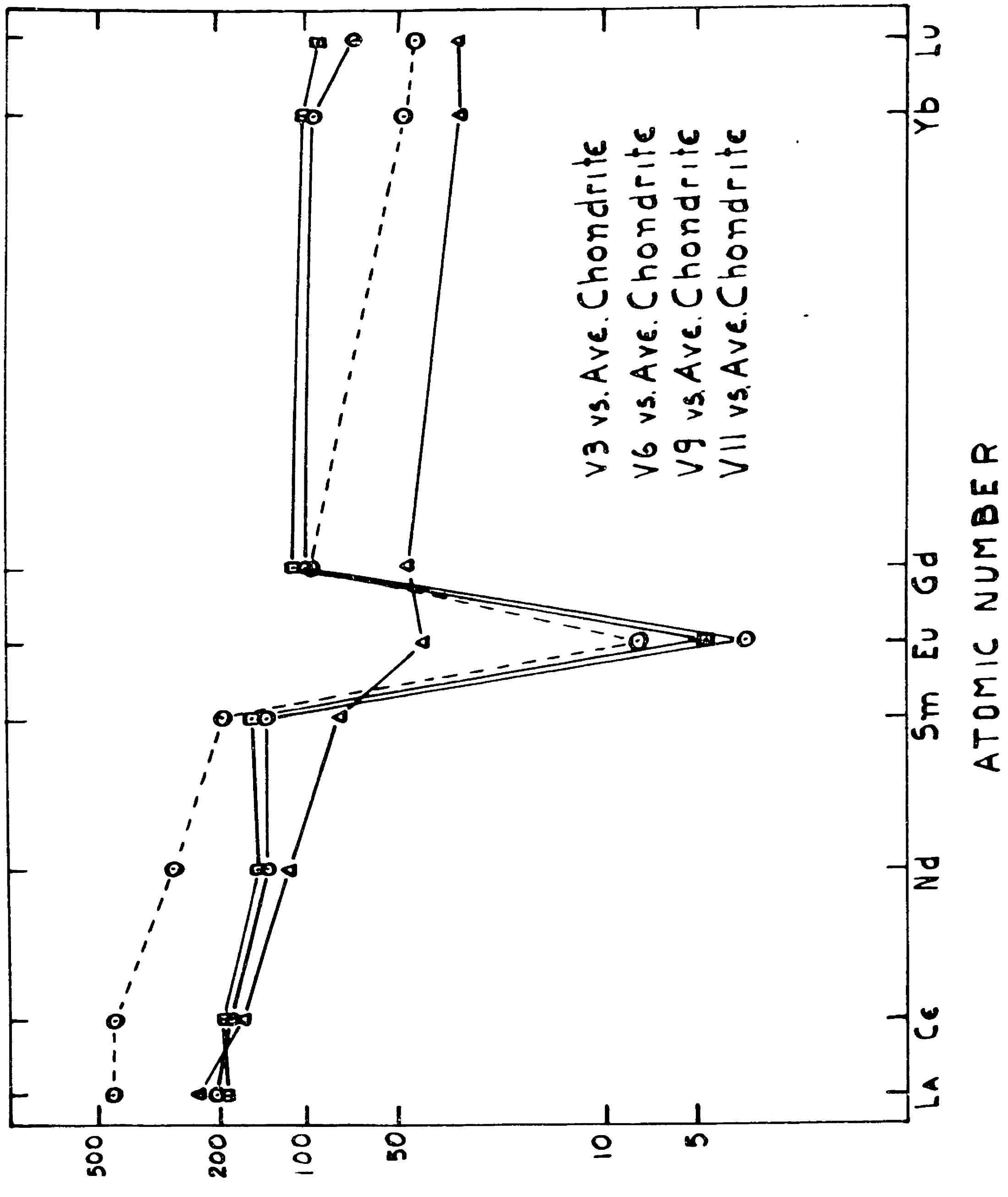

V3 vs. Ave. Chondrite
V6 vs. Ave. Chondrite
V9 vs. Ave. Chondrite
V11 vs. Ave. Chondrite
500
200
100
50
10
5
LA
Ce
Nd
Sm
Eu
Gd
Yb
Lu
ATOMIC NUMBER

Figure 6. Rb, Ba and Sr abundances for Virginia's samples plotted versus their respective Eu/Eu* ratio.

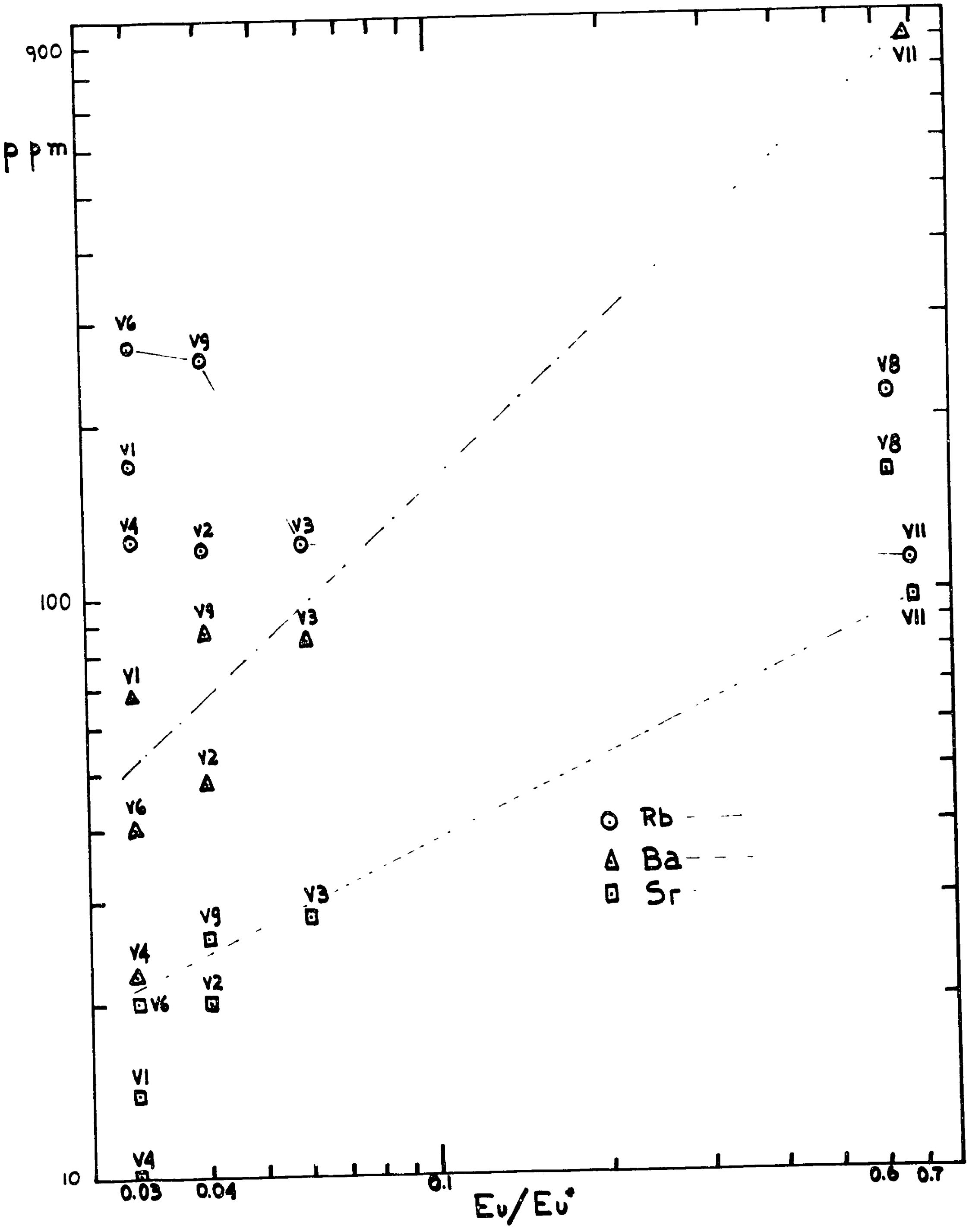

ppm
900
100
10
0.03
0.04
0.1
0.6
0.7
Eu/Eu*
V6
V9
V1
V4
V2
V3
V8
V11
Rb
Ba
Sr

Figure 7. REE abundance pattern for samples V3, V6 and V9 normalized element by element to sample VII.

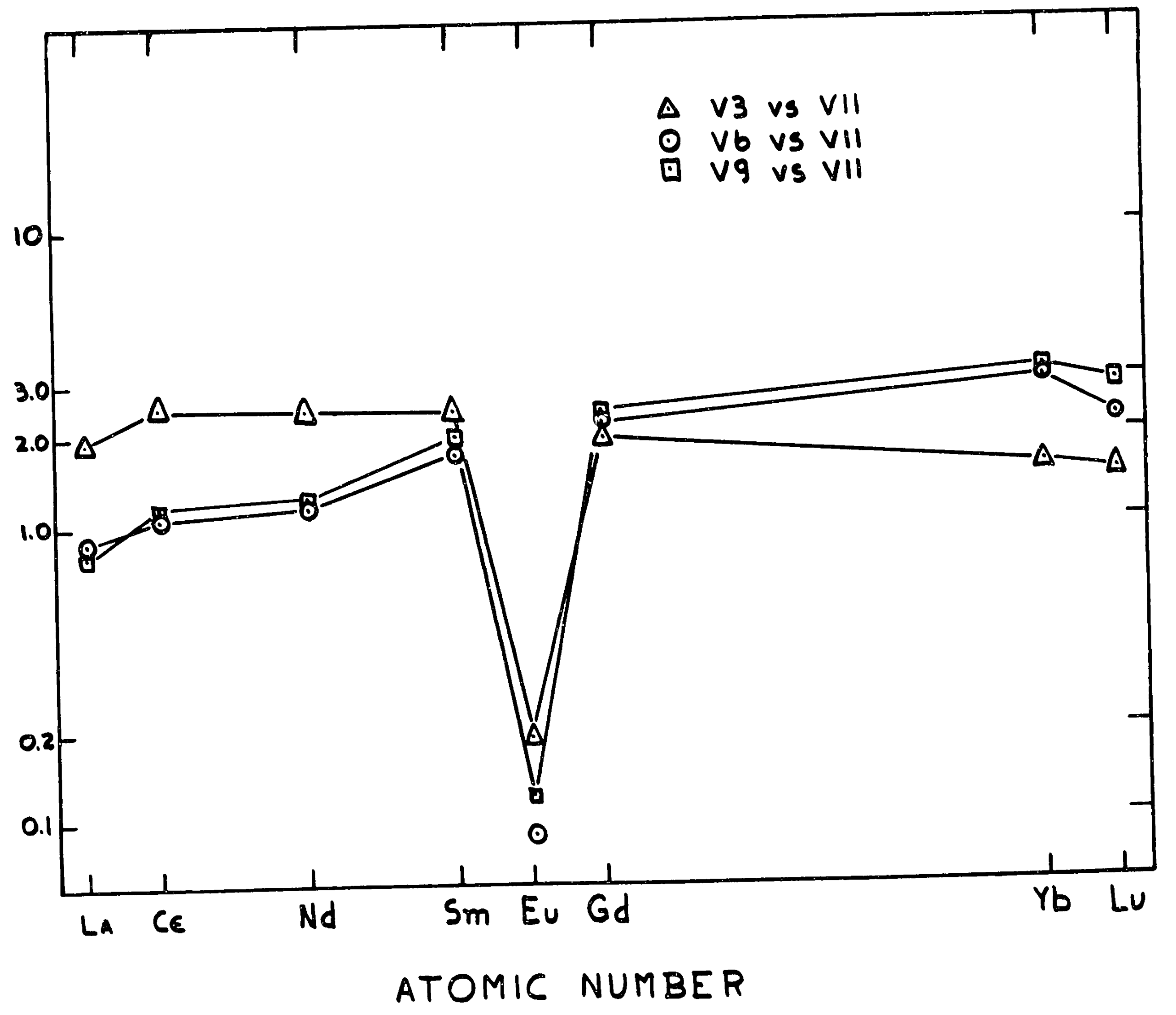

△ V3 vs V11
⊙ V6 vs V11
⊡ V9 vs V11
10
3.0
2.0
1.0
0.2
0.1
LA
Ce
Nd
Sm
Eu
Gd
Yb
Lu
ATOMIC NUMBER

Figure 8. Eu distribution coefficient values versus plagioclase composition.

Note: ⊙ from Schnetzler and Philpotts (1970)

◬ from Dudas *et al.* (1971)

⊡ from Nagasawa and Schnetzler (1971)

⊗ k-feldspar, from Schnetzler and Philpotts (1970)

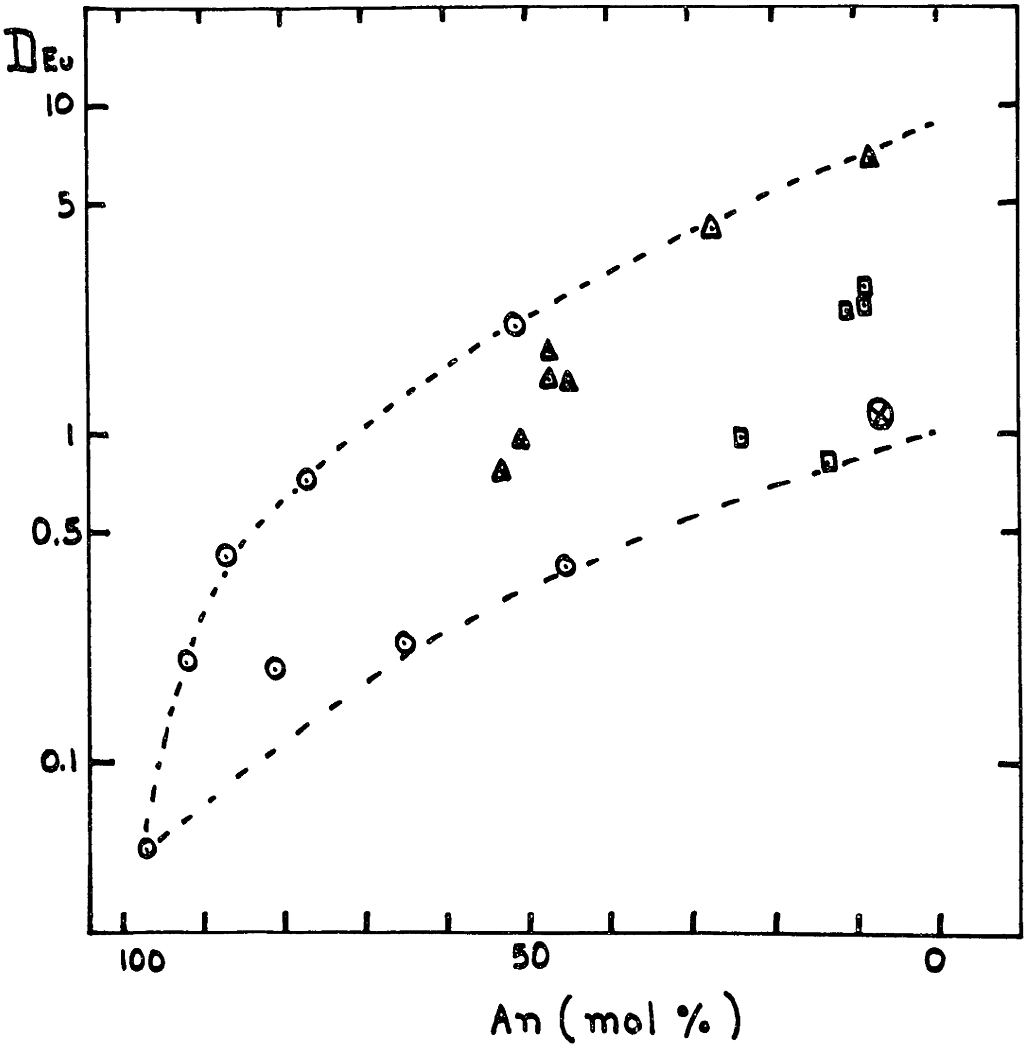

D_{Eu}
10
5
1
0.5
0.1
100
50
0
An (mol %)

Figure 9. Sr distribution coefficient values versus plagioclase composition (see note in Figure 8).

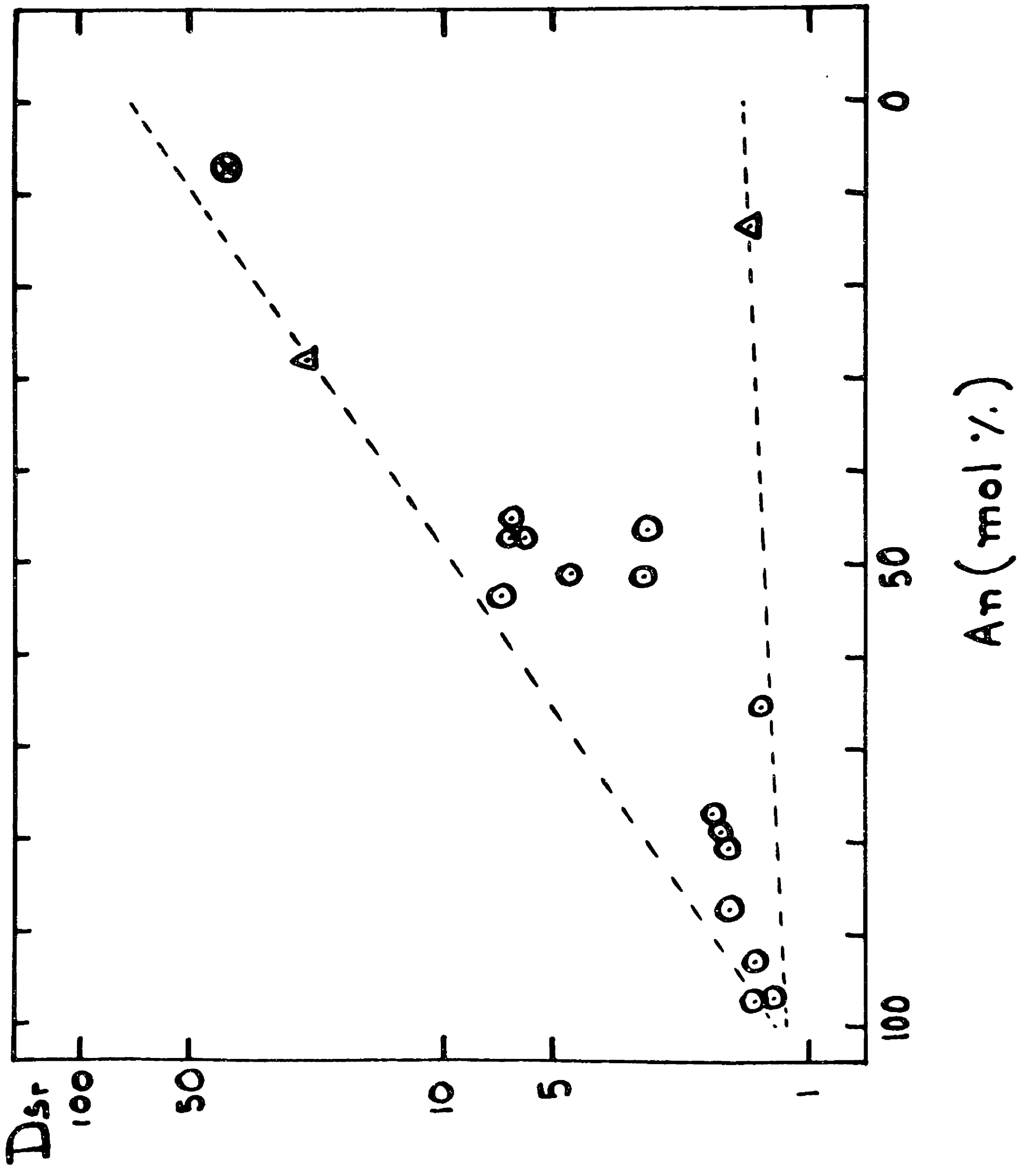

D_sr
100
50
10
5
1
0
50
100
An (mol %)

Figure 10. Ba distribution coefficient values versus plagioclase composition (see note in Figure 8).

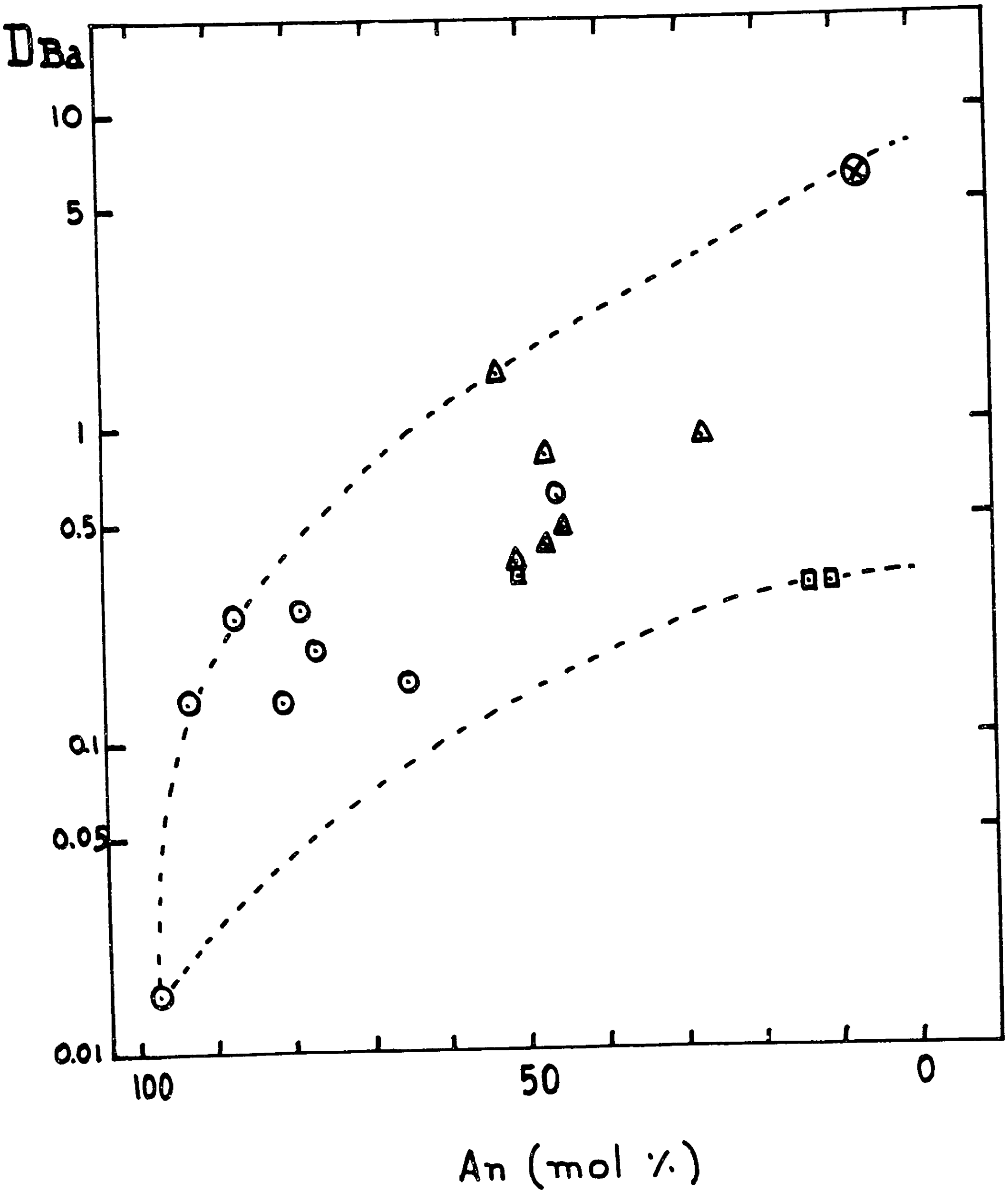

DBa
10
5
1
0.5
0.1
0.05
0.01
100
50
0
An (mol %)

Figure 11. REE abundance pattern for Mt. Rogers rhyolites normalized element by element to rock sample V11.

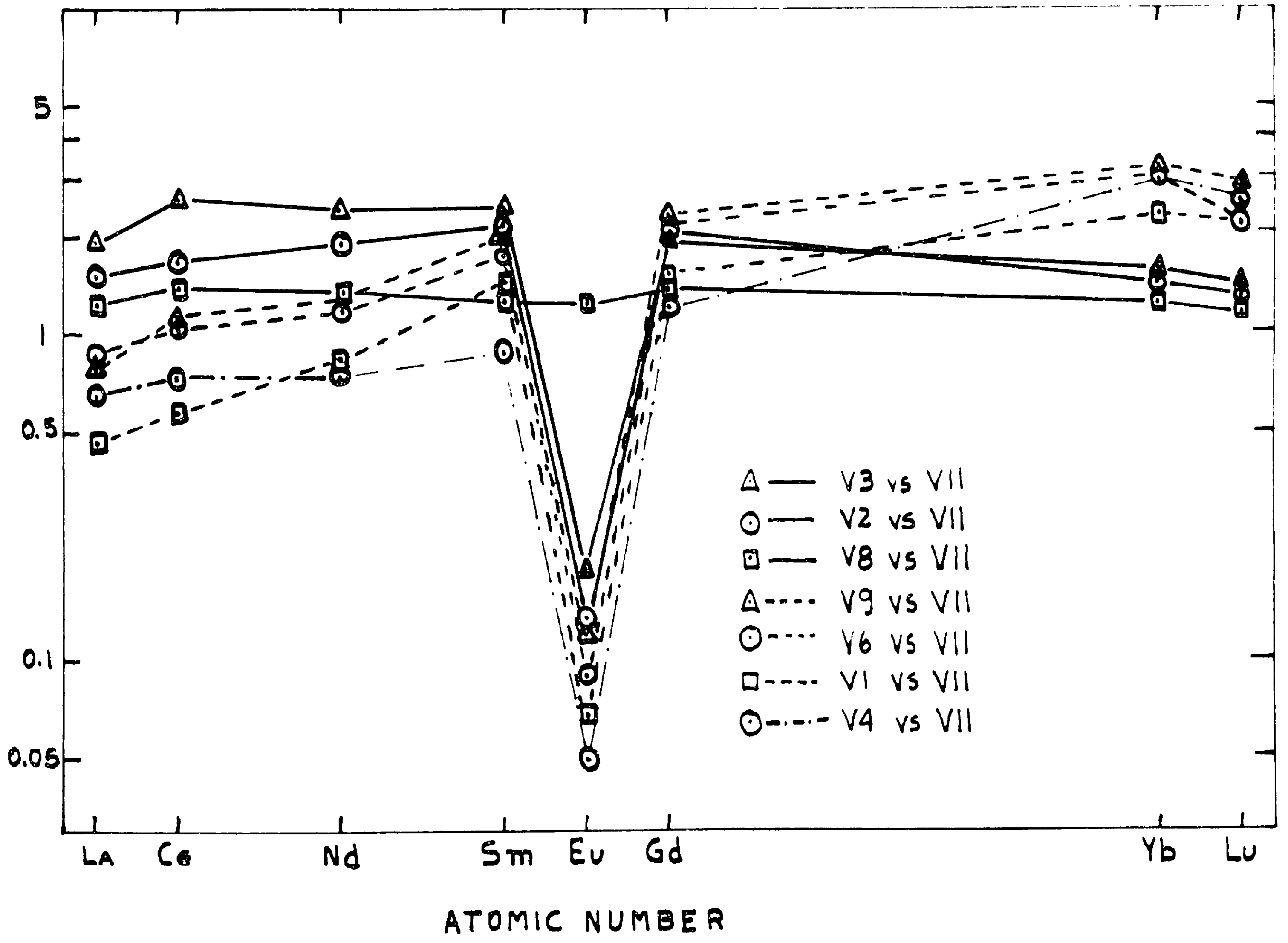
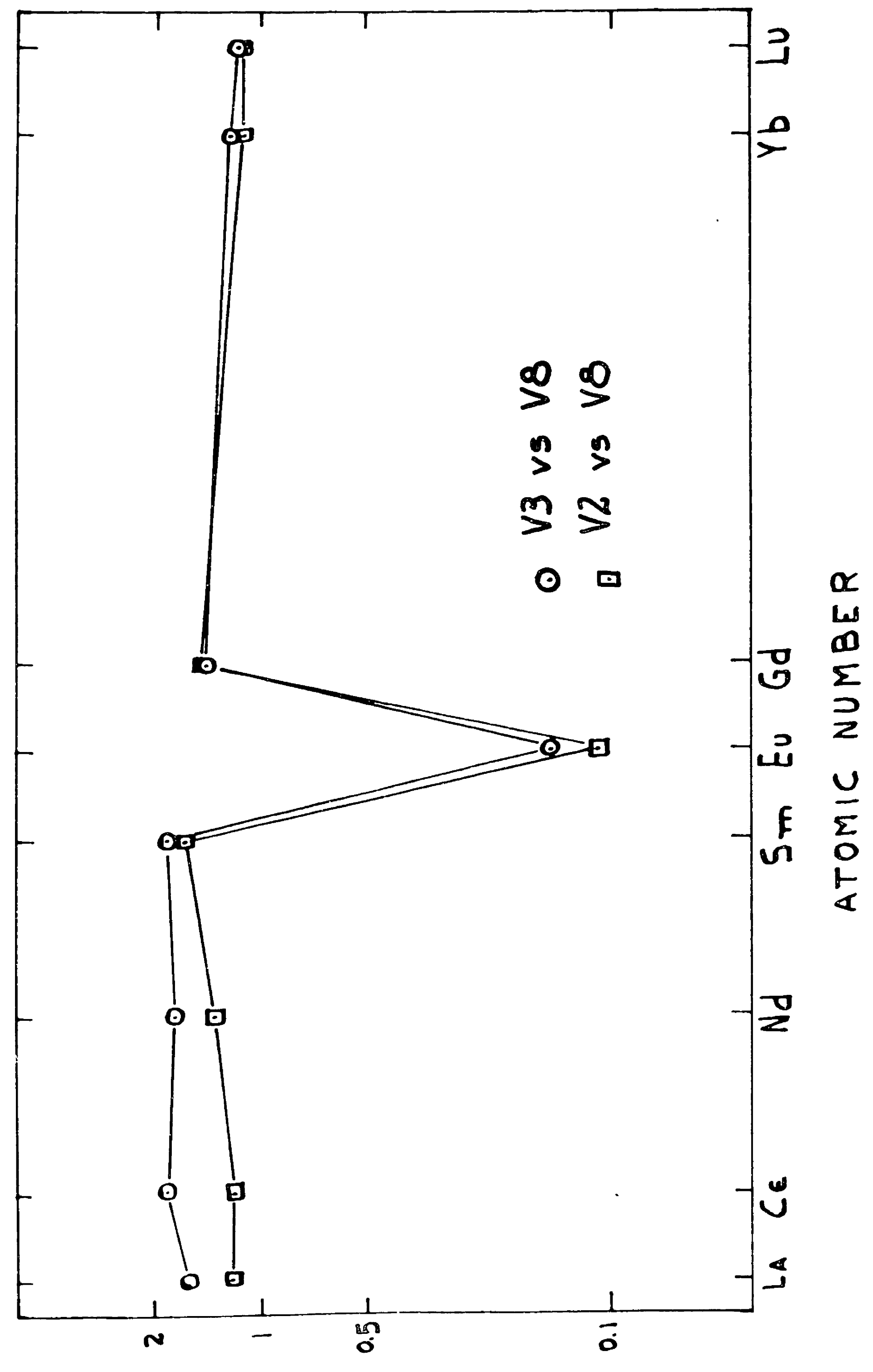

5
1
0.5
0.1
0.05
LA
Ce
Nd
Sm
Eu
Gd
Yb
Lu
ATOMIC NUMBER
V3 vs V11
V2 vs V11
V8 vs V11
V9 vs V11
V6 vs V11
V1 vs V11
V4 vs V11

Figure 12. REE abundance pattern for samples V2 and V3 normalized element by element to rock sample V8.



2
1
0.5
0.1
La
Ce
Nd
Sm
Eu
Gd
Yb
Lu
ATOMIC NUMBER
⊙ V3 vs V8
⊡ V2 vs V8

Figure 13. REE abundance pattern for samples V1, V4 and V9 normalized element by element to rock sample V6.

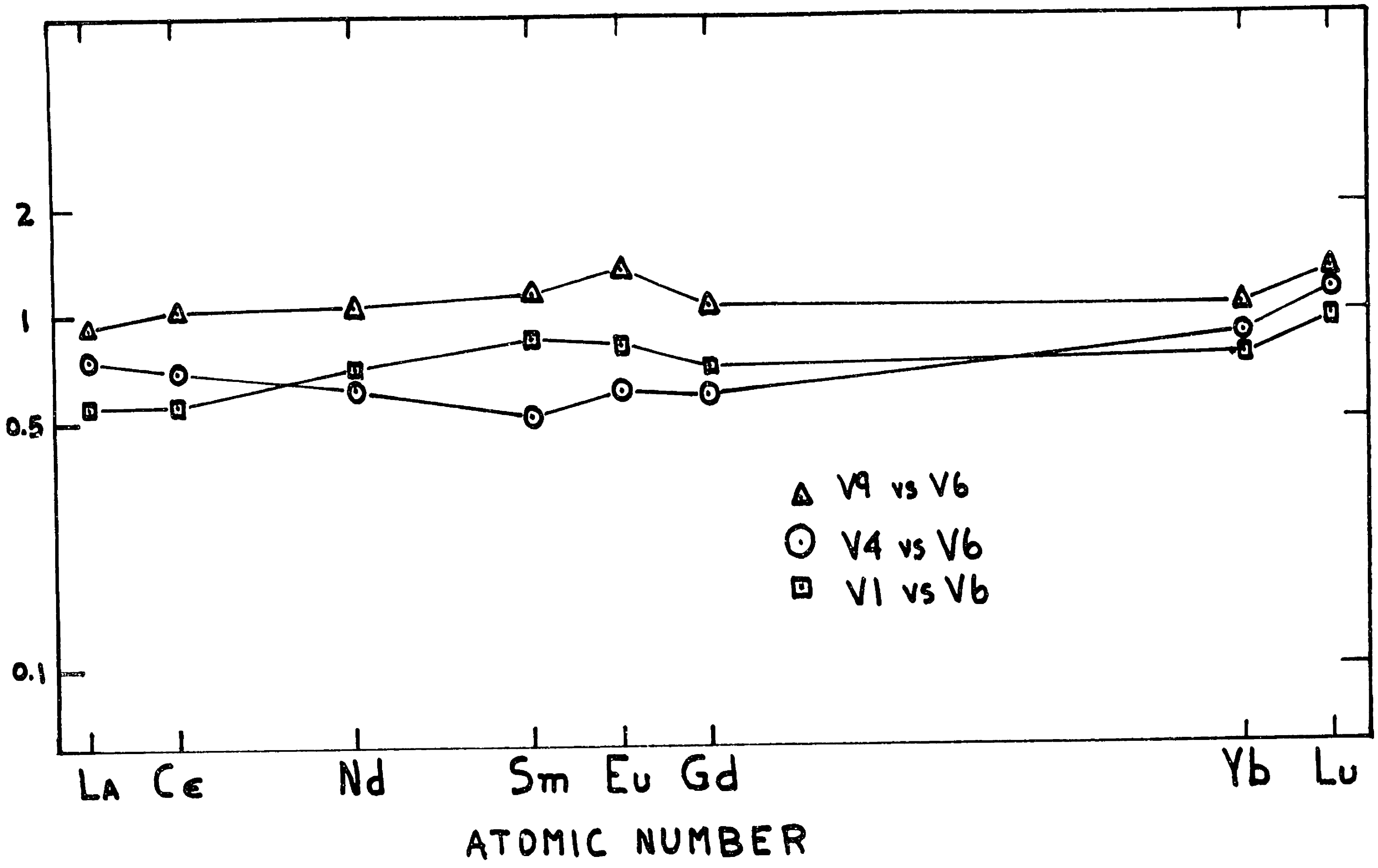

2
1
0.5
0.1
V9 vs V6
V4 vs V6
V1 vs Vb
LA
Ce
Nd
Sm
Eu
Gd
Yb
Lu
ATOMIC NUMBER

Figure 14. Eu^{+3} distribution coefficient values versus plagioclase composition (see note in Figure 8).

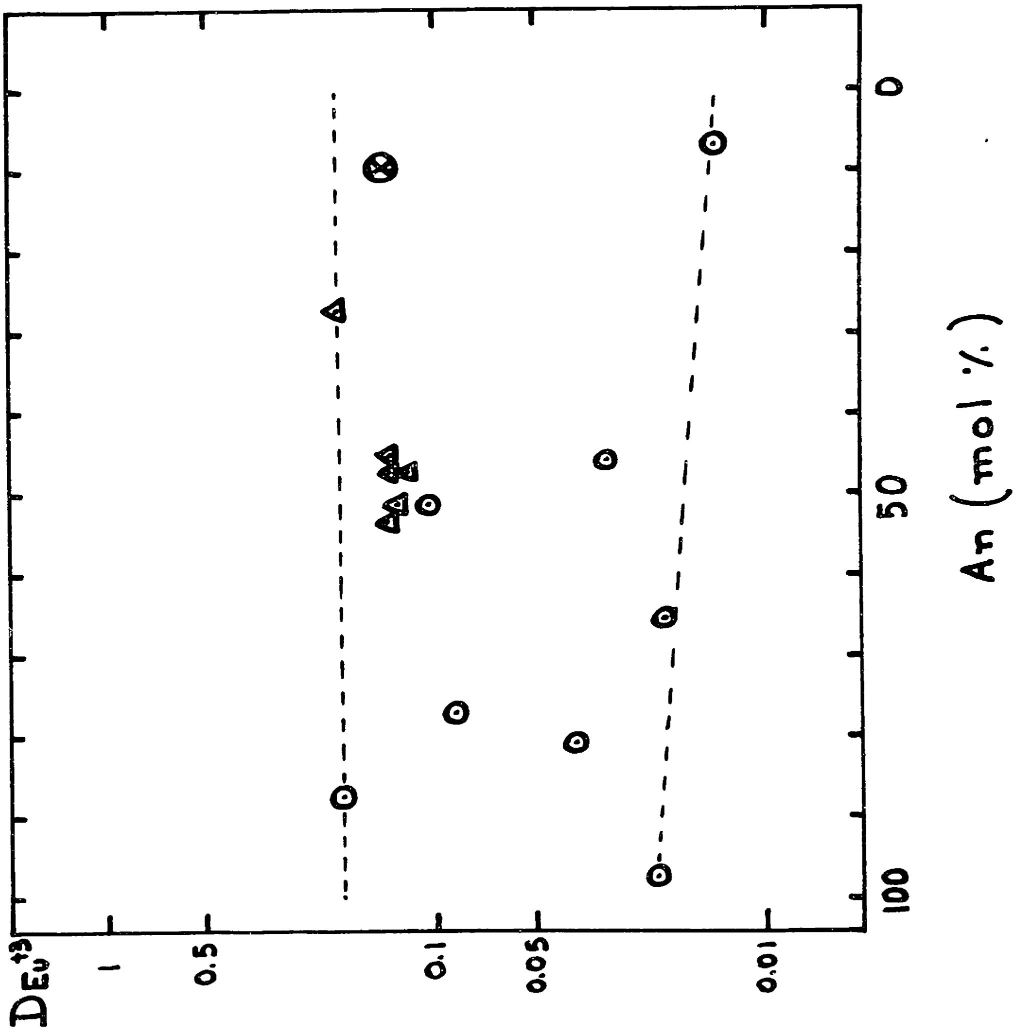

$D_{Eu^{+3}}$
1
0.5
0.1
0.05
0.01
100
50
0
An (mol %)

Figure 15. Range REE abundance pattern for Traveler Mtn. rhyolites normalized element by element to chondrites.

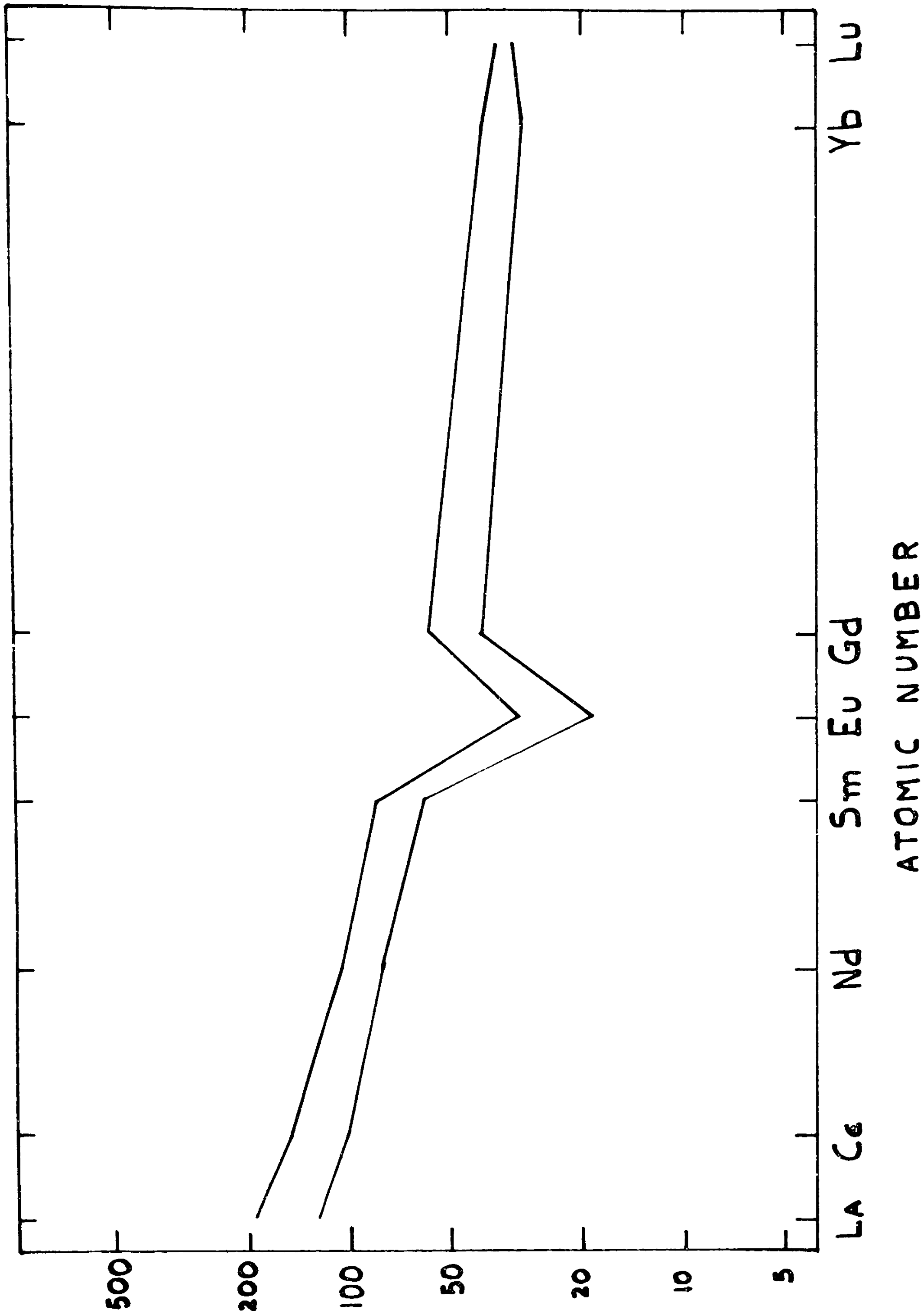

500
200
100
50
20
10
5
LA
Ce
Nd
Sm
Eu
Gd
Yb
Lu
ATOMIC NUMBER

Figure 16. REE abundance pattern for samples V5, V7 and V10 normalized element by element to chondrites.

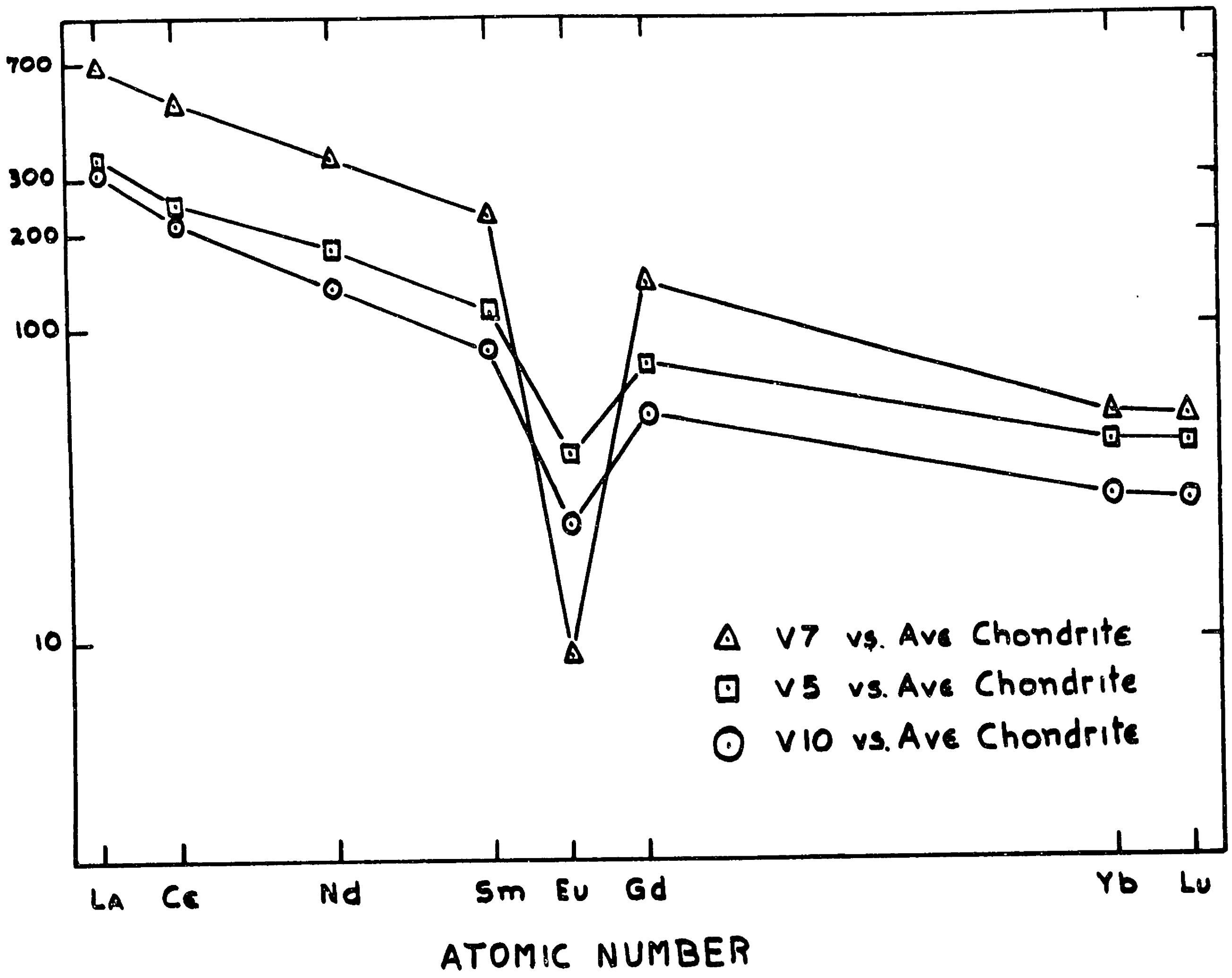
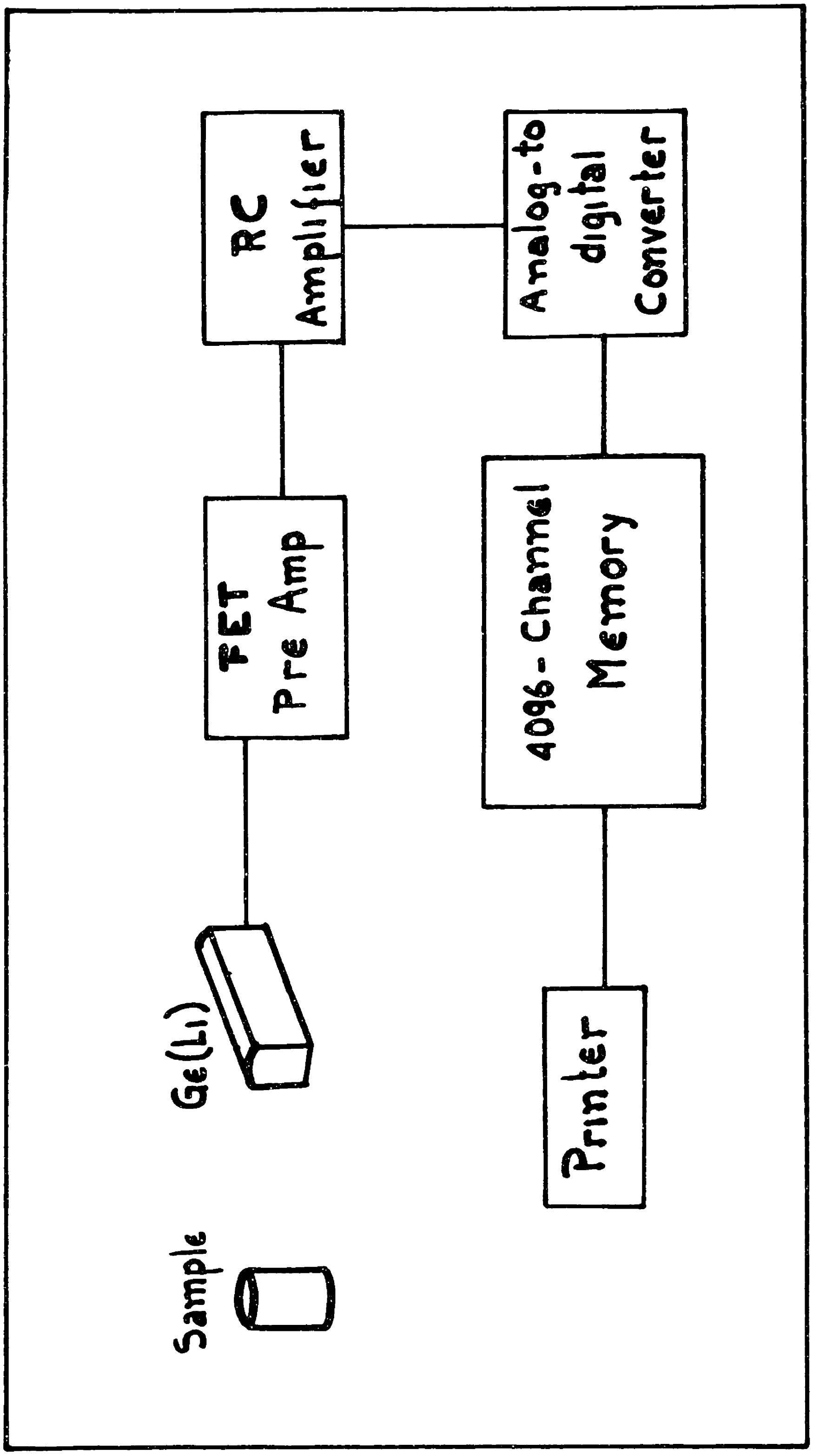

700
300
200
100
10
LA
Ce
Nd
Sm
Eu
Gd
Yb
Lu
ATOMIC NUMBER
△ V7 vs. Ave Chondrite
⊡ V5 vs. Ave Chondrite
⊙ V10 vs. Ave Chondrite

Figure I (Appendix II) Schematic diagram of γ-ray spectrometry equipment used.


Sample
Ge(Li)
FET
Pre Amp
RC
Amplifier
Analog-to
digital
Converter
4096-Channel
Memory
Printer