THALLIUM-RUBIDIUM-POTASSIUM RELATIONSHIP

IN

NEPHELINE SYENITE

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NEPHELINE SYENITE

BY

SING ZEON LAI

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ABSTRACT

Nepheline syenite samples were collected from the Bancroft and Blue Mountain areas, Ontario, Canada, and were analysed for K, Rb, and Tl contents by atomic absorption spectrophotometry. The results for these elements and the corresponding K/Rb, K/Tl and Rb/Tl ratios were compared with those of nepheline syenites in various localities, and were found to be similar.

The Tl, Rb, K contents and the K/Rb, K/Tl and Rb/Tl ratios in this study were determined to be 825 ppb, 110 ppm, 3.28%, 298, 4.11×10^4 and 135 respectively for the Bancroft nepheline syenite gneisses, and 574ppb, 93ppm, 3.28%, 353, 5.71×10^4 and 162 reapectively for the Blue Mountain nepheline syenites. From these data, the nepheline syenite rocks in this study were probably originated as continental plutonics.

ACKNOWLEDGEMENT

The author is indebted to Professor D.M. Shaw for his proposal and supervision without which this study cannot be possible. Thanks are also extended to Industmin Limited for allowing the study on its properties, and to Mr. P.C. Fung and Mr. J.R. Muysson for their helpful advices throughout this study.

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INTRODUCTION

The nepheline syenite bodies in the Bancroft and the Blue Mountain areas, Ontario have been studied by various workers. Two theories have been proposed for their origin: (1) intrusion and crystallisation of nepheline syenite magma into the country rocks; and (2) in situ replacement of the older rocks by metasomatic nephelinisation brought forth by aqueous solutions enriched in alkalis and alumina. Gittins (1961) and Tilley and Gittins (1961) studied the Bancroft nepheline syenite and proposed that metasomatic nephelinisation was probably the cause of some of the nepheline-bearing rocks, but others were igneous. Payne (1968) studied the Blue Mountain body and suggested a metasomatic origin was unrealistic and supported the hypothesis of igneous intrusion. This study attempts to examine the two areas of nepheline syenites by investigating their Tl-Rb-K relationships.

AREAS OF STUDY

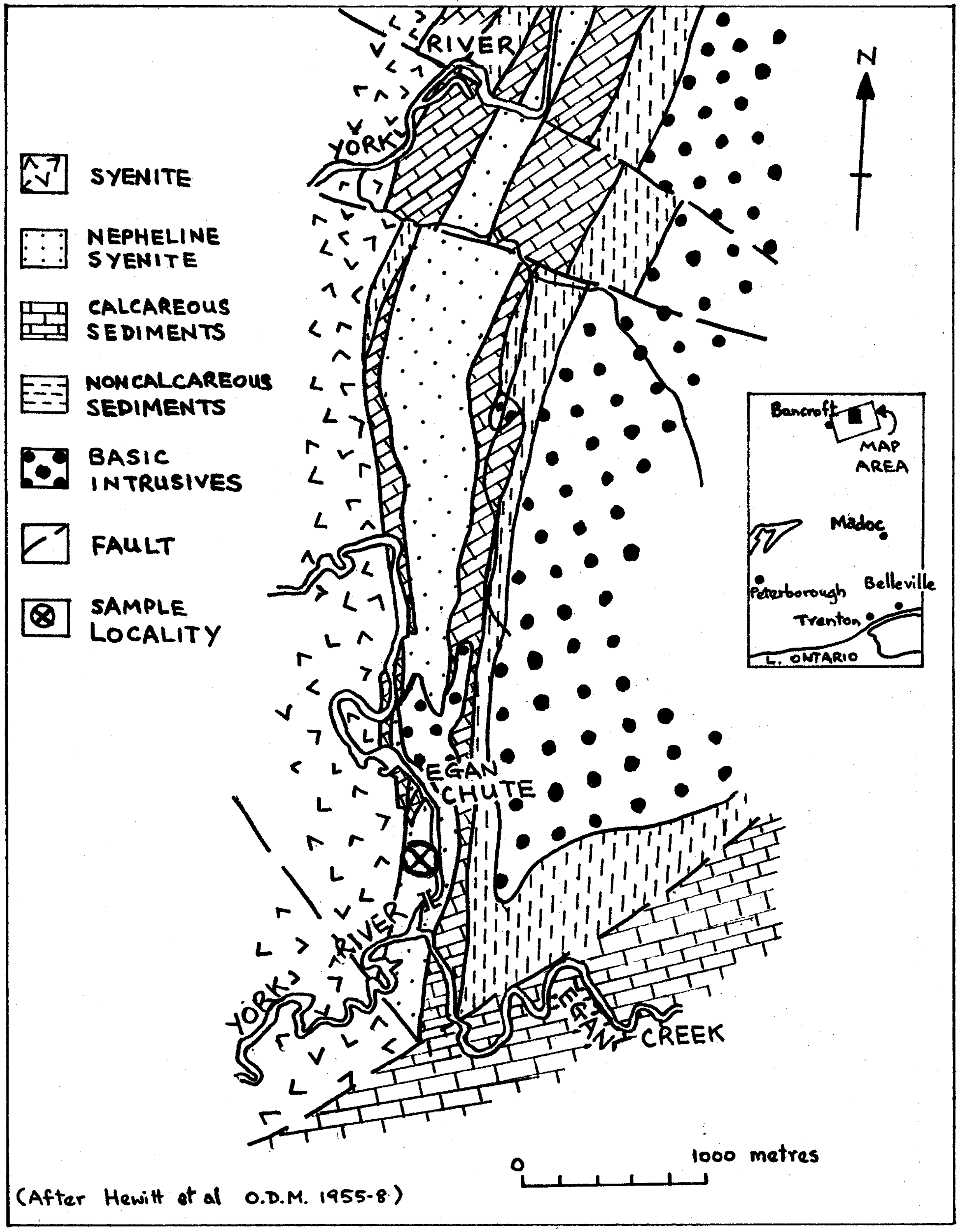
The samples NS1-NS6 were collected from the York River nepheline gneiss band in Lot 12, Concession XI and Lot 12, Concession XII, Dungannon township about 1/4 mile north of the East Road on the west bank of the York River (Map 1).

The township of Dungannon is divided into two parts geologically: The Hasting Highland gneiss complex lying to the north, from which samples NS1-NS6 were collected, and the Hasting Basin to the south. The Hasting Highland gneiss complex is a terrain of high-grade metamorphic gneisses, characterised by rocks of the amphibolite and granulite metamorphic facies. The Precambrian bedrocks consist of the Grenville-type metasediments and metavolcanic rocks, which were intruded by acidic and basic plutonic rocks (nepheline syenites, syenites, granites and gabbros). Later folding and high grade metamorphism produced a strong gneissic structure in all the rocks. Structurally the strike of the intruded rocks follows the trend of the York River and the dips are steeply to the south and the east.

The samples BM1-BM11 were collected from Lot 12 and Lot 13, Concessions XI and XII, Methuen township, Ontario, that is, the southwest arm of the nepheline syenite body on the Cabin Ridge quarries operated by Industmin Limited, Nepheline Syenite Company (Map 2).

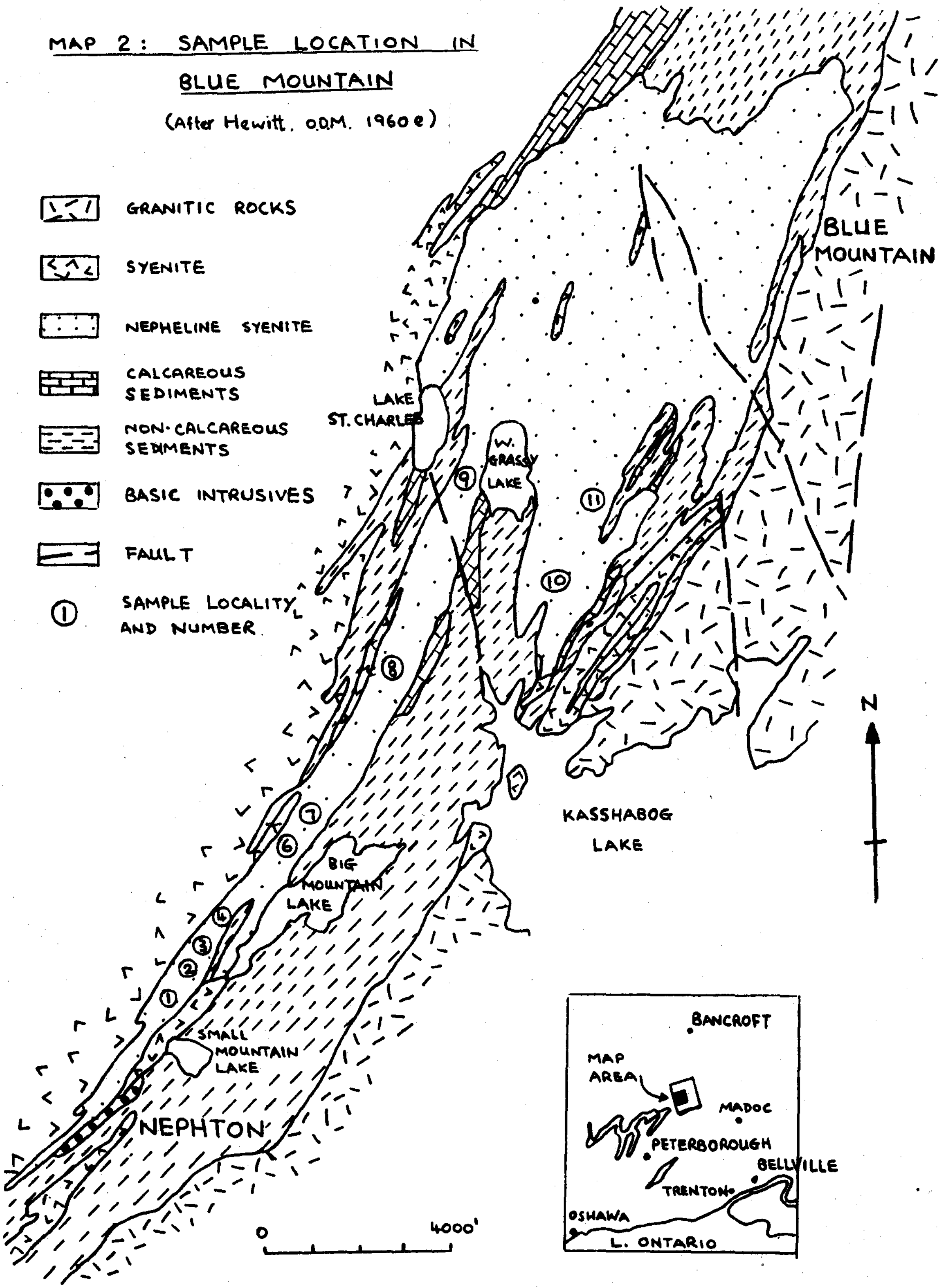
The nepheline syenite body here occurs in one single body in the west-central Methuen township and consists of an elongated, irregular stock intruding and partially replacing the para-amphibolite, paragneiss

MAP 1 : SAMPLE LOCATION IN YORK RIVER



MAP 2: SAMPLE LOCATION IN BLUE MOUNTAIN

(After Hewitt, O.D.M. 1960e)



and marble of the Blue Mountain metasedimentary band. The nepheline syenite itself is intruded and replaced by pink syenite and syenite pegmatite. Structurally the nepheline syenite body is well foliated near the contact and appears to occupy the trough of a syncline plunging gently southwest.

SAMPLE PREPARATION

Fratta's method (1973) was employed and slightly modified for Tl, Rb and K determinations. The sample preparation procedure is summarised in Figure 1.

Tl Standard Preparation

About 0.5 gm. of an rock powder similar to the sample being analysed was dissolved as in Figure 1 and reextracted for Tl with isopropyl ether saturated with 0.5 N HBr. The Tl-free aqueous portion was made up with water, or evaporated, to 30 ml. When cool, 5 ml. of 100 ppb Tl solution were added with 3 drops of Br_2 liquid, and excess Br_2 was then boiled off. The solution was then made up to 50 ml. in a separating funnel and Tl was extracted with 10 ml. isopropyl ether saturated with 0.5 N HBr.

Rb Standard Preparation

6.47 mg. of Spec pure RbCl were dissolved in about 20 to 30 ml. water. 5 ml. of HBr were added and the solution was boiled for 1 to 2 minutes. When cool, it was made up to 500 ml. with water. Then, 500 ml. working standard solutions were prepared, containing 20 ml. Na buffer, 12.5 ml. HBr and 0, 5, 10, 25, 50 and 100 ml. aliquots of the above RbCl solution, and were stored in polyethylene bottles.

The values of these standard solutions in terms of ppm oxide and ppm Rb in the samples were given in Table 1.

FIGURE 1 : SAMPLE PREPARATION

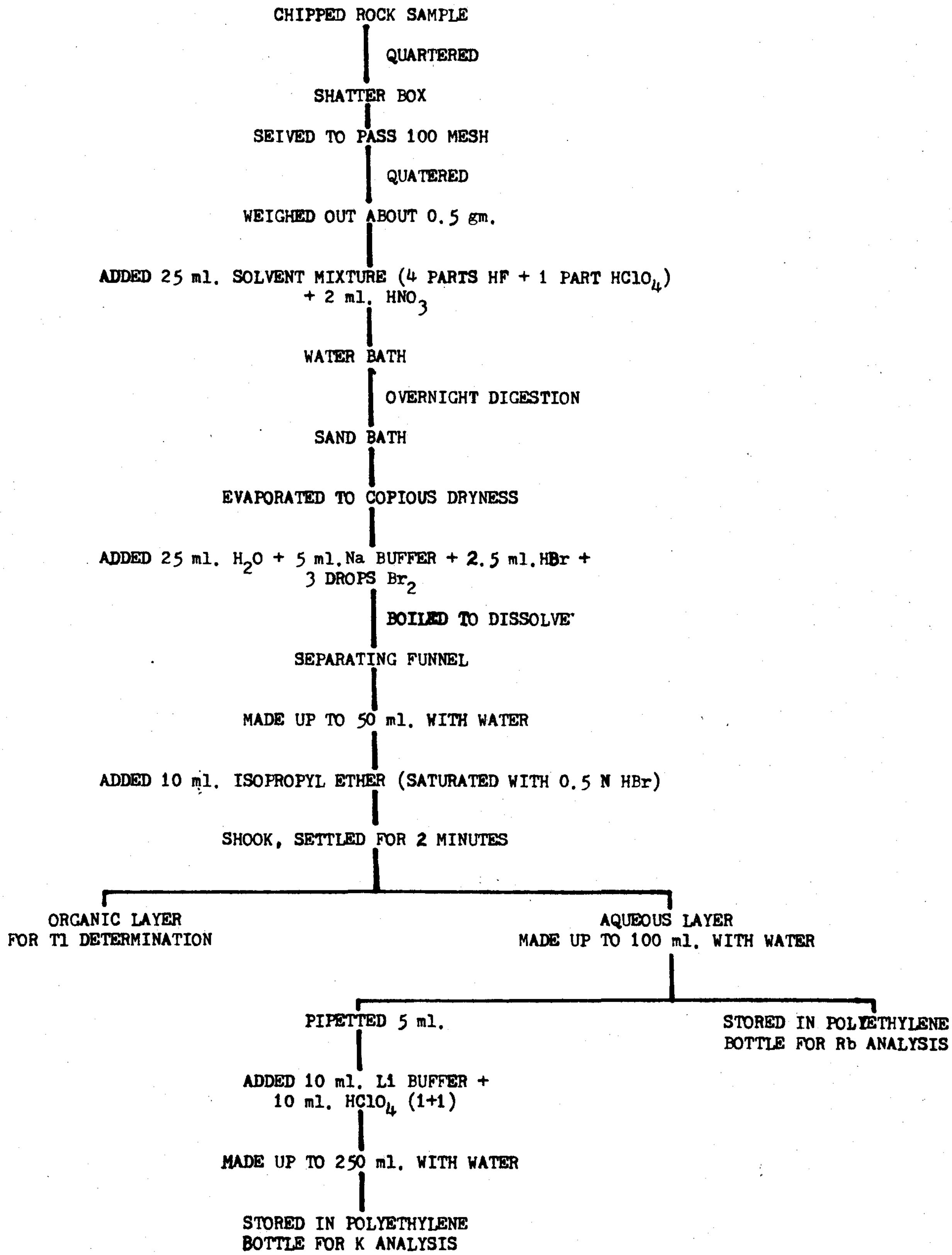


TABLE 1 : VALUES OF RB_2O AND RB OF STANDARD SOLUTIONS

STANDARD	ALIQUOTS ml.	RB_2O ppm	RB ppm
A	0	0	0
B	5	10	9.14
C	10	20	18.29
D	25	50	45.72
E	50	100	91.44
F	100	200	182.88

TABLE 2 : VALUES OF K_2O AND K OF STANDARD SOLUTIONS

STANDARD	ALIQUOTS ml.	K_2O %	K %
BLANK	0	0	0
MEDIUM	5	2.21	1.83
HIGH	10	4.42	3.67

K Standard Preparation

About 70 mg. of Spec pure KCl were weighed accurately and dissolved in water acidified with a few drops of HCl, then it was made up to 200 ml. with water. 250 ml. working solutions were prepared, containing 10 ml. Li buffer, 10 ml. (1+1) $HClO_4$, 2.5 ml. HBr, and 0, 5, 10 ml. aliquots of the standard KCl solution. The solutions prepared were stored in polyethylene bottles.

The equivalent percentages of K_2O and K in the standard solutions were calculated from the amount of KCl weighed out. The values were tabulated in Table 2.

SAMPLE ANALYSES

Tl Determination

Fratta's method (1973) was followed.

The analysis was performed on a Perkin-Elmer Model 303 atomic absorption spectrometer coupled to a record readout and thence to a fast response Perkin-Elmer Hitachi Model 56 strip chart recorder. Aliquots of sample or standard Tl extracts were transferred into a tantalum boat, and were introduced directly into the atomic absorption flame after the organic liquid was completely evaporated. Peaks were produced on the chart recorder upon instantaneous absorption, with the heights of the peaks proportional, with some limit, to the amounts of Tl present in the boat. These peak heights were tabulated and averaged. From the results of the standard, a working curve was produced from which the unknown Tl concentrations in the samples could be determined. In order to prevent aging of the Tl extracts, the analysis was done over a 2-day period.

The analytical conditions for Tl are shown in Table 3.

Rb and K Determinations

Conventional aspiration techniques were used for Rb and K analyses. The sample and standard solutions were suctioned into the atomic absorption flame at a constant flow rate for a constant time period. The results were averaged by a Perkin-Elmer DCR-1 recorder

TABLE 3 : ANALYSIS CONDITIONS FOR TL

Perkin-Elmer Atomic Absorption Spectrophotometer Model 303

Range	UV
Slit	4
Gain	5.3
Wavelength	277
Lamp	Perkin-Elmer Intensitron Lamp, Element Tl
Absorption	0
Lamp Current	20 mA

Recorder Perkin-Elmer Model 56 Chart Recorder

Scale Expansion	1
mV Range	20

Flame Acetylene-air

and printed out on a Perkin-Elmer PR-4 printer. The results were tabulated and working curves were produced from the standards, so that the unknown concentrations of the samples could be determined.

The analytical conditions for Rb and K analyses were shown in Tables 4 and 5 respectively.

TABLE 4 : ANALYSIS CONDITIONS FOR RB

Perkin-Elmer Atomic Absorption Spectrophotometer Model 303

Range	VIS
Slit	5- Filter
Gain	4.3
Wavelength	390
Lamp	Osram Lamp
Absorption	0
Lamp Current	350 mA

Recorder Perkin-Elmer DCR-1 Recorder
Perkin-Elmer PR 4 Printer

Flame Acetylene-air

TABLE 5 : ANALYSIS CONDITIONS FOR K

Perkin-Elmer Atomic Absorption Spectrophotometer Model 303

Range	VIS
Slit	4 - Filter
Gain	5.9
Wavelength	383
Lamp	Perkin-Elmer Intensitron Lamp Element K
Absorption	0
Lamp Current	12 mA

Recorder Perkin-Elmer DCR-1 Recorder
Perkin-Elmer PR 4 Printer

Flame Acetylene-air

RESULTS OF ANALYSES

Three working curves for Tl, Rb, and K were constructed as in Figures 2, 3 and 4 respectively, from which the results were calculated.

The results of the individual samples are tabulated in Table 6 and their Tl-Rb-K relationships are plotted in logarithm-logarithm graphs in Figures 5, 6 and 7.

Table 7 shows a comparison of the results of the standards with their corresponding recommended values. It can be seen that the results of the standards obtained in this study are reasonably close to the recommended values.

Table 8 attempts to summarize the results of this study.

It was also noted that sample BM10 has a lower Tl content than the other leucocratic nepheline syenites.

FIGURE 2: TL WORKING CURVE

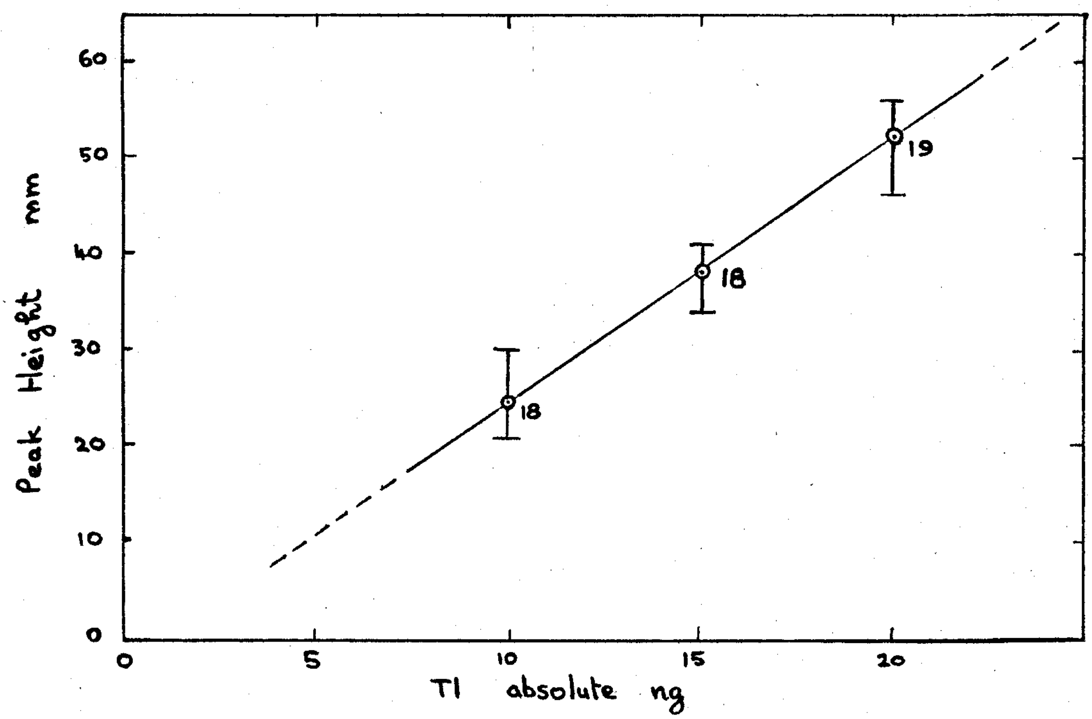


FIGURE 3: RB WORKING CURVE

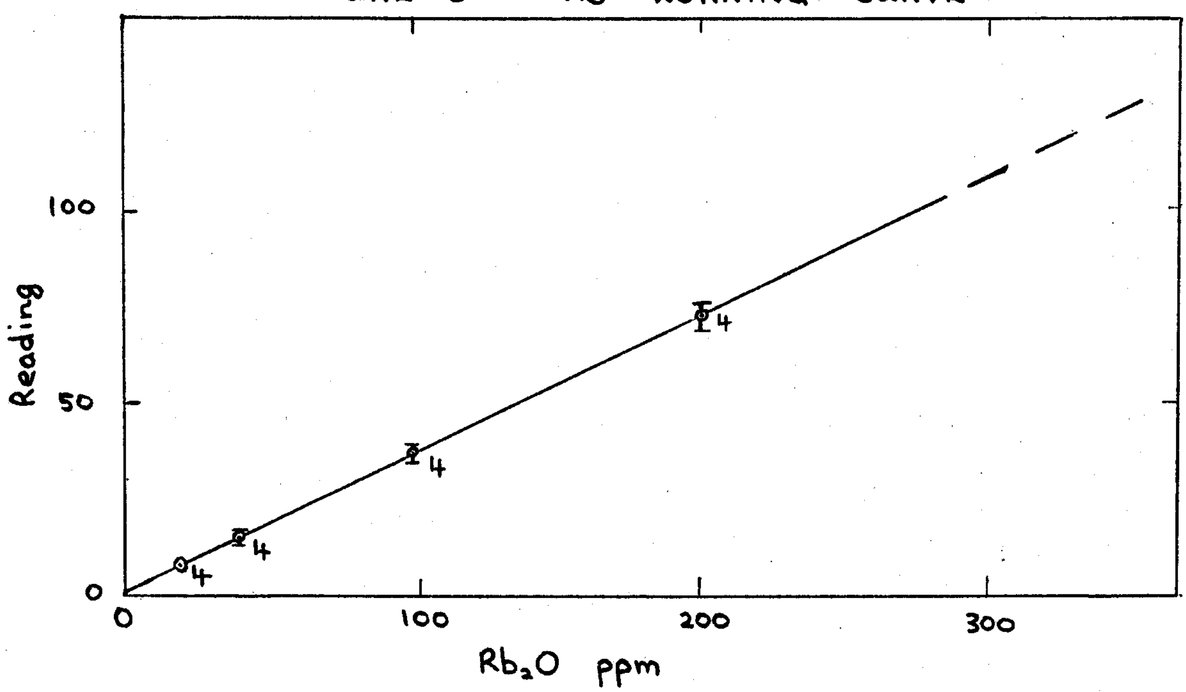


FIGURE 4 : K WORKING CURVE

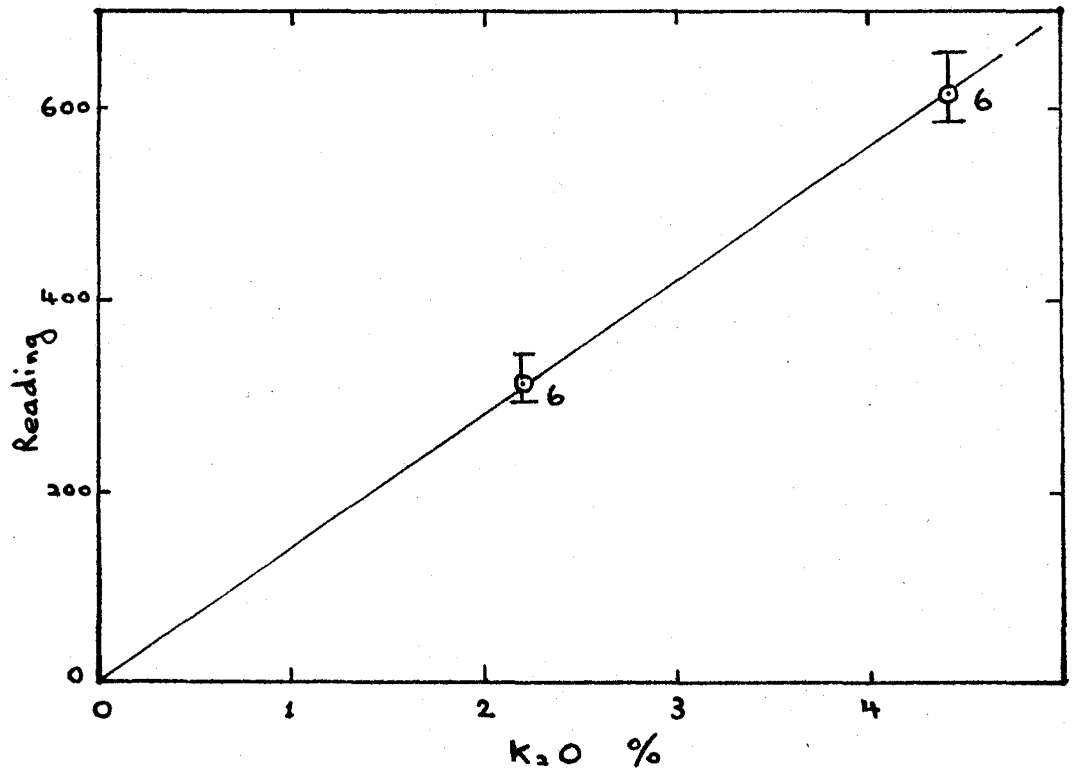


TABLE 6 : RESULTS OF ANALYSES

Locality/ Rock	Sample No.	Tl ppb	Rb ppm	K %	K/Rb	K/Tl (10^{-4})	Rb/Tl
Standard	SY-2	1029	231	3.28	142	3.19	224
		1104	221	3.48	157	3.15	200
Standard	SY-3	956	206	3.20	155	3.35	213
Standard	G-2	529	182	3.30	181	6.24	345
		765	174	3.42	197	4.47	227
BANCROFT :	NS 1	582	91	3.38	371	5.81	152
Nepheline		844	90	3.55	394	4.21	106
gneiss	NS 2	697	72	3.00	417	4.30	103
		710	68	3.12	459	4.39	96
	NS 5	685	113	3.39	300	4.95	165
		817	91	3.26	358	3.99	111
	NS 6	811	72	2.76	383	3.40	89
		730	68	2.86	421	3.92	93
Nepheline	NS 3	1306	119	3.72	313	2.85	91
pegmatite		1049	104	3.73	359	3.56	99
Biotitic	NS 4	849	244	3.21	132	3.78	287
Neph. Gneiss		814	184	3.38	184	4.15	226

TABLE 6 : RESULTS OF ANALYSES (CONT'D)

Locality/ Rock	Sample No.	Tl ppb	Rb ppm	K %	K/Rb	K/Tl (10^{-4})	Rb/Tl
BLUE MOUNTAIN:							
Leucocratic	BM 1	353	57	2.78	488	7.88	160
Nepheline		415	54	2.80	519	6.75	131
Syenite	BM 4	364	59	3.24	549	8.90	162
		493	57	3.19	560	6.47	117
	BM 7	528	73	2.64	362	5.00	138
		624	65	2.68	412	4.30	104
	BM 8	505	80	3.16	395	6.26	158
		682	65	2.99	460	4.38	96
	BM 9	484	72	3.60	500	7.44	149
		589	65	3.51	540	5.96	110
	BM 10	297	64	3.22	503	10.84	217
		280	64	3.04	475	10.86	229
	BM 11	579	87	4.33	498	7.48	150
		701	81	4.36	538	6.22	115
Pink Neph.	BM 3	454	95	2.44	257	5.37	210
Syenite		506	75	2.46	328	4.86	147
	BM 6	634	112	3.08	275	4.86	176
		717	88	2.96	336	4.13	123

TABLE 6 : RESULTS OF ANALYSES (CONT'D)

Locality/ Rock	Sample No.	Tl ppb	Rb ppm	K %	K/Rb	K/Tl (10^{-4})	Rb/Tl
BLUE MOUNTAIN:							
Biotitic	BM 2	1304	316	4.76	151	3.65	242
Neph. Sye.		967	221	4.33	196	4.48	229

FIGURE 5: K-RB TRENDS IN IGNEOUS ROCKS. (After Payne and Shaw 1967)

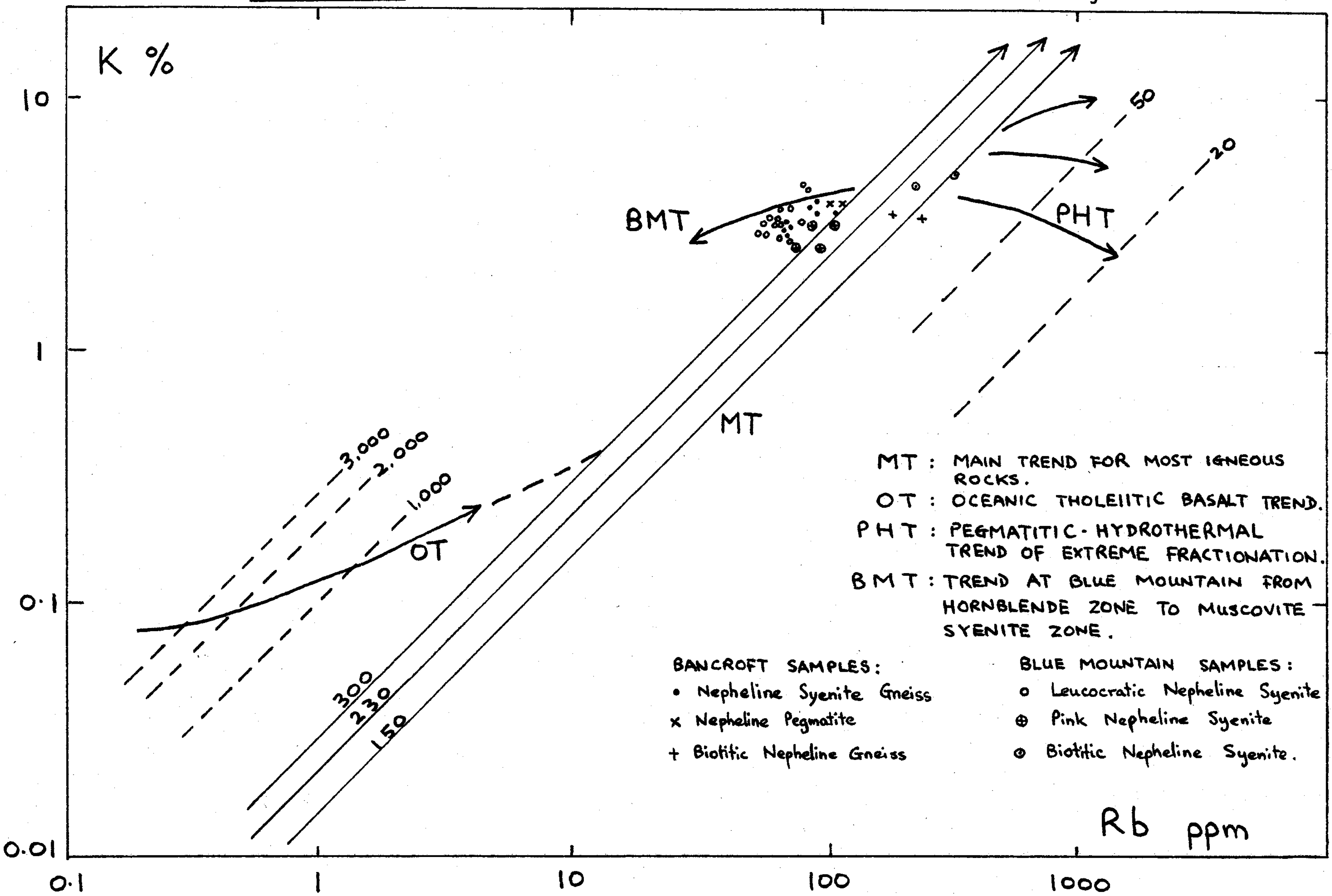


FIGURE 6 : RB-TL SCATTER DIAGRAM (After Shaw et al 1973)

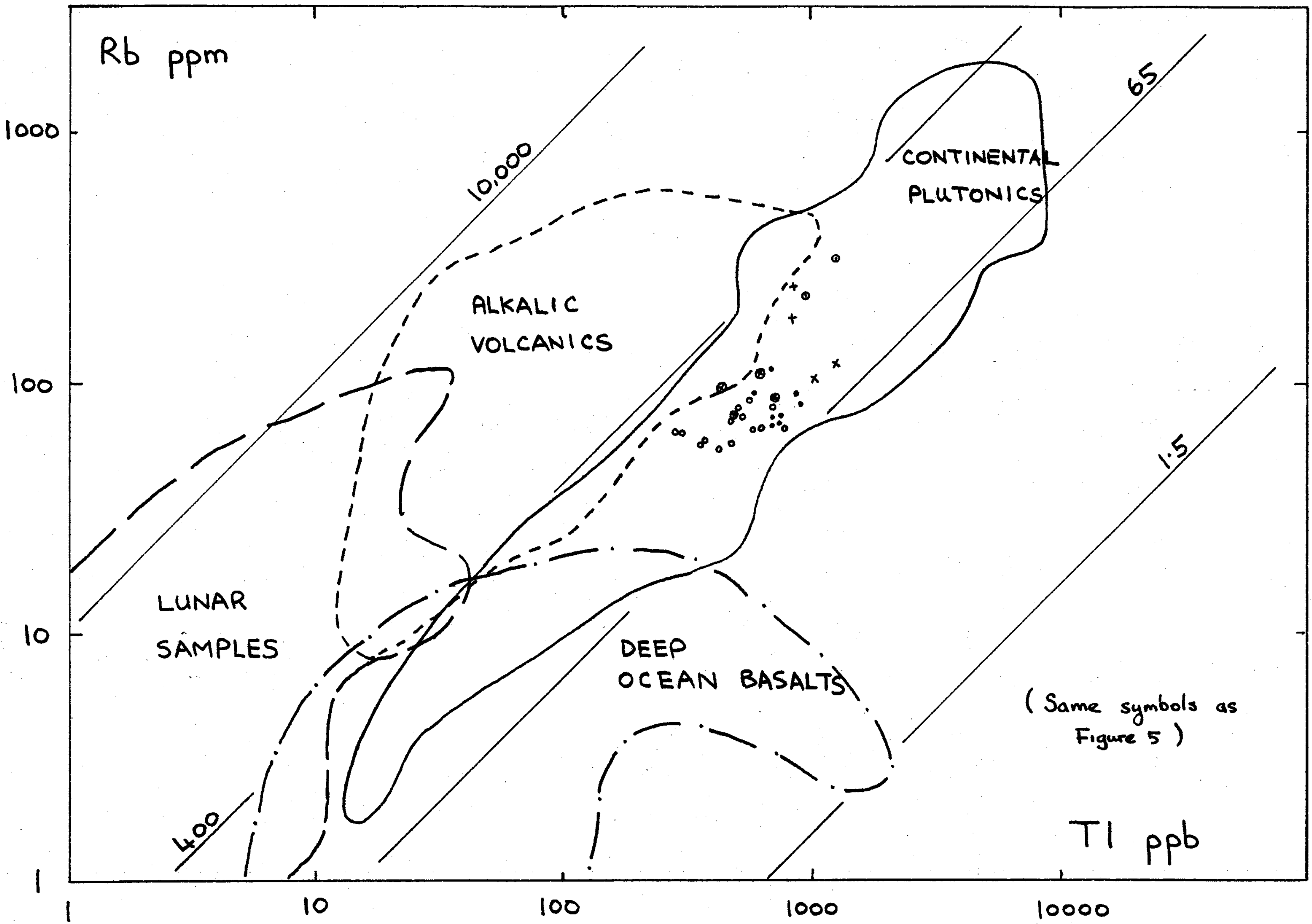


FIGURE 7: K-TL SCATTER DIAGRAM (After Shaw et al 1973)

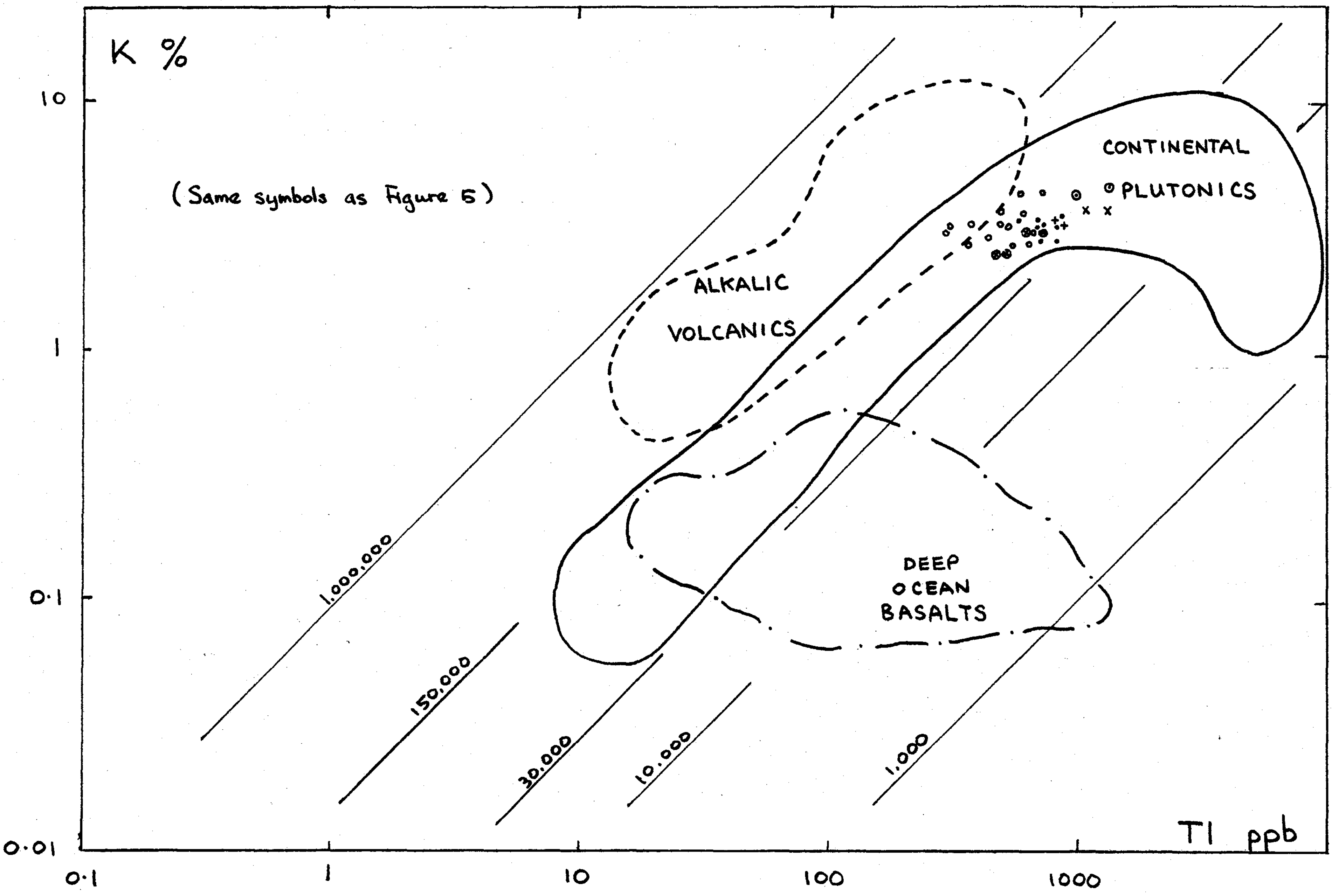


TABLE 7 : TL, RB AND K VALUES FOR STANDARD ROCKS

	SY-2			SY-3			G-2		
	Tl	Rb	K	Tl	Rb	K	Tl	Rb	K
	ppb	ppm	%	ppb	ppm	%	ppb	ppm	%
Flanagan (1973)							1000	168	3.74
Previous estimates by J.R. Muysson and the author	1150-1680	246	3.46-3.74	1240-1500	225	3.30-3.47	647-1200	183-193	
This study	1029-1104	221-231	3.28-3.48	956	206	3.20	529-765	174-182	3.30-3.42

TABLE 8 : SUMMARY OF RESULTS

Rocks	No. averaged	Tl ppb	Rb ppm	K %	K/Rb	K/Tl (10^{-4})	Rb/Tl
BANCROFT:							
Nepheline Gneiss	8	735	83	3.17	388	4.37	114
Nepheline Pegmatite	2	1178	112	3.73	336	3.21	95
Biot. Neph. Gneiss	2	832	214	3.30	158	3.97	257
BLUE MOUNTAIN :							
Leucocratic Neph. Sye.	14	492	67	3.25	486	6.61	136
Pink Nepheline Syenite	4	578	93	2.74	299	4.81	164
Biotitic Neph. Syenite	2	1135	269	4.55	169	4.07	236
REGIONAL AVERAGES :							
BANCROFT	12	825	110	3.28	298	4.11	135
BLUE MOUNTAIN	20	574	93	3.28	353	5.71	162

DISCUSSION

The Tl contents in this study range from 582 ppb to 1306 ppb in Bancroft, averaging 825 ppb; and from 280 ppb to 1304 ppb in Blue Mountain, averaging 574 ppb. These values are comparable to the Tl contents of nepheline syenites in various localities as shown in Table 9. The Tl contents in this study indicate that Tl seems to concentrate in the pegmatitic and biotitic rocks. This observation can be attributed by both the high volatility and the larger ionic size of Tl (than that of K). During fractional crystallization of the intruding nepheline syenite magma, the high volatility enables Tl to concentrate in the later phase of magmatic crystallization as well as to migrate from the central part of the intrusive body to the endocontact zones. Thus Tl tends to accumulate more in the pegmatite than in the leucocratic nepheline syenites outcropping in the central part of the intrusion. The larger ionic size of Tl^+ (1.44 Å) over K^+ (1.33 Å) enables the substitution of Tl for K in the sheet-like biotite. As a result, the biotitic nepheline syenites will expect more Tl. This explains the higher Tl content of BM2 over the other Blue Mountain samples as well as that of NS4 over the other nepheline gneisses in Bancroft.

The Rb contents seem to follow the same trend of Tl because the two have approximately equal ionic radii (1.45 Å for Rb^+). As a result of the accumulation of the larger ions towards the end of the crystallization process, Rb tends to accumulate in the biotitic

TABLE 9 : TL CONTENT OF NEPHELINE SYENITE IN VARIOUS LOCALITIES

Locality	Tl ppb		Reference
	Range	Mean	
Lovozero Massif, USSR	800-1400	1180	Gerasimovskii et al 1968
Mt. Sandyk Massif, USSR	1500-4400	2900	Zlobin and Lebedev 1960
Methuen twp., Ontario		2200	Shaw 1952
Vishnevyye Gory, Ural		600	Voskresenskaya 1961
Keivy, Kola Peninsula		200	Voskresenskaya 1961
Yenisei Range, USSR		1200	Voskresenskaya 1961
Central Kazakhstan, USSR		2700	Voskresenskaya 1961
Pareisis Complex, S.W. Africa		590	Brooks & Ahrens 1961
Bancroft, Ontario	582-1306	824	This study
Blue Mountain, Ontario	280-1304	550	This study

and pegmatitic rocks (refer Table 8). In this study, it is shown that the Bancroft gneisses have higher Tl and Rb contents than the Blue Mountain nepheline syenites. This may be due to metamorphic effect; the nepheline syenite gneisses in Bancroft are more severely metamorphosed and contain a larger amount of the metamorphic minerals such as micas and amphiboles which can accommodate more Tl^+ and Rb^+ in their loosely-packed crystal lattices, hence higher Tl and Rb contents may be expected. However, this proposal requires further investigation and more data for support.

Table 10 compares the Rb contents and the K/Rb ratios determined in this study with those in various localities. It can be seen that the values are comparable except for the biotitic rocks which have very high Rb and very low K/Rb ratios.

The K contents of nepheline syenites in this study are also compared with those determined elsewhere in Table 11.

K-Rb-Tl Relations

It has been shown that the geochemistry of K, Rb and Tl are similar due to their similarities in ionic radii. Generally, the K/Rb and Rb/Tl ratios remain fairly constant during a range of geological processes. However, deviations from this generalisation do occur and have been demonstrated (for example, Erlank 1968, Voskresenskaya 1964), especially in rocks formed in the later stages of magmatic differentiation or by metasomatism.

In this study, the K/Rb ratios of the nepheline syenites are

TABLE 10 : RB CONTENT AND K/RB RATIO OF NEPHELINE SYENITE IN VARIOUS LOCALITIES

Locality	Rb ppm	K/Rb	Reference
Lovozero Massif, USSR	130	287	Gerasimovskii 1966
Stjernøy, Norway	115	579	Heier 1964
Blue Mountain, Ontario	44	795	Heier 1965
	70	560	Heier 1965
	70	737	Heier 1965
	85	490	Payne & Shaw 1967
Blue Mountain, Ontario			
Nepheline Syenite	67	486	This study
Pink Neph. Syenite	93	299	This study
Biotitic Neph. Sye.	269	169	This study
Bancroft, Ontario			
Nepheline Gneiss	83	388	This study
Nepheline Pegmatite	112	336	This study
Biotitic Neph. Gneiss	214	158	This study

TABLE 11 : AVERAGE K CONTENT OF NEPHELINE SYENITE IN VARIOUS LOCALITIES

Locality	K %	Reference
Nosy Kombe, Madagasca	4.53	Daly 1933
Average rock	4.59	Johansen 1949
Average rock	4.43	Nockolds 1954
Lovozero Massif, USSR	4.79	Gerasimovskii 1963
	5.21	Gerasimovskii 1963
	4.28	Gerasimovskii 1963
	4.08	Gerasimovskii 1963
Ilimansuk Massif, USSR	2.42	Ussings 1911
Khibiny Massif, USSR	5.23	Vlasov et al 1959
Vishnevyye Gory Massif, USSR	4.98	Vlasov et al 1959
Blue Mountain, Ontario	4.16	Payne & Shaw 1967
	3.28	This study
Bancroft, Ontario,	3.28	This study

slightly higher than the average range for most terrestrial rocks (160 to 300 as suggested by Ahrens et al 1952), except the biotitic nepheline rocks which have low K/Rb ratios and high Rb contents. This accumulation of Rb may be due to the crystallization and separation of biotite which accommodates more Rb than K, thus causing an impoverishment in Rb in the magmatic rocks, which will then have high K/Rb, while the biotitic rocks, such as the biotitic nepheline gneiss in Bancroft (NS4) and the biotitic nepheline syenite in Blue Mountain (BM2), will have low K/Rb ratios. Another theory of the accumulation of Rb is the enrichment of Rb, which has a larger ionic radius than K, in the low temperature potassic minerals and in the residual fluid magma, both of which represent the later differentiation stage in fractional crystallization. As a result, the pegmatitic nepheline rocks, which represent the fluid magma, also have high Rb contents and low K/Rb ratios. These two theories can also explain the unusual trend of the Blue Mountain nepheline syenite noted by Payne and Shaw (1967) and in this study (Figure 5). The Blue Mountain trend is from low K/Rb in the hornblende zone to high K/Rb ratios in the muscovite-syenite zone.

Due to the accumulation of Tl at the later stage of magmatic differentiation by virtue of its high volatility as discussed before, the Rb/Tl and K/Tl ratios also decrease towards the end of the magmatic differentiation. However, it should be noted that these ratios may not remain constant, probably as a result of autometasomatism (that is, deuteric alteration) of the originally magmatic nepheline syenite by the residual melt. During the autometasomatism of the magmatic rocks, part of the Tl originally fixed in the minerals may be displaced into the melt due to its high volatility, causing a Tl impoverishment in the solid phase, whereas the Rb content increases with the increasing degree of autometasomatism by the residual melt, replacing both K, which has a smaller ionic radius, and Tl, which is more volatile. As a result, the K/Rb, Rb/Tl and K/Tl ratios may show variations. These effects are shown in Table 8.

Despite the above effects, Shaw et al (1973) were able to construct scatter diagrams for the K-Tl and Rb-Tl relationships. They also noted that igneous rocks of different origins occupied different fields in the logarithmic diagrams. Following their observations, it seems that the nepheline syenites in this study are continental plutonic in origin (Figures 6 and 7).

CONCLUSION

Nepheline syenite samples were collected from the Bancroft and Blue Mountain areas, Ontario, Canada, and were analysed for K, Rb and Tl contents by atomic absorption spectrophotometry. The results for these elements and the corresponding K/Rb, K/Tl and Rb/Tl ratios were compared with those of nepheline syenites in various localities, and were found to be similar.

The Tl, Rb, K contents and the K/Rb, K/Tl and Rb/Tl ratios in this study were determined to be 825 ppb, 110 ppm, 3.28%, 298, 4.11×10^4 and 135 respectively for the Bancroft nepheline gneisses; and 574 ppb, 93 ppm, 3.28%, 353, 5.71×10^4 and 162 respectively for the Blue Mountain nepheline syenites. From these data, the nepheline syenite rocks in this study were probably originated as continental plutonics.

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