THALLIUM AND RELATED ELEMENTS
IN
A METAMORPHIC ROCK

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A METAMORPHIC ROCK

BY

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ABSTRACT

A scapolite-hornblende-biotite schist from the Grenville province of the Canadian Shield has been analysed for Tl by an atomic absorption technique with a high sensitivity. K, Rb and some major oxides were determined by wet chemistry. Tl, K/Rb, K/Tl and Tl/Rb were compared to several other rocks and for this report were found to be 432ppb, 429, 4.85×10^{3} and 88.4×10^{-3} respectively. These values are similar to those quoted for other rocks.

ACKNOWLEDGEMENTS

The authoress is greatly indebted to Dr. D. M. Shaw for his proposal of this project and for his thoughtful guidance and great patience throughout the study.

The assistance of M. Fratta and J. R. Muysson is greatly appreciated.

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INTRODUCTION

Thallium was discovered in 1861 by W. Crookes who thought it was similar to sulphur. Later study by A. Lamy showed the element to be a metal whose compounds resembled both lead and alkali metals. Thallium is now grouped with boron, aluminum, gallium and indium in the periodic table.

The distribution of thallium in metamorphic rocks has had little study. The purpose of this problem is to determine the distribution of thallium among the minerals of a metemorphic rock from the Grenville province of the Camadian Shield.

Due to the small amounts of thallium expected in some of the minerals in the sample, the aspiration technique of atomic absorption spectrophotometry would not give the required sensitivity. Prior to the start of this project, M. Fratta developed a highly sensitive technique using an organic extracting solvent and a tantalum boat in the atomic absorption apparatus. This method was chosen for the project.

AREA OF STUDY

The sample, field number 630628-1 SCA was collected from Lot 26, Concession VI in Chandos Township (Fig. 1, enclosed) during the summer of 1963 by D. M. Shaw.

Chandos township lies within the Hastings Basin structural subdivision of the Haliburton-Bancroft area which forms part of the Grenville province of the pre-Cambrian shield in Canada. The area is underlain by marble, gneiss, amphibolite, schist, arkose and basic volcanics of the Mayo group. These metasediments and metavolcanics have been intruded by gabbro, diorite, syenite and granite. The principal intrusive body in the area is the Loon Lake Pluton--a granite-syenite body located in southern Chandos township.

The area was highly folded during the Grenville orogeny. The main fold axis trends NE-SW, parallel to regional fold trends. Cross-folding has developed along axes trending NW-SE.

Other studies on the rocks in this area are concerned with rare earth elements and are being carried out by J. Dostal.

SAMPLE PREPARATION

The crushing and mineral separation method used for this analysis is summarized in Fig. 2 (enclosed). A Bico pulverizer, a Braun chipmunk, Shatterbox, metal seives, and a Frantz Isodynamic Separator were used. The chemicals were all reagent grade.

Approximately one gram each of the 100-200 mesh rock and mineral powders and a sample piece of biotite from a pegmatite and a sample hornblende (both crushed by agate mortar and pestle to less than 100 mesh) were dissolved with 8 ml. aqua regia (prepared just before dissolution) and 16 ml. HF (hydrofluoric acid) in teflon crucibles. The crucibles and dissolved powder were then set on a sandbath with a temperature of approximately 150° C. The powders were allowed to digest fpr 30 minutes; the lids were then removed and the liquid evaporated to dryness overnight, leaving a brittle white cake in the bottom of the crucible. The cake was cooled and 2 ml. HBr were added with a few ml. of water and allowed to digest for 30 minutes. The dark brown solution was quantitatively transferred to a beaker and once more placed in a sandbath. A 4-8 ml. aliquot of a solution of boric acid and 2-3 drops bromine were added and the solution heated. This step facilitated the dissolution of the sample cake. After cooling, again, the solution was quantitatively transferred to a 60 ml. separation funnel with teflon stopcock and plug. Water was added to dilute the HBr to between 0.25 and 0.5N for selective extraction. Approximately 10 ml. isopropyl ether (reagent grade), previously saturated with 0.5N HBr, was added to the separation funnel. The mixture was agitated for 2 minutes and allowed to separate for 20 minutes. The aqueous solution was let out the bottom of the funnel into a labelled container, care being taken not to run out any organic solvent, and the ether was poured out the top of the funnel into labelled glass sample vials. The vials were placed on a warm sandbath (80-100°C) and the ether evaporated. The aqueous solution was returned to the separation fummel and a second extraction was carried out with exactly 10 ml. isopropyl ether. The same procedure was followed for separating the aqueous solution and the ether. The organic extract for each sample was then placed in the corresponding vial used for the first extraction.

Standard solutions were prepared in a similar way. A depleted rock solution was prepared by extracting three times from a solution prepared as above from a mixture of rocks. To 40 ml. amounts of the solution, 2, 4, and 8 ml. aliquots of 100 ppb Tl solution were added. A stock solution of 100 ppm Tl had been prepared from solid Tl_2O_3. Two to three drops of liquid bromine were also added and the solution heated. After cooling, the solution was quantitatively transferred to the separation funnels and extraction was carried out as for the rock and mineral samples. The resulting solutions of 10 ml. isopropyl ether contained 200ng, 400ng, and 800ng of thallium.

SAMPLE ANALYSIS

Samples and standard solutions were analysed on a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. (Table 1) The aspiration technique was not used. Instead, the sample was introduced into the atomic absorption flame after evaporation of a known volume of the ether extract in a tantalum boat near the flame. The boat was supported on a stand not attacked to the base of the atomic absorption unit, but to the table, in order to cut down movement when the boat was moved into the flame. Peaks were recorded on a chart recorder. Atomic absorption analyses were done over a two day period in order to cut down on any aging of the solutions.

Chemical analyses for some major oxides as well as Li, Rb, Sr, Ba, and SO_3 were carried out by J. Muysson on the whole rock and some mineral samples.

Petrographis analyses were done on four randomly selected thin sections taken from the sample pieces.

TABLE 1. ANALYSIS CONDITIONS

Perkin-Elmer	Atomic Absorption Spectrophotometer Model 303	
	Range	UV
	Slit	4
	Gain	6
	Wavelength	277
	Lamp	Perkin-Elmer Intensitron Lamp: Element Tl
	Absorption	0
Recorder	Perkin-Elmer Model 56 Chart Recorder	
	Scale Expansion	1
	mV Range	10
Flame	Acetylene-air	

RESULTS

The atomic absorption results are summarized in Table 2. For the whole rock powder, all analyses are shown as well as the average. Values for the other samples, including range and mid-range, are given.

BCR-1

Special attention is brought to the Tl determinations made on BCR-1. The value is higher than most recorded values. (Table 3) During the preparation of the solution of ether and Tl, a step involving drying of the ether was done. If the Tl compound dried on the bottom and sides of the vial did not completely redissolve, this would affect the results. However, unless some complexing with other ions in the solvent occured, this would lower the results. Another possibility is the inclusion of a drop of aqueous solution in the organic extract which would raise the value. As only one solution was made, the reason for this hight value is difficult to determine. Owing to the high value of BCR-1 in this report and the wide range of values, the precision would be difficult to determine. Using the value of 280 ppb the precision is on the order of 30%.

Working curves for the calculation of Tl in the samples were constructed from the standard solutions used. An enrichment of the solutions prepared on the first day appeared on the second day. As a result, two working curves were drawn, the slopes were the same.

TABLE 2 ATOMIC ABSORPTION RESULTS

Sample	Sample wt.	No. of Analyses	Range (ppb/gm)	Tl Content (ppb/gm)	Midrange (ppb/gm)
630628-1SCA	1.15430	12	235-580	277	
				277	
				345	
				235	
				345	
				535	
				535	
				535	
				390	
				580	
				560	
				560	
				av. 430	427
BCR-1	1.02859	10	195-555	414	375
Whole rock lt. fr.	1.09021	5	155-320	220	235
K-feldspar	0.99807	8	600-850	785	725
Plag. scap	0.98709	6	170-260	210	215
Biotite	0.99435	6	1900-2300	2050	2100
Hbd-tourm	0.98844	5	210-280	250	245

TABLE 3 Tl VALUES FOR BCR-1

Reference	Value (ppb)
Flanagan (1960)	360
Ganapathy et.al. (1970)	274
	283
Laul, Pelly, Lipschutz (1970a)	330
(1970b)	290
Marowsky & Wedepohl (1971)	350
de Albuquerque et. al. (in press)	267
Laul et. al. (1972)	258
	280
this report	375

Calculation of the Tl content of solutions prepared on the first day, and run on the second was carried out using the second curve. All other calculations were made using the first curve. (Fig 3a,3b)

Petrographic analyses were made by point counting on four randomly chosed thin sections. The rock is generally fine-medium grained, and is irregularly schistose and porphyroblastic. The porphyroblasts are plagioclase, scapolite, amphibole and K-feldspar. The matrix is biotite, amphibole, plagioclase, K-felspar, quartz with accessory tourmaline, apatite and opaque minerals. Observation of the ground powder revealed some sulphide in the opaque fraction and sphene and zircon as heavy, less magnetic minerals. Plagioclase was determined to be An_{50} by the Michel-Levy method. Petrographic results are summarized in Table 4. The rock type is "porphyroblastic hornblende-microcline biotite-quartz schist".

Chemical analyses are shown in Table 5. Thallium distribution is calculated in Table 6. Table 7 summarizes the results determined by the various analysis methods.

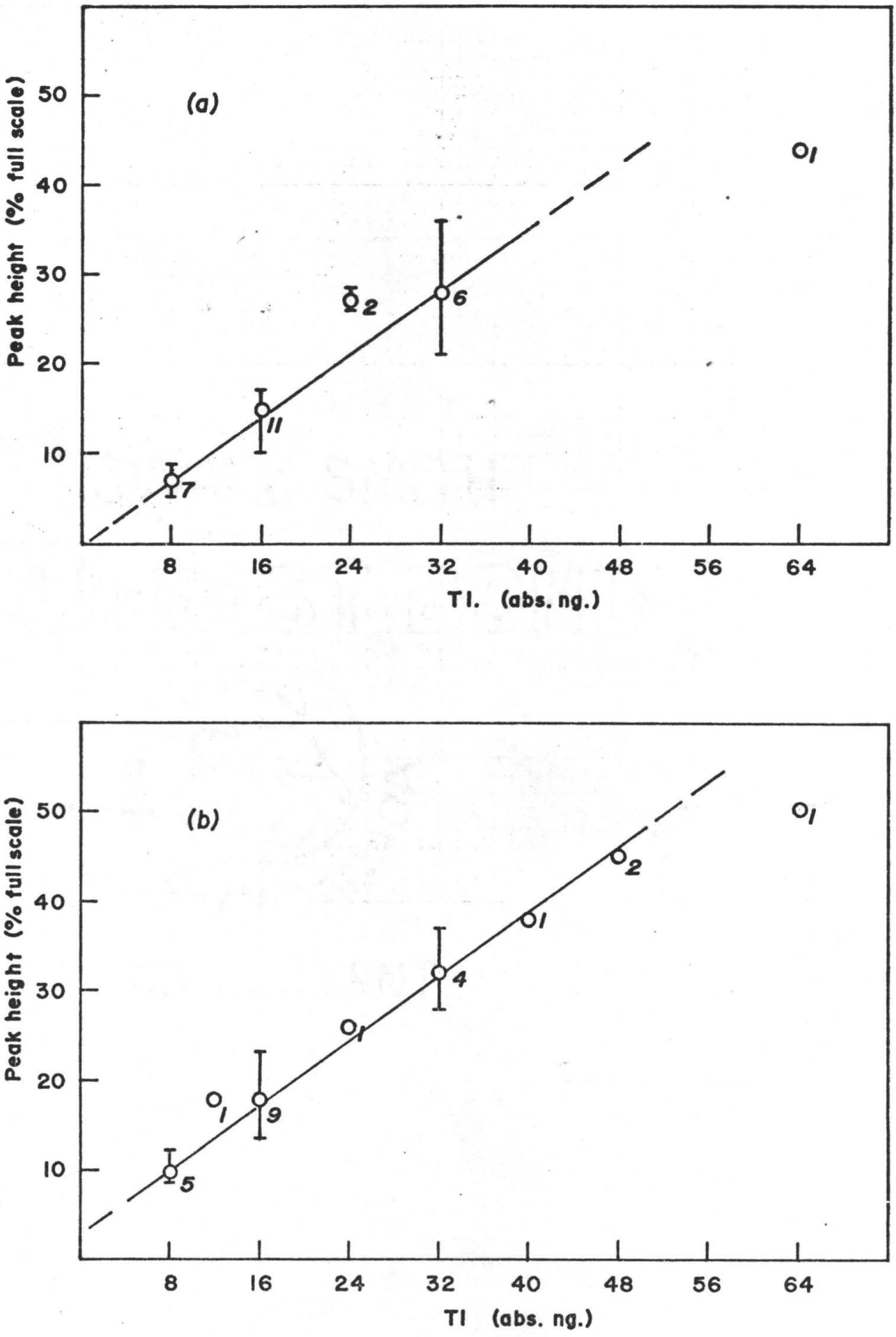


FIGURE 3 WORKING CURVES - (a) first day, (b) second day. Vertical bars represent the range; subscripts, the number of values used to calculate the average.

TABLE 4 PETROGRAPHIC RESULTS

Thin Section	Plag.	K-spar	Qtz	Scap	Biot	Amph	Apat	Tourm	Opaq.
630628-1									
-HAM	17.4	11.9	19.5	8.3	31.6	9.9	1.1	-	0.4
-MAH	2.3	65.7	8.8	-	18.3	2.6	-	2.3	-
-AHM	14.1	52.9	13.2	6.3	14.0	-	-	-	-
-2	36.3	11.1	8.8	8.3	24.8	11.4	-	-	-
TOTAL	70.1	141.6	50.3	22.9	88.7	23.9	1.1	2.3	0.4
AVERAGE	17.5	35.4	12.5	5.7	22.2	6.0	0.3	0.6	0.1

MINERAL	Whole rock light fraction	K-spar	Plagioclase + scapolite	Biotite	Hornblende + Tourmaline
Modal %	71.1	35.4	23.2	22.2	6.6

TABLE 5 CHEMICAL ANALYSES*

	Whole rock	Biotite	Hornblende +tourm.	K-feldspar
SiO_2	60.94	-	-	-
TiO_2	0,65	-	-	-
Al_2O_3	14.92	-	-	-
Fe_2O_3	0.99	-	-	-
FeO	5.14	-	-	-
MnO	0.034	-	-	-
CaO	5.09	-	-	-
Mgo	4.18	-	-	-
Na_2O	1.36	-	-	-
K_2O	3.82	9.28	1.89	14.39
P_2O_5	0.21	-	-	-
H_2O^+	1.16	-	-	-
H_2O^-	0.11	-	-	-
CO_2	0.22	-	-	-
Li_2O	0.0211	0.0695	0.0160	0.0013
Rb_2O	0.0089	0.0332	0.0016	0.0146
SrO	0.0237	0.0022	0.0039	0.0701
BaO	0.040	0.040	0.006	0.350
SO_3	0.60	-	-	-
F	0.12	-	-	-
Cl	0.25	-	-	-

*Analyst: J. R. Muysson, McMaster University.

TABLE 6 Tl DISTRIBUTION IN THE ROCK

Mineral	Tl content ppb	Modal vol%	Density gm/vol	Modal wt%	Tl content in whole rock ppb
whole rock		100			432
light fr.	220	71.1	2.6	44	96.8
k-spar	788	35.4	2.6	22	173.4
plag-scap	211	23.2	2.6	14	29.5
biotite	2062	22.2	3.0	16	329.9
hbd-tourm	251	6.6	3.2	5	12.6

TABLE 7 SUMMARY OF RESULTS

	Whole rock	Biotite	Hornblende +tourmaline	K-spar
Modal vol%	100	22.2	6.6	35.4
wt%	100	16	5	22
K %	3.82	9.28	1.89	14.39
Rb ppm	89	332	16	146
Tl ppb	432	2062	251	788
K/Rb	429	280	1181	986
Tl/Rb (10^3)	4.85	6.21	15.7	5.39
K/Tl (10^{-3})	88.4	44.6	75.5	184

DISCUSSION

For the rocks used in this study, the Tl concentrations range from 251-2062 ppb. Table 8 lists the Tl content of several other types of rocks. The authoress' results are similar to those for gneissic rocks, schist, amphibolite, and microcline. From Table 6, it can be seen the "sum of the parts is greater than the whole": Whole rock light fraction + biotite + hornblende and tourmaline ≐ 439.3 ppb. K-feldspar + plagioclase and scapolite + biotite + hornblende and tourmaline = 545.4 ppb. The whole rock light fraction as well as the other minerals are mineral separates, which may not be equivalent to the modal percent as calculated by the point-count method. The modal percentages shown in Table 4 show that the rock is very inhomogeneous, so the calculation of modal weight percent may not mean much. Differences in ease of crushing the minerals may tend to concentrate high Tl minerals in the 100-200 mesh fraction which would raise the value of the sum of the parts.

The high value obtained for BCR-1 in this study is noteworthy.

Very few data on Tl ratios with K or Rb are known for metamorphic rocks. Ratios for igneous rocks would not be expected to be similar as Tl is thought to be highly mobile during metamorphism. The values obtained in this study do fall within the ranges quoted.

TABLE 8 Tl CONTENTS OF VARIOUS ROCKS

Rock	Method of analysis	Value	Reference
K-fspar (granodiorite gneiss-amph. facies)	Spectroscopy	range 0.6-0.9ppm average 0.8ppm	1
K-fspar (monzonitic gneiss)	"	range 0.9-1.0ppm average 1.0ppm	1
m/m schist	chemical	average 2.0ppm	2
biot-hbd schist	spectroscopy	average 0.35ppm	3a
amphibolite	"	average 0.4ppm	3b
garnet gneiss	"	average 0.37ppm	3c
hbd-gneiss	"	average 1.1ppm	3d
peg. microcline		range 1-70ppm	4
peg. biotite		average 37ppm	4
BCR-1		range 258-360ppb	5
crustal abundance		1.3ppm	3
most igneous rocks		K/Rb range - average 230 $Tl/Rb \times 10^3$ range 3.3-159 average 5.6 $K/Tl \times 10^{-3}$ range 13-149 average 41.4	6

References for TABLE 8.

1. Heier, K. S. (1960) Langoy, Norway
2. Slepnev, Y.S. (1961) Sayan Mts. USSR
3. Shaw, D. M. (1952) a.Danbury Quadrangle, N. Y.
   b.Impilahti, KFSSR
   c.N. Isatog, Greenland
   d.S. Stronfjord, Greenland
4. Riber, J. I. unpublished Masters thesis, Rice University, Texas
5. low value-Laul et al (1972)
   high value-Flanagan (1969)
6. de Albuquerque, Muysson and Shaw (in press) Chem. Geol.

The most dominant feature of Tl geochemistry is the resemblance to potassium and rubidium. Because of the similarities in ionic size (Table 9), it is thought that Tl and Rb follow one another closely. In the results of this project, this can be seen by the relatively constant value of Tl/Rb (approximately 5.3×10^{-3}) with the exception of hornblende.

TABLE 9 IONIC SIZE

Element	Ionic Size (A)
k^{+}	1.33
Tl^{+}	1.49
Rb^{+}	1.49

In plagioclase, Tl will replace wither Na or K, but not Ca due to size and charge relationships. In amphiboles, replacement is flexible with regards to valency and radius. Amphiboles have a defect structure where Tl^{+3} can replace Ca^{+2}, but Tl^{+} probably replaces K^{+}. The micas have the greatest flexibility of all silicates for accomodating trace elements. Tl^{+} replaces K^{+} during enrichment in late stage micas. Biotites show a wide range of values due to environmental conditions.

Distribution coefficients for biotite, hornblende and k-feldspar were determined and are listed in Table 10.

TABLE 10 DISTRIBUTION COEFFICIENTS

	D^{bi-hb}	D^{hb-kf}	D^{kf-bi}
K	4.9	0.13	1.55
Rb	21	0.11	0.44
Tl	8.2	0.32	0.38

D^{a-b} = concentration in a/concentration in b

In looking at the coefficients for K, the element preferentially goes into K-feldspar, then biotite, then hornblende. From the chemical similarities, Rb and Tl would be expected to follow the same pattern. However, both Rb and Tl preferentially go into biotite, then K-feldspar and hornblende to a much smaller degree. The structure of biotite is quite flexible; both Rb and Tl have a slightly larger ionic size than K and would therefore probable fit into the biotite structure more easily.

Concrete conclusions are difficult to present due to the relatively small amount of specific reference values and the few analyses done on the sample used for this report. However, the method devised for the Tl determination appears to have good reproducibility as can be seem by the standard solution working curves. A better method could be devised for introducing the sample into the atomic absorption flame, as the peak heights appear to be sensitive to manual speed of introduction. Other rocks from the same area could be analysed for comparison, although due to differences in mineralogy and degree of metamorphism, the results may not be of any value.

SUMMARY

A scapolite-hornblende-biotite schist from the Grenville province of the Canadian Shield has been analysed for Tl, Rb, K, and some major oxides in order to add to the data on thallium in metamorphic rocks. The method used involved thallium extraction by an organic solvent and analysis by atomic absorption spectrophotometry on whole rock and some mineral separates. Major oxides were analysed by wet chemistry. Tl, K/Rb, K/Tl and Tl/Rb were determined and compared to other rocks. The whole rock analyses for the above determinations gave 432 ppb, 429, $4.85 x 10^3$, and $88.4 x 10^{-3}$ respectively. Biotite analyses were found to be 2062 ppb, 280, $6.21 x 10^3$, and $44.6 x 10^{-3}$; hornblende, 251 ppb, 1181, $15.7 x 10^3$, and $75.5 x 10^{-3}$; k-feldspar, 788 ppb, 986, $5.39 x 10^3$ and $184 x 10^{-3}$. These values were compared to other rocks and found to be similar.

REFERENCES

de Albuquerque, C. and Shaw, D. M., (in press) Chapter 81, Handbook of Geochemistry.

Shaw, D. M., 1952, The Geochemistry of Thallium. Geochim. et Cosmochim. Acta, 2, 118-154.

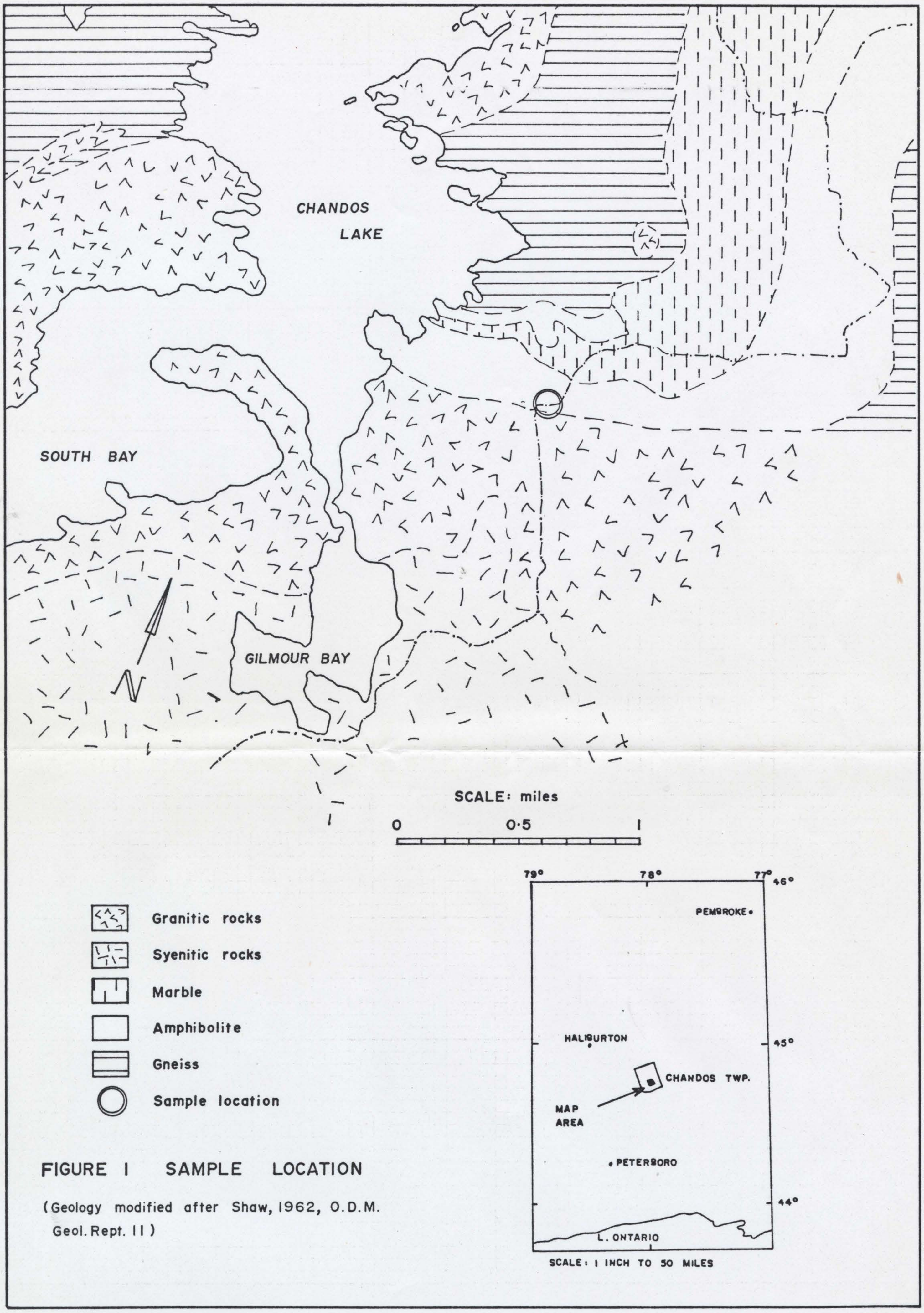
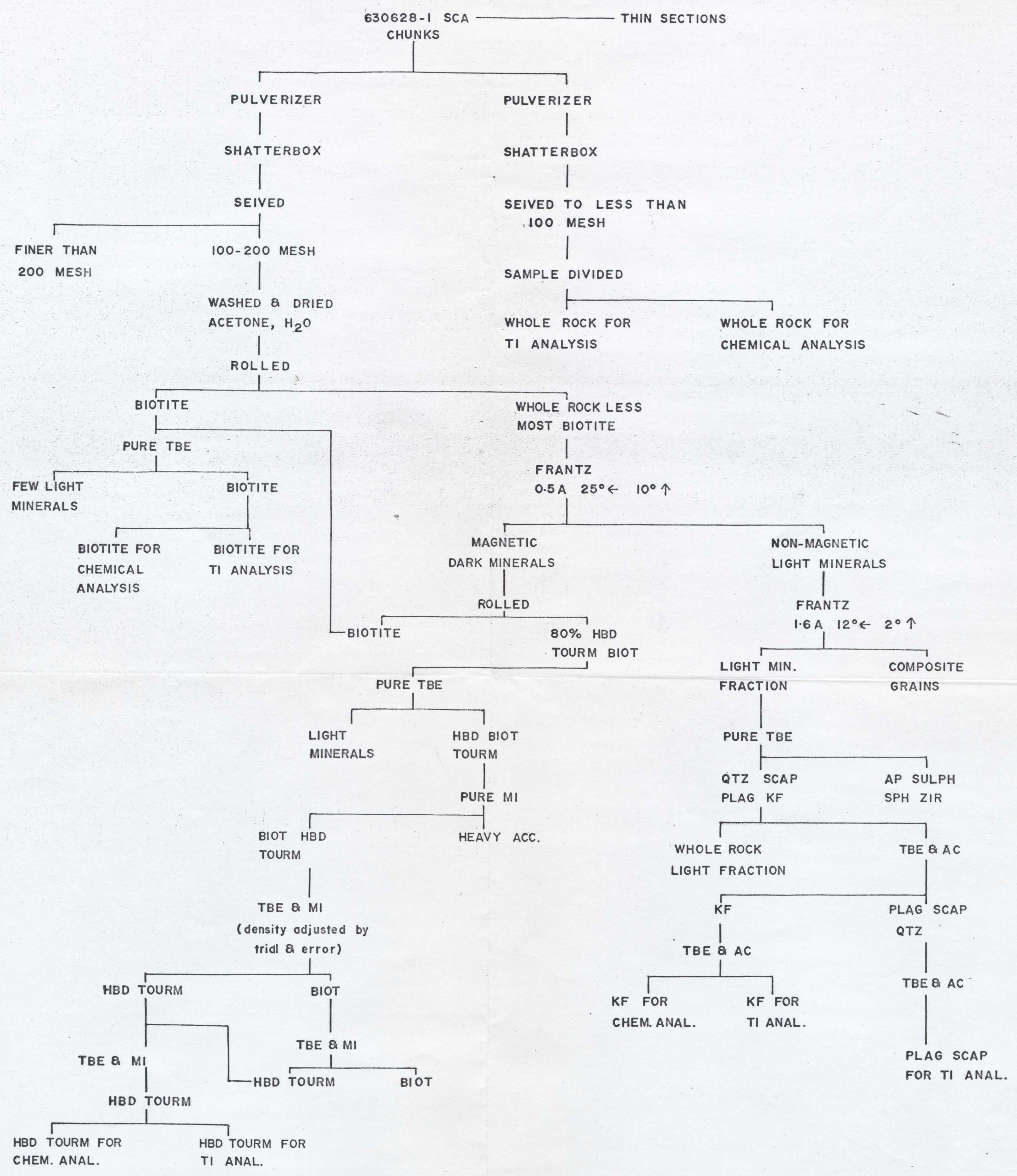


FIGURE 1 SAMPLE LOCATION

(Geology modified after Shaw, 1962, O.D.M.
Geol. Rept. 11)

FIGURE 2 SAMPLE PREPARATION



LEGEND

TBE	TETRABROMOETHANE	KF	K-FELDSPAR	AP	APATITE	FRANTZ	
MI	METHYLENE IODIDE	QTZ	QUARTZ	SULPH	SULPHIDES	x° ↑	side wheel setting
AC	ACETONE	SCAP	SCAPOLITE	SPH	SPHENE	x° ←	back wheel setting
TOURM	TOURMALINE	PLAG	PLAGIOCLASE	ZIR	ZIRCON		
BIOT	BIOTITE	HBD	HORNBLENDE				