GEOCHRONOLOGY AND K/RB RATIOS OF AN ANORTHOSITE NEAR PARRY SOUND, ONTARIO

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A Thesis
Submitted to the Faculty of Arts and Science
in Partial Fulfilment of the Requirements
for the Degree
Bachelor of Science

McMaster University
(April) 1968

ABSTRACT

The primary purpose of this study was to date the last metamorphism of a metanorthosite near Parry Sound, Ontario, by the Rb-Sr method on the mineral phases: biotite, hornblende and plagioclase. Due to problems with the mass spectrometer, the prepared samples could not be run.

K/Rb ratios on biotites and plagioclase give a calculated K/Rb whole rock ratio for the mafic rich bands of about 230, consistent with the main trend of igneous rocks. The plagioclase K/Rb ratio, however, is much higher, and the anorthosite body as a whole may have a much higher K/Rb ratio, consistent with oceanic tholeiites and achondritic meteorites and indicating a possible lower crustal or mantle origin.

ACKNOWLEDGEMENTS

I wish to thank Professor R.H. McNutt, McMaster University, for proposing this study and for his unstinting assistance and constructive criticism given throughout this project. I am also indebted to Mr. R. Mitchell for aid given during my work in the isotope laboratory and to Mr. J. Muyson who patiently directed me through the atomic absorption analyses. Special thanks are due to Professor D. M. Shaw who kindly allowed the use of his summary paper on K/Rb ratios and of its figures although this is not yet published.

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I INTRODUCTION

This study was undertaken to determine the age of the last metamorphism of an anorthosite near Parry Sound, Ontario, by Rb-Sr methods. Biotite and plagioclase were used to give a good spread of Rb/Sr ratios. Whole rock samples, due to the high Sr content of the abundant plagioclase, would have given an inadequate spread. Due to problems with the mass spectrometer the isochron could not be determined after the samples were prepared. K/Rb ratios were determined on biotite and plagioclase in an attempt to determine the origin of the anorthosite magma.

II SAMPLE LOCALITY

General Geology

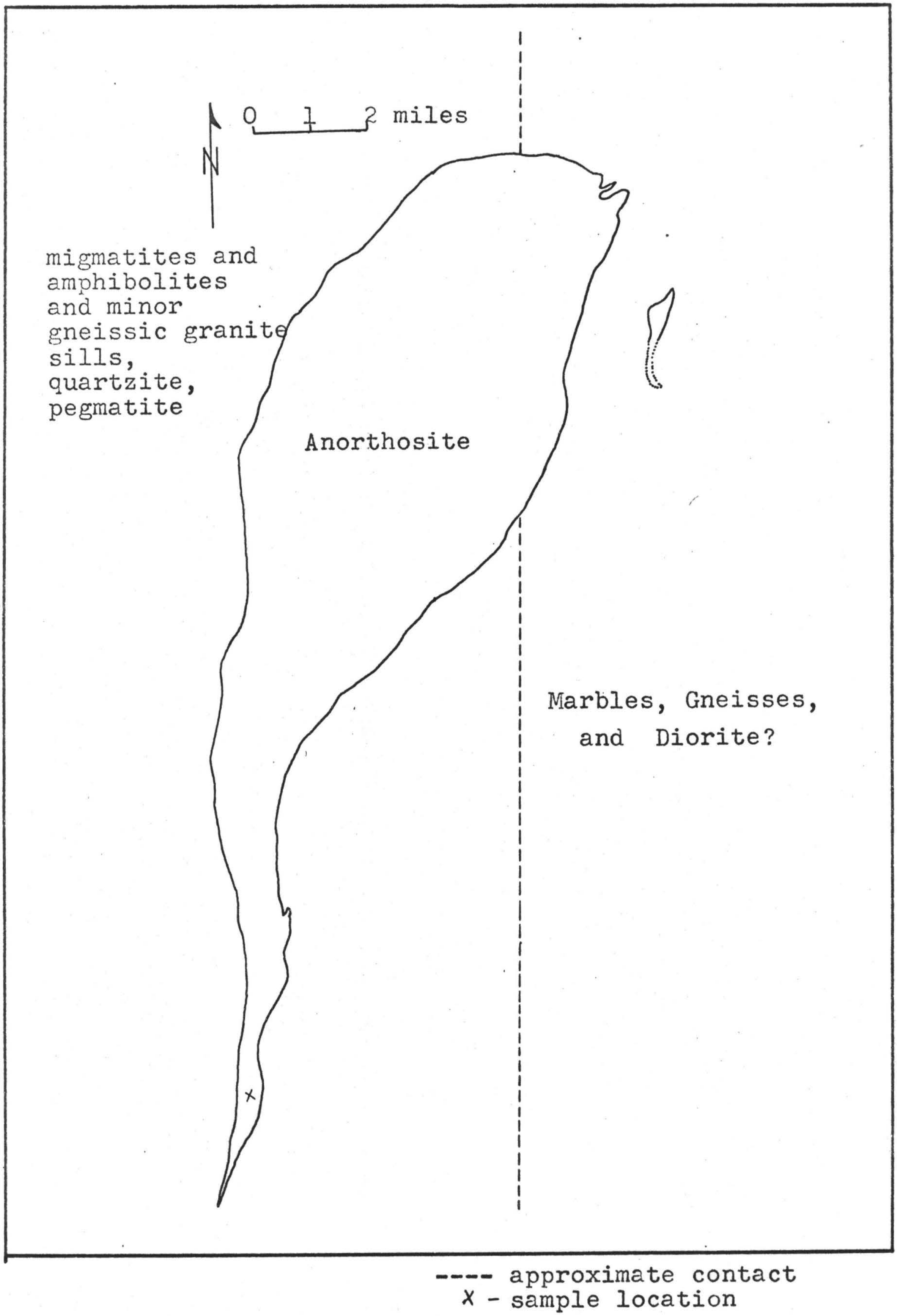
The anorthosite body, as described by Mason (personal communication), lies about ten miles northeast of Parry Sound, Ontario, in the Grenville Province of the Canadian Shield. It is intrusive into a series of metamorphosed igneous and sedimentary rocks of the hornblende granulite or upper amphibolite facies of regional metamorphism. Fig.-1 shows the general geology of the area. The regional strike is approximately north-south, with the country rocks being divided into a migmatite-amphibolite complex with the minor gneissic granite sills, quartzite, and pegmatite in the west; and marbles, quartz-plagioclase-hornblende and pyroxene-hornblende-biotite-plagioclase gneisses and units of badly sheared rock, tentatively identified as diorite, in the east. The regional dip is approximately 65° to the east. Where the anorthosite is sheared, the mafics are concentrated together in bands subparallel to the country rock contact. These bands in the west, dip at about 65° to the east, but in the east are much shallower,dipping only about 20° E.

Sample Collection

Samples F-1 and F-2 were collected from the narrow neck at the southern end of the anorthosite (see Fig.-1) by the writer and sample L2-2 was previously collected by Mr. I. Mason at the same location. Care was taken to see that the samples were all fresh, unweathered rock. The samples were of mafic rich bands and are in no way representative of the outcrop.

Fig.-1

Sample Locations and General Geology



Petrography

Sample F-1

Sample F-1 was collected from a medium grained biotite rich, foliated band. The mode as determined from a 650 point count, on the thin section is:

Plagioclase	76%
Epidote	12%
Quartz	1%
Biotite	10%
Muscovite	2%
Chlorite	trace

Plagioclase occurs as 0.6-1.6 mm interlocking anhedral grains and exhibits twinning in about half the grains according to the albite, carlsbad and pericline laws. Traces of sericitic alteration are found along the cleavage. The Michel-Levy method gives a composition of An_{56}. Rounded inclusions of quartz and other minerals are found.

Biotite occurs as elongated, large (2.0 mm) to small subparallel books and is dominately fresh,showing alteration to chlorite only rarely. It is often intergrown with muscovite which has an identical occurence but both appear to be primary. Some of the large 2 mm muscovite grains contain abundant inclusions of other minerals.

Epidote is concentrated in the biotite rich bands but also occurs throughout the plagioclase rich areas. The minor alteration of biotite to chlorite appears to be concentrated where the biotite is in contact with the epidote.

Quartz,besides forming rounded inclusions in the plagioclase,forms small interstitial grains,but quantitatively is unimportant.

Sample F-2

Sample F-2 was collected from a biotite-hornblende rich band about 50 feet to the south-west of Sample F-1. The mode as determined from a 700 point count, on the thin section is:

Plagioclase	73%
Hornblende	12%
Biotite	8%
Epidote	6%
Quartz	1%
Chlorite	trace

The plagioclase is similar in occurence as in F-1 but has a composition of An_{59}, some of the twins deformed, and some of the grains exhibit strained extinction. The small rounded quartz inclusions are slightly more numerous than in F-1.

Hornblende occurs as irregular grains, often with elongate habit, subparallel to the biotite foliation in mafic rich bands which vary in their proportions of biotite to hornblende, from dominately one to the other. Minor inclusions of quartz are contained in the hornblende which appears to be fresh and primary. The biotite exhibits the same relations as in F-1 and shows very minor alteration to chlorite. Epidote and quartz, like the biotite, are similar to F-1.

Features Indicative of Metamorphism

Samples F-1 and F-2 both show various features which are indicative of a metamorphic origin for the textures and minerals which are now observed. The granoblastic texture with plagioclase, biotite, hornblende and epidote all being approximately the same average grain size and with none of the minerals, with the possible exception of quartz, a very minor phase, being in any sense interstitial to the others, points to a metamorphic texture. The presence of epidote as a major and primary phase also indicates this. Epidote where found in igneous rocks is usually deuteric or late magmatic. Thus it would be expected to form interstitial grains or be seen to be altering from the plagioclase. It does not occur this way so this points to the epidote as being a primary mineral due to the metamorphism.

These features indicate that this anorthosite has been metamorphosed along with the country rocks after it was intruded. Thus the isochron obtained from the various mineral phases will likely date the last stage of metamorphism when the temperature dropped below a critical point at which Rb and Sr were no longer able to diffuse and were locked in the various mineral phases. A whole rock isochron would be needed to date the age of the intrusion.

III MINERAL SEPARATION

The samples were first crushed in a jaw crusher, transferred to the disc crusher and ground to -100 mesh. After coning and quartering, half the sample was set aside for whole rock analysis. The other half was washed several times in distilled water to remove fines, dried with acetone and heated under a heat lamp. The strongly magnetic fraction was removed by passing a hand magnet, wrapped in paper, over the dry samples.The minerals were separated using a Franz Isodynamic Magnetic Separator at the following settings:

a. 1 ampere, 15° side slope, and 40° forward slope.

b. The nonmagnetic portion from (a.) was rerun at 1.6 amperes, 15° side slope, and 40° forward slope, several times until a satisfactory plagioclase concentrate was obtained.

c. The magnetic portion from (a.) was rerun several times at 0.65 amperes, 20° side slope, and 37° forward slope until a satisfactory biotite concentrate was obtained for F-1 and a satisfactory biotite and hornblende concentrate for F-2. Sample L2-2 was run at 0.45 amperes, 10° side slope and 38° forward slope until a satisfactory biotite concentrate was obtained.

The purity of each concentrate,as determined by point counting,is shown in Table-1.

Table -1

Purity of Mineral Concentrates

Min. Conc.	Plag. %	Epid. %	Bio. %	Hn B %	Others %	no. of grains counted
L2-2 Plag.	97	3	-	-	-	200
L2-2 Bio.	3	1	96	-	-	250
F-1 Plag.	96	3	trace	-	1*	200
F-1 Bio.	3	1	96			300
F-2 Plag.	96	3	-	-	1*	200
F-2 Bio. + Hn B	1	-	15	85	-	550

* - quartz
Min. - mineral
Conc. - concentrate
Plag. - plagioclase

Epid. - epidote
Bio. - biotite
Hn B - hornblende

IV PRELIMINARY X-RAY FLOURESCENCE ANALYSIS:Rb, Sr

The mineral concentrates were analyzed semiquantitatively for Rb and Sr to determine the amount of Rb and Sr spike needed for each concentrate in the following isotope dilution step,in preparation for the mass spectrometer. The concentrates were analyzed on a Philips Manual Vacuum X-Ray Flourescence Spectrograph,with a Philips P 1011, 1600 watt generator.

The mineral concentrates were crushed to about -300 mesh in a Spex Mixer Mill and then pressed into pellets with borax backings. The Sr content of each plagioclase was determined at 50 KV, 30 mA with a W x-ray tube, and a LiF crystal, using a previously analyzed plagioclase concentrate as a standard. The Rb and Sr content of each biotite concentrate and the hornblende-biotite concentrate were determined at 40 KV, the other variables as above. A biotite previously analyzed fo Sr was used as a standard to determine the Sr content of the concentrates and indirectly the Rb content by comparing the Rb/Sr count ratio.

The results are given in Table-2.

Table - 2

Semi Quantitative Rb and Sr Analyses
by X-ray Flourescence

Conc.	Plagioclase	Biotite*		
Sample	Sr (ppm)	Rb(ppm)	Sr(ppm)	Rb/Sr
L2-2	840	160	50	3.1
F-1	740	450	50	9.0
F-2	750	450	60	7.1
Std.	820	1564	40	39.1

Conc. - concentrate
* - a hornblende and biotite concentrate
for sample F-2

V CHEMICAL PREPARATION FOR MASS SPECTROMETRIC ANALYSIS

1. Strontium Isotope Ratio: Using a 5 place Mettler balance, 100 milligram samples of plagioclase and 500 milligram samples of biotite were weighed out into tephlon dishes. 20 ml. of concentrated, distilled HF and approximately 1 ml. of concentrated, distilled $HClO_4$ were added to the samples which were allowed to digest overnight on a steam bath at about 90° C. In the morning the samples were evaporated down to about 15 ml. with the steam bath on high. 2 N HCl was added to convert to chlorides, the samples were evaporated down to 15 ml., more 2 N HCl added and again evaporated. The samples were then taken up to about 100 ml. with D D H_2O and evaporated down to about 50 ml. If, upon cooling, some precipates formed, these were removed by centrifuging for about 5 minutes. About 1 ml. of Sr^{89} tracer was added to each sample which was then put on the ion exchange column. The samples were eluted with 2 N HCl. When the radioactivity at the base of the resin in the column was up to 20 mr/hr, 8 successive 20 ml. samples were collected in 30 ml. disposable,polyethelene beakers. The samples were evaporated down to about 2 ml., the radioactive material collected and transferred to a vycor vial, and evaporated to dryness. 2 ml. of 1:1 HNO_3 were added to convert to nitrates and the samples evaporated to dryness. The vial was covered with parafilm and stored for mass spectrometric analysis.

2. Strontium Isotope Dilution: 100 milligram samples of biotite and plagioclase were weighed accurately into tephlon dishes. Enough Sr spike was added to give a normal

Sr/spike Sr ratio of approximately 2. These samples plus a blank containing only Sr spike were then dissolved and processed in the same manner as the isotope ratio samples.

VI ATOMIC ABSORPTION ANALYSIS:K,Rb, and Sr

The mineral concentrates were analyzed quantitatively for K, Rb and Sr to determine the K/Rb and Rb/Sr ratios of the various minerals.

Two sets of calibration standards, 0.5 gm samples of the concentrates, and the internal standards G-1 and Or-1 were accurately weighed out into the tephlon containers. These were then wetted with DDH_2O, and oxidized by the addition of 2 ml. of reagent grade HNO_3. After about one half hour 20 ml. of a 3:1 mixture of HF and $HClO_4$ respectively, each of reagent grade, was added and the samples placed on a steam bath to digest overnight at about 90°C. After digestion, they were evaporated down to about 2 ml., quantitatively transferred to clean 500 ml. vycor beakers, and finally to 100 ml. volumetric flasks. 2 ml. of a 10,000 ppm NaCl buffer solution were added to each flask before the solutions were made up to 100 ml. with DDH_2O. The solutions were transferred to 250 ml., soft polyethelene bottles ready for running on the atomic absorption spectrophotometer.

The analyses were all made with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. The Rb was determined using a Rb Osran vapour discharge lamp and an air-acetylene flame. The Sr was determined using a Perkin-Elmer hollow cathode, single element, Sr lamp and a nitrous oxide-acetylene flame.

To determine K the solutions had to be diluted by a factor of 5 and more NaCl buffer added. After dilution the K was determined using a K Orsan vapour discharge lamp and an air-acetylene flame.

The results are given in Table-3.

Table-3

K, Rb, Sr Analyses by Atomic Absorption

Oxide / Mineral		K_2O (Wt. %)		Rb_2O (Wt. %)		Rb	SrO (Wt.%)		Sr	Rb/Sr	K/Rb
		Dup.	Av.	Dup.	Av.	(ppm)	Dup.	Av.	(ppm)		
L2-2 Plagioclase		0.34 0.35	0.35	0.000 0.000	0.000	0	0.084 0.085	0.085	720	0.0	580*
L2-2 Biotite		8.14 8.04	8.09	0.034 0.032	0.033	300	0.004 0.004	0.004	30	10.0	220
F-1 Biotite		8.05 8.09	8.07	0.040 0.042	0.041	370	0.005 0.005	0.005	40	9.3	180
F-2 Biotite and Hornblende		1.88 1.84	1.86	0.009 0.009	0.009	80	0.004 0.005	0.005	40	2.0	190
G-1	O	-		0.022		200	0.029		250	0.8	
	L	4.58		0.024		220	0.031		260	0.8	250
Or-1	O	-		0.023		210	0.040		340	0.6	
	L	14.92		0.03		270	0.035		300	0.9	410

Dup.-Duplicate
Av.-Average
O-experimentally determined
L-Literative Value

*-a minimum value as calculated using Rb=5 ppm, the sensitivity limit
- not determined

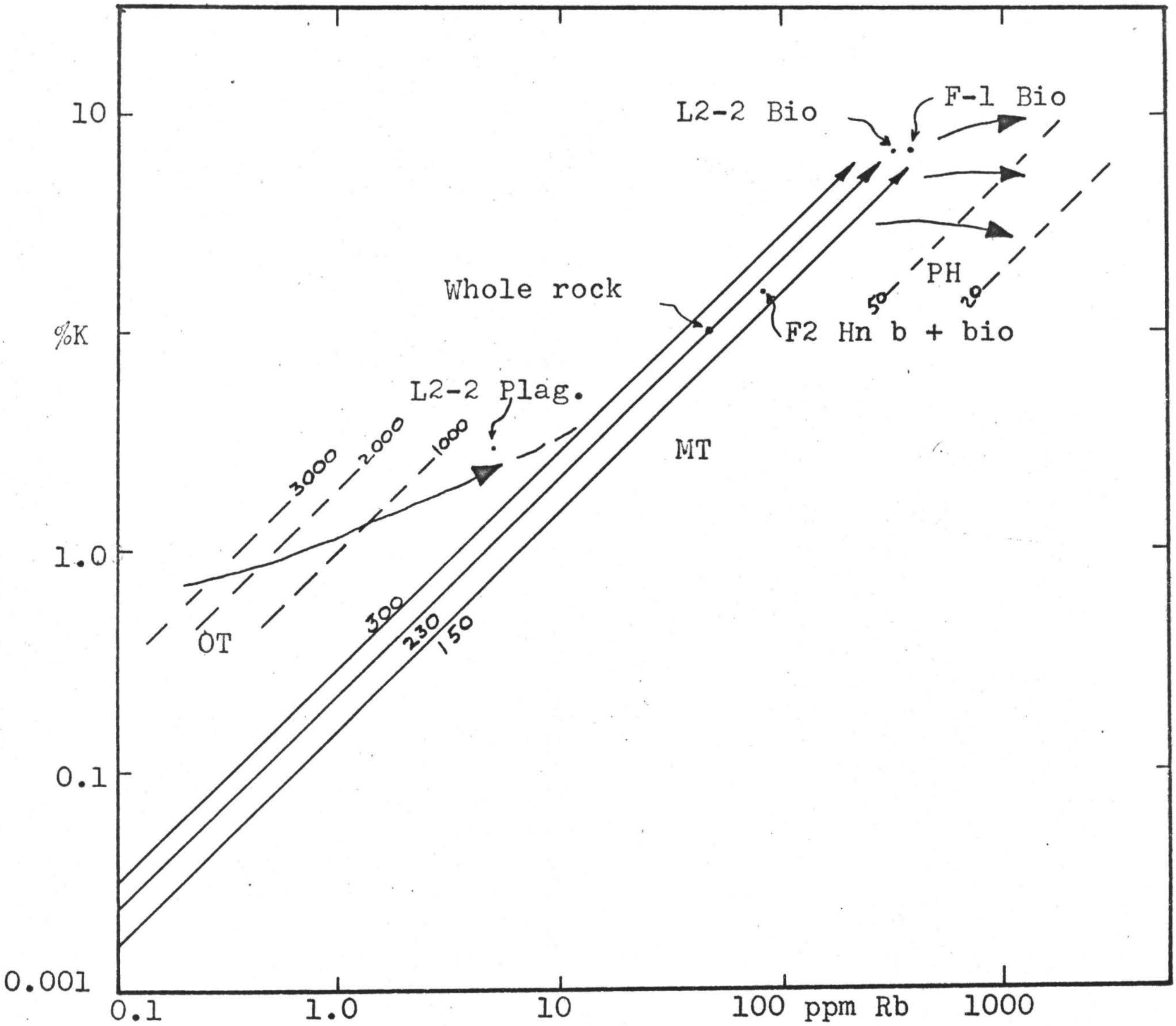
VII DISCUSSION

Due to difficulties with the mass spectrometer, the samples prepared, as described earlier, could not be run. If the samples were run, the initial Sr^{87}/ Sr^{86} ratio would probably fall in the range 0.703 to 0.706 as found by Heath (1966) and Phinney (1966) for similar occurences. The isochron determined from the samples would likely give an age of metamorphism of about 1100 m.y. as found by Silver (1966) and Heath (op. cit.).

The K/Rb ratios of the four mineral concentrates, determined by atomic absorption, are plotted on Fig.-2 (after Shaw, Fig.-4, 1968). This figure shows the K-Rb trends for igneous rocks. The main trend (MT) is linear on a log-log plot and is approximated by a K/Rb ratio of 230 for most igneous rocks, although a decrease in the ratio is found with increasing differentiation. The oceanic tholeiite trend (OT) is characterized by high K/Rb ratios decreasing from >3500 and merging with the main trend. The pegmatitic-hydrothermal trend (PH) is characterized by extreme Rb concentration relative to nearly constant or decreasing K concentration. The biotite and biotite-hornblende concentrates all fall on the main trend as determined by Shaw (op. cit.), but the plagioclase lies on or above the oceanic tholeiite trend.

The biotite concentrates have K/Rb ratios of 180 and 220 which are cosiderably higher than the ratio of 80 which Shaw estimates as the average for biotites. Although these are high, they are still within the range of normal variation found in the various investigations cited by Shaw. For sample F-2, if the biotite K/Rb ratio is assumed

Fig.-2
Mineral K/Rb Ratios



(After Shaw Fig.-4, 1968)

to be 180 as is the case for the biotite in sample F-1, collected about 50 feet away, then the hornblende K/Rb ratio calculated from the percentages of biotite and hornblende, given in Table-1, is 230. This too lies on the main trend and again is considerably different from Shaw's reported average of about 1100. The partition of Rb between hornblende and biotite suggested by Shaw's average K/Rb ratios suggests that a different K/Rb ratio for the biotite of sample F-2 may be possible. Thus if the biotite in this hornblende-biotite mixture has a K/Rb ratio considerably lower than 180, then the K/Rb ratio for the hornblende might approach Shaw's average value of 1100. This larger partition seems likely on crystal chemical grounds as the large alkali cation site in hornblende, in which the K substitutes, is , according to Deer, Howie, and Zussman (1964), a 10 fold coordination site while that in biotite is a 12 fold site. Consequently the small difference in ionic radii between K^+ (1.33A°) and Rb^+ (1.47A°), as given by Ahrens (1953), would be expected to produce a large fractionation of K^+ from Rb^+, with the larger Rb^+ cation preferentially going into the larger 12 fold site in biotite. With the apparent equilibrium between hornblende and biotite observed in the thin section,these differences in ionic radii presumably could have produced a large fractionation of Rb from K.

The plagioclase K/Rb ratio could not be determined as the Rb content proved to be below the sensitivity limit for atomic absorption analysis. However using a Rb content equal to the sensitivity limit of 5 ppm, a K/Rb ratio of 580 is obtained. This is a minimum and the ratio is certainly much higher. Again this result disagrees with Shaw's average plagioclase value, which he suggests " must not be greatly different from the overall rock averages 200-400."

Shaw does, however, suggest a reason for the lower K/Rb ratios in biotites as compared to feldspars. The difference in atomic radii between K and Rb makes possible a fractionation, as micas " have more tolerance for Rb, since the coorination of alkali metals are 12 and 8-10, " for micas and feldspars respectively.

Thus the larger Rb^+ ion favours the larger alkali site in the micas. This is also in agreement with the relative bonding energies given by Nockolds (1966) of 200, 100, 90 and 85 K cal/mole for Ca^{+2}, Na^{+1}, K^{+1} and Rb^{+1} respectively, for cation-oxygen bonds.*

As the whole rock was not analyzed for K and Rb an approximation to the whole rock K/Rb ratio was calculated using the modal analysis determined for the thin section of sample F-1, and the K and Rb contents of the F-1 biotite concentrate, and the L2-2 plagioclase concentrate. The L2-2 plagioclase analysis had to be used as the F-1 plagioclase was not analyzed. Assuming the epidote as having the same K-Rb composition as the plagioclase a K/Rb whole rock ratio of 235 is obtained, assuming the Rb content of the plagioclase to be 0 ppm. This will give the highest possible K/Rb ratio for the whole rock. If a Rb content of 5 ppm is assumed for the plagioclase a K/Rb ratio of 225 is obtained.

Thus the whole rock K/Rb ratio falls on the main trend in Fig.-2. This is unlike the K/Rb ratios reported by Phinney (1966) and Reynolds (1966) of 2600 and 1470 respectively. This may or may not represent a significant difference. These samples are all taken from mafic rich bands in a dominately

* These bonding energies are for 6 fold co-ordination hence do not strictly apply. However, they suggest that the K would probably be preferentially incorporated by the plagioclase, giving it a higher K/Rb ratio, causing a relative enrichment of Rb in the biotite and hence a lower biotite K/Rb ratio.

plagioclase rock. They thus may have greatly different K/Rb ratios from the anorthosite as a whole, where the plagioclase content is greater and the biotite content is minor or nonexistent. The biotite with its high concentration of K and Rb with respect to the plagioclase tends to determine the whole rock K/Rb ratio where present in any abundance, and swamps the small contribution of K and Rb from the plagioclase. However where biotite is minor or absent, the high K/Rb ratio of plagioclase may become much more important and values approaching those found by Phinney and Reynolds may be found.

If the low K/Rb ratio for the whole rock calculated, does represent the anorthosite ratio for the area around the sample location then this may be due to contamination from the country rocks which are reasonably close to the sampled location. Alternatively, this narrow southern neck may represent the last magma differentiate intruded, which had a lower K/Rb ratio than the main anorthosite body.

The low abundance of biotite in the main portion of the anorthosite probably means that the anorthosite as a whole does have a high K/Rb ratioas found for the other anorthosites by Phinney and Reynolds. This would plot on Fig.-2 off the main trend and approach the oceanic tholeiite trend. If so, then this would point to an origin in the crust or upper mantle for this anorthosite.

VIII SUGGESTIONS FOR FURTHER STUDY

The results of this study have pointed out several areas where further investigation would seem to be profitable. Much more work on the distribution of K and Rb is necessary before any conclusions can be drawn about the average K/Rb ratio of this anorthosite. Whole rock analyses should be made of the average anorthosite body rather than from mafic rich bands of the southern neck. These would give a much better idea of the K/Rb ratio of the body as a whole and would presumably indicate whether a mantle or lower crustal origin is probable. The analysis of the biotite and hornblende, individually, from sample F-2, would enable their individual K/Rb ratios to be determined and might show that a greater partition of K from Rb, as suggested, does take place between the hornblende and biotite. This would also indicate whether the K/Rb ratios of each mineral vary considerably with varying mineral assemblages as the biotites from mafic bands consisting only of biotite could be compared with the biotite of mafic bands consisting of both biotite and hornblende

Analyses from the narrow southern neck could also be analyzed and compared with the analyses of the main anorthosite body. Such a comparsion would indicate whether there is a change across the body, due to wall rock contamination or differentiation, of the K/Rb ratios.

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