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WHOLE-ROCK Rb-Sr STUDIES OF VOLCANICS AND SOME RELATED GRANITES

by

MICHAEL LOUIS BOTTINO
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Signature of Author ____________________
Department of Geology and Geophysics, February, 1963

Certified by ____________________
Thesis Supervisor

Certified by ____________________
Thesis Supervisor

Accepted by ____________________
Chairman, Departmental
Committee on Graduate Students

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by Michael L. Bottino

Submitted to the
Department of Geology and Geophysics
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degree of Doctor of Philosophy

Abstract

The determination of radioactive ages for events in the geological or fossil time scale is one of the challenging problems in geochronology. Volcanic rocks are well suited for this purpose because of their conformable relation to the strata. The recent developments of Rb-Sr whole-rock age studies indicates that whole rocks are less susceptiblethan minerals to loss of radiogenic strontium. These two factors combined suggest that whole-rock investigations of volcanic sequences should be a powerful tool for time scale studies.

A series of geologically dated volcanic rocks from the northern Appalachians have been analyzed for their Rb, Sr, and Sr isotopic composition. For each suite a series of whole-rock samples with different Rb/Sr ratios were analyzed and an isochron constructed. Satisfactory isochrons were obtained for most areas studied. The age results are internally consistent and do not contradict field evidence.

The ages reported here are approximately 8 % lower than the recent time scale estimates for the Silurian and Devonian. The discrepancy apparently increases in the Pennsylvanian. In the areas studied the ages overlap the published biotite ages from intrusives in the section, suggesting a rapid sequence of sedimentation, burial and intrusion.

A series of isochrons for the Cape Ann granite, the Quincy granite, and the Blue Hills porphyry and aporhyotite yield three different ages for the alkaline granites and rhyolite, all of which have been correlated and considered contemporaneous. These

results extend the alkaline igneous activity in New England back to the Ordovician or Silurian.

The initial ratios determined from the isochrons show that four of the eight granites and rhyolites crystallized with Sr^{87}/Sr^{86} ratios well above the value for basaltic rocks. This is interpreted as indication that these rocks are partially or wholly of crustal origin. Six basalts, a rhombenporphyry, and four rhyolite and granite isochrons gave initial ratios in the basaltic range.

Summary of Whole-rock Rb-Sr ages and $\left(\frac{Sr^{87}}{Sr^{86}}\right)_0$

$(\lambda_{Rb} = 1.39 \times 10^{-11}\ yr^{-1})$

Localities	Age(M.Y.)	$\left(\frac{Sr^{87}}{Sr^{86}}\right)_0$
Cape Ann granite (Mass.)	415 ± 10	0.709 ± 0.002
Post-Lower Cambrian		
Arisaig volcanics (N. Scotia)	405 ± 10	0.709 ± 0.001
Basal Silurian		
Kineo volcanics (Maine)	360 ± 10	0.715 ± 0.001
Upper Lower Devonian		
Newbury volcanics (Mass.)	345 ± 10	0.709 ± 0.001
late Silurian or early Devonian		
Blue Hills complex (Mass.) post-middle Cambrian to pre-middle or late Pennsylvanian		
Quincy granite	325 ± 15	0.728 ± 0.008
Blue Hills aporhyolite	248 ± 10	0.708 ± 0.004
Blue Hills porphyry	245 ± 10	0.722 ± 0.002
Rhombenporphyry	--- --	0.707 ± 0.003
Wamsutta volcanics (Mass.) Middle or late Pennsylvanian		
Rhyolite	225 ± 25	0.721 ± 0.002
Basalts	--- --	0.708 ± 0.001

Thesis Supervisor: Harold W. Fairbairn
Title: Professor of Geology

Thesis Supervisor: William H. Pinson Jr.
Title: Associate Professor of Geology

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PART I

(Intended for Publication)

WHOLE-ROCK Rb-Sr STUDIES OF VOLCANICS AND SOME RELATED GRANITES

Abstract

A series of geologically dated volcanic rocks from the northern Appalachians have been analyzed for their Rb, Sr, and Sr isotopic composition. For each suite a series of whole-rock samples with different Rb-Sr ratios were analyzed and an isochron constructed. Satisfactory isochrons were obtained for most areas studies. The age results are internally consistent and do not contradict field evidence.

The ages reported here are approximately 8 % lower than the recent time scale estimates for the Silurian and Devonian. The discrepancy apparently increases in the Pennsylvanian. In the areas studied the ages overlap the published biotite ages from intrusives in the section, suggesting a rapid sequence of sedimentation, burial and intrusion.

A series of isochrons for the Cape Ann granite, The Quincy granite, and the Blue Hills porphyry and aporhyolite yield three different ages for the alkaline granites and rhyolite, all of which had previously been correlated and considered contemporaneous. These results extend the alkaline igneous activity in New England back to the Ordovician or Silurian.

The initial ratios determined from the isochrons show that four of the eight granites and rhyolites crystallized with Sr^{87}/Sr^{86} ratios well above the value for basaltic rocks. This is interpreted as indicating that these rocks are partially or wholly of crustal origin. Six basalts, a rhombenporphyry, and four rhyolite and granite isochrons gave initial ratios in the basaltic range.

Summary of Whole-rock Rb-Sr Ages and $\left(\frac{Sr^{87}}{Sr^{86}}\right)_0$

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Wamsutta volcanics (Mass.)		
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Introduction

The determination of radioactive ages for events in the geologic or fossil time scale is one of the challenging problems in geochronology. Volcanic rocks are well suited for this purpose because of their conformable relation to the strata. In this investigation a series of volcanic rocks of different geologic ages from the northern Appalachians were studied. These included the basal Silurian (Arisaig, Nova Scotia), Lower Devonian (Kineo, Maine), late Silurian or early Devonian (Newbury, Mass.), and Pennsylvanian (Wamsutta, Mass.) volcanic suites. (See Figure 1.1 p. 95). The Pennsylvanian volcanics (Wamsutta) occur in the Narragansett basin of Massachusetts and Rhode Island. The Blue Hills complex ,which includes the Quincy granite and the Blue Hills porphyry and aporhyolite, stratigraphically underliesthe Narragansett basin and thus defines a maximum age for the basin. Therefore , it was possible to directly compare the results for the Wamsutta volcanics, interbedded with the sediments, to the maximum age for the sediments from the complex. In addition,both of these results were compared to the minimum ages for the basin reported by Hurley et al. (1960). Since the Cape Ann granite (Cape Ann, Mass.)

has been correlated with both the Blue Hills complex and the Newbury volcanics, it was also included in the study. The Cape Ann granite, the Blue Hills complex and the Newbury volcanics are all considered part of the extensive alkaline igneous province of New England.

The age results for the volcanics and granites are compared with their known or inferred geologic ages and to other available radioactive ages. In addition, the geologically well dated suites are compared with the recent time scale estimates by Kulp (1960), Holmes (1960) and Faul (1960).

The initial Sr^{87}/Sr^{86} ratios obtained from the isochrons are compared with the Sr^{87}/Sr^{86} ratios for basaltic rocks reported by Faure and Hurley (1962), and Gast (1960). Based on the premise that the basaltic values are representative of the strontium isotopic composition of the upper mantle or base of the crust, and that the sialic regions of the crust have a Sr^{87}/Sr^{86} ratio equal to or greater than the basaltic value, then the following conclusions can be drawn: (1) if the initial Sr^{87}/Sr^{86} ratio of a suite is greater than the basaltic value, then the source magma for that suite was partially or wholly of crustal origin; (2) if the initial Sr^{87}/Sr^{86} ratio of a suite is equal to the basaltic value, then the source magma for that suite may have been of subcrustal orogin.

In addition the initial ratios of the acid and basic members of a suite are compared as an indication of whether or not they were co-magmatic.

Analytical Procedures

In general, the laboratory procedures and instruments used in this investigation were the same as described by Herzog and Pinson (1956), Herzog et al. (1958) and Faure and Hurley (1962). Datails of the particular procedures can be found in Bottino (1963). The rubidium and strontium were determined by isotope dilution techniques using Rb^{87} and Sr^{86} spikes, respectively. The weighed samples were spiked at the beginning of the procedures. The samples were dissolved in a mixture of HF and $HClO_4$. Rubidium was separated by precipitation of the alkali perchorates and strontium was purified on a cation exchange column of Dower 50, 8 % cross linked, 200-400 mesh, using 2N HCl as eluant. Strontium blank determinations were made and a blank correction applied. Rubidium blank corrections were unnecessary. Replicate analyses for rubidium and strontium indicate a precision of ± 2 % except for strontium concentrations of 15 ppm or less where the precision is ± 6 %. New shelf solutions were prepared for spike calibrations. The new calibrations were indentical within analytical precision with the previous calibrations. This is a satisfactory indication of the accuracy of the analyses. For a detailed review of the spikes see Pinson (1962). In addition to isotope dilution analyses some samples were analyzed by X-ray spectrography. These samples were converted to fluorides for the X-ray analysis. If quantitative results were sought, the analysis was standardized against a sample of similar bulk chemical composition of known rubidium and strontium content. In some cases only the relative intensity was needed and no standardization was used. The sample powder itself was analyzed if a semi-quantitative result was sufficient. All of these values are noted in the tables.

Separate, unspiked samples were analyzed for their strontium isotopic composition. The chemical procedure was the same as that for spiked strontium samples. The mass spectrometer used was a 6 inch radius, 60 sector, single filament, thermal ionization, magnet sweep instrument with a Faraday cup collector and vibrating-reed electrometer. The Sr^{87}/Sr^{86} ratios were normalized to 86/88 = 0.1194. For a justification of this procedure see Faure and Hurley (1962). The precision of a single analysis as determined from duplicates of samples and six replicate analyses of a standard strontium carbonate is approximately ± 0.002 or 0.25 %. The value of the $(Sr^{87}/Sr^{86})_{.1194}$ ratio of a standard strontium carbonate, Eimer and Amend, Lot # 492327, is identical within analytical precision to the previous results on this instrument. For six analyses the results were: 86/88 = 0.1199, 87/86 = 0.7093 and $(87/86)_{.1194} = 0.7108$. The overall averages for 24 analyses, including the six above, over the period, May 1960 to November 1962 were as follows

$$\frac{86}{88} = 0.1195 \pm 0.0001$$

$$\frac{87}{86} = 0.7110 \pm 0.0005$$

$$\left(\frac{87}{86}\right)_{.1194} = 0.7114 \pm 0.0004$$

The uncertainty attached to the ages reported in this work represent the range of ages compatible with the points on the diagram rather than a calculation of the standard deviation of the mean, which it is felt, is not necessarily the best estimate of uncertainty when there is no assurance that the deviations are random. The error of individual isochron points is ± 3 % Rb^{87}/Sr^{86} and ± 0.25 % for Sr^{87}/Sr^{86}, except for samples wherein the strontium content was less then 25 ppm.. For those samples ± 5 % for Rb^{87}/Sr^{86} was assigned as a reasonable error. The age and initial ratio were determined by the age equation:

$$\left(\frac{Sr^{87}}{Sr^{86}}\right)_p = \left(\frac{Sr^{87}}{Sr^{86}}\right)_o + \left(\frac{Rb^{87}}{Sr^{86}}\right) \lambda t$$

where

$$\lambda_{Rb^{87}} = 1.39 \times 10^{-11} \text{ yr}^{-1}$$

The Arisaig Volcanics

The Arisaig volcanics make possible an age investigation of the base of the Silurian in northeastern North America. They are in the Arisaig-Antigonish district of Nova Scotia at the base of the Silurian Arisaig series. These rocks outcrop along Northumberland strait, from Malignant Cove to Mc Aras Brook in an area approximately 6 by 1 ½ miles. Twenhofel and Schuchert (1909) and Mc Learn (1918, 1924) are prominent amongst those who worked on the paleontology of the Arisaig series. The geology is described by Fletcher and Fairbault (1886) and Williams (1911, 1912, 1914).

The sediments of this Silurian section are highly fossiliferous and range in age from lower Llandovery to Ludlow. The fossils are correlated with European rather than North American types (Twenhofel and Schuchert, 1909; Williams, 1914; and McLearn, 1924).

The geologic age of the Arisaig volcanics can be summarized as follows: The volcanics occur at the base of the Silurian sediments. The oldest formation, the Beechhill Cove formation of Lower Llandovery (Lower Silurian) age was deposited on the irregular surface of the Arisaig volcanics with no apparent angular unconformity. The contact is irregular, with local conglomerates composed of the underlying volcanics. Therefore the minimum geologic age for the volcanics is pre or basal Lower Silurian. There are no field relations to directly determine the maximum geologic age. The oldest formation in the area, which unconformably underlies all the other formations, is Lower Ordovician. Therefore a post-Lower Ordovician age is a reasonable maximum age for the Arisaig volcanics, and the most probable geologic age is basal Silurian.

Results and Discussion. Five rhyolite and one basic volcanic whole-rock samples have been analyzed.

The results are reported in Table I and the isochron is shown in Figure 4.1 (p.154). The isochron indicates an age of 405 ± 10 M. Y. and an initial ratio of 0.709 ± 0.001 for both the basic volcanic and the rhyolites. The single initial ratio for the acid and basic volcanics is consistent with a common genetic history for the two rock types in this sequence, and falls within the range for basaltic rocks (Faure and Hurley, (1962), and Gast, (1960)). The 405 ± 10 M. Y. age is consistent with the 360 ± 10 M. Y. age for the upper Lower Devonian Kineo volcanics which is reported in the next section. Assuming that the Devonian-Silurian boundry is approximately 370 M. Y., based on the Kineo age, then the length of the Silurian is approximately 35 M. Y., which is not an unreasonable value.

There are no geologically dated granitic intrusives listed by Kulp (1960) or Faul (1960) to date the Silurian-Ordovician boundry. Based on interpolation, Kulp estimates 430 M. Y. and Holmes (1960) estimates 440 M. Y. for this boundry. The age reported here is approximately 8 % lower than these estimates, assuming its most probable age to be basal Silurian. Faul (1960) reported an age of 420-450 M. Y. for the Middle Ordovician of Alabama and Tennessee. Adams and Rogers (1961)

Table I

Arisaig Volcanics, Arisaig, Nova Scotia

Sample		Rb ppm.	Sr ppm.	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})_{.1194}$	$\frac{Rb^{87}}{Sr^{86}}$
R4634	Andesite	14.7	328.0	0.1198[a]	0.7081[a]	0.7093[a]	0.13
R4635	Rhyolite	73.4	96.0	0.1197	0.7203	0.7212	2.02
R4635	Rhyolite	99.9	128.0	0.1213	0.7151	0.7208	2.26
R4637	Rhyolite	226.0[c]	13.33[b]	0.1202[a]	0.9756[a]	0.9787[a]	50.4
R4638	Rhyolite	274.0	64.0 [a]	0.1202[a]	0.7780[a]	0.7806[a]	12.5
R4639	Rhyolite	186.0	72.o	0.1198	0.7477	0.7490	7.5

a. average of two analyses.
b. average of three analyses.
c. average of four analyses.

summarized much of the same data and concluded that the 447 ± 10 M. Y. average of five U^{238}-Pb^{206} ages is the best estimate. The result for the Arisaig is reasonably consistent with these Middle Ordovician estimates. The Kulp-Holmes estimate of 430-440 M. Y. for the base of the Silurian only allows a maximum of approximately 15 M. Y. for the interval between Lower Silurian and Middle Ordovician. Faul (1960, 1961) reported four biotite K-Ar ages of 405 M. Y. for a group of granites south of Calais, Maine, one of which is post-upper Silurian. There is a contradiction between this and the 405 M. Y. age for the Arisaig volcanics. This is the only North American intrusive granite age that is incompatible with the ages reported in this work.

The Kineo Volcanics.

The Kineo volcanics occur in the Moose River synclinorium in west-central Maine and consist of a variety of volcanic rock types, including massive felsite, tuffs, agglomerates and garnet rhyolites. For a complete description of the Kineo volcanics and the geology of the Moose River synclinorium see Boucot(1961).

The geologic age of the Kineo volcanics is precisely defined as early Onondaga to late Oriskany (upper Lower Devonian).

Results and Discussion. Five whole-rocks and one mineral from the Kineo volcanics have been analyzed. The analyzed samples are massive conchoidally fractured felsites with the exception of R4565 and R5051 which are garnet felsites. The hornblende sample Hb3061, was separated from sample R3061. In addition to the isotope dilution analyses for rubidium and strontium, an analysis was done by X-ray spectrograph for relative intensity of the Rb/Sr weight ratio in this series of samples. These values are plotted against the Sr^{87}/Sr^{86} ratios to obtain an initial ratio independent of the isotope dilution analyses. The results are reported in Table II. The isochron is shown in Figure 3.1 (p.139) and the plot of relative intensity X-ray Rb/Sr versus Sr^{87}/Sr^{86} is shown in Figure 3.2 (p.140). The isochron indicates an age of 360 ± 10 M. Y. and an initial Sr^{87}/Sr^{86} ratio of 0.715 ± 0.001. The initial ratio from Figure 3.2 is 0.715 and confirms the value obtained from the isochron.

The initial ratio for the KIneo is higher than the basaltic value of 708 $^{+0.002}_{-0.003}$ (Faure and Hurley, 1962) and indicates that this volcanic sequence is partially

Table II

Kineo Rhyolite

Sample	Location	Rb ppm.	Sr ppm.	$\frac{Rb^{87}}{Sr^{86}}$	Intensity X-ray $\frac{Rb}{Sr}$	$\frac{Sr^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$(\frac{Sr^{87}}{Sr^{86}})_{.1194}$
R3061	Felsite	206^{b}	61.5^{b}	9.75	2.27^{d}	0.7613^{a}	0.1194^{a}	0.7611^{a}
Hb3061	Hornblende	152	527.0	0.83	----	0.7175	0.1195	0.7178
R4565	Garnet felsite	135	64.3	6.10	1.58^{b}	0.7454^{a}	0.1200^{a}	0.7471^{a}
R4566	Felsite	191	44.7	12.44	3.10^{b}	0.7765^{a}	0.1194^{a}	0.7775^{a}
R4567	Felsite	143	84.8	4.91	1.26^{c}	0.7397^{a}	0.1192^{a}	0.7391^{a}
R5051	Garnet felsite	---	-----	-----	0.907^{a}	0.7297	0.1206	0.7334

a. is the average of two analyses.
b. is the average of three analyses.
c. is the average of four analyses.
d. is the average of five analyses.

or wholly of crustal origin.

Holmes, Kulp and Faul give an estimate of 400 M. Y. for the Devonian-Silurian boundry. The age for the upper Lower Devonian would be approximately 390 M. Y.. The Kineo age is approximately 8 % lower than these estimates. A critical inspection of the individual values that determine this boundry shows that in North America only the 405 M. Y. granites south of Calais, Maine are incompatible.

In Nova Scotia, (Fairbairn et al.,1960) two localities are close to intrusive contacts with upper Lower Devonian fossiliferous strata. The K-Ar and Rb-Sr biotite ages from those localities are discordant but their mean value is in good agreement with concordant results from several other localities. The results suggest a 365 M. Y. minimum age for the upper lower Devonian which overlaps the Kineo result. Another critical locality for comparison is the Seboomook slate (Oriskany, middle Lower Devonian) near Jackman, Maine (Hurley et al., 1959). The biotite K-Ar ages from the quartz monzonite average 360 M. Y.. This includes three biotites from two localities and replicate analyses from two laboratories.The whole-rock K-Ar ages (four samples) on the Seboomook slate range from 350-377 M. Y.. If one assumes that these sediments lost all of their inherited argon at the time of intrusion then their mean K-Ar age of 365 M. Y. is a minimum age. A single biotite Rb-Sr age of 360 ± 28 M.Y. is also reported. This locality is north of the Kineo area and the slate stratigraphically underlies the Kineo volcanics. A possible explanation of this overlap for the minimum and Kineo ages is that the interval of time between sedimentation, burial and intrusion was on the order of the uncertainites of the measurements and is **undetectible.**

In the British Isles, the Shap adamellite, the Creetown granite and the Leinster granite give biotite Rb-Sr ages of 423 ± 10 ($\lambda = 1.39 \times 10^{-11}$) and K-Ar ages of 390 ± 10 M. Y. (Lambert and Mills, 1961). However there is some question as to whether or not these granites are really Lower Devonian intrusives. According to Lambert and Mills (1961) the assignment of these granites to the Lower Devonian depends on their correlation with volcanics of Lower Devonian age which are part of the post-orogenic calc-alkaline suite. The intrusive relations only show that they are post-Lower Silurian. The dikes associated with the Shap adamellite intrude the upper Silurian. If these dikes and the Shap adamellite are contemporaneous, then the Shap is post-Upper Silurian. Finally, if the Shap and the Lower Devonian volcanics are contemporaneous then the granite is Lower Devonian. It is very difficult to asses this situation. The difference between apparent inconsistency or consistency for the two sets of data (Shap and Kineo) depends on whether the Shap adamellite is Lower Devonian, post-Upper Silurian or post-Lower Silurian. A whole-rock isochron study of the Lower Devonian volcanics which are correlated with the British granites would help clarify the situation. In this paper there are reported whole-rock ages for volcanics and granites from a well-known alkaline suite in eastern Massachusetts. These are also correlated on petrologic grounds and the ages for individual intrusions and extrusions are 415, 345, 325, and 245 M. Y.. This lends weight to the need for great caution in assigning geologic ages to intrusive rocks.

The Wamsutta Volcanics.

The volcanics of the Wamsutta formation occur south of Hoppin Hill near the town of South Attleboro, in southeastern Massachusetts. The formation is part of the Pennsylvanian Narragansett basin of Massachusetts and Rhode Island. An unpublished map by Coomaraswamy and Ray (1954) was used for collecting samples for this investigation.

The formations of the basin in ascending order, are the Pondville, the Wamsutta, the Rhode Island and the Dighton (see Table III). These formations partly overlap. In particular the upper part of the Wamsutta is probably equivalent to the lower part of the Rhode Island formation (Knox, (1944)). In the Hoppin Hill area the volcanics occur near the base of the formation and are interbedded with conglomerates. Three flows, two of basalt, and one of rhyolite, are separated by conglomerate beds. 85 to 550 feet thick (Coomaraswamy, 1954). The unmetamorphosed rhyolite has a red aphanatic groundmass and quartz and feldspar phenocrysts. The northern end of the basin, unlike the southern end, is unmetamorphosed.

Quinn and Oliver reviewed the geology and paleontology of the basin. The flora and fauna of the basin have been correlated with both the early middle and late Pennsylvanian sediments elsewhere. (see Table IV for the names and relations of the major divisions of the Pennsylvanian). Knox (1944) compared the flora from the Wamsutta formation with the Cherokee shales of

Table III

Stratigraphy of the Narragansett Basin, Rhode Island.

After Quinn and Oliver (1962), Hurley et al. (1960), Moore (1959), Nichols (1956) and Knox (1944).

Age	Formation	Description
Late or post Pennsylvanian	Westerly granite	Light-gray, pink or tan fine grained massive granite; quartz, oligoclase, potash feldspar and biotite.
	Narragansett Pier granite	Pink, tan, gray medium-to coarse-grained granite; chiefly massive, locally weakly foliated; quartz, oligoclase, potash feldspar and biotite.
Pennsylvanian (middle or late, Quinn and Oliver, 1962)	Dighton and Purgatory conglomerate (1000-1500 feet)	Coarse, poorly sorted, quartzite and granite roundstone conglomerates
	Rhode Island formation (10,000')	Gray sandstone, conglomerates, shale, black shale and coal.
	Wamsutta formation (1000 feet)	Red, locally green and brown, sandstone, shale and conglomerate; interbedded rhyolite and basalts.

Table III, continued

Age	Formation	Description
Pennsylvanian	Pondville conglomerate	Fine grained to coarse gray conglomerate, includes "giant" conglomerate containing Blue Hills porphyry pebbles.
(unconformity)		
Pre-middle or late Pennsylvanian Mississippian (?)	Quincy granite	Light to dark, bluish gray, medium-to-coarse-grained massive granite, quartz, microperthite, riebeckite, aegirite.
	Blue Hills granite and quartz porphyries	Gray, quartz, feldspar, riebeckite, aegirite.
	Blue Hills aporhyolite	Dark red, purplish rhyolite showing flow structure.
Pre-Pennsylvanian Devonian (?) or older	Fine-grained granite	Pinkish, gray, tan, fine-grained, partly massive, partly lineated or foliated; quartz, plagioclase, potash feldspar and biotite.
	Scituate granite gneiss	Pinkish-gray to pink medium-to-coarse granite gneiss, oval splotches of biotite, quartz, potash feldspar, plagioclase and biotite.
	Hope Valley alaskite gneiss	Pink, pinkish gray, medium-to-coarse grained alaskite gneiss, rod shaped aggregates of quartz, quartz, potash feldspar, plagioclase, biotite; other varieties.
(unconformity)		
Pre-Cambrian (?)	Blackstone series	Quartz biotite schist; gray pinkish quartz feldspar biotite gneiss.

Table IV

Major Divisions of Pennsylvanian Time
from Branson (1962)

	Appalachian Mts.	Mid-continent	Western Europe	Russia
Permian	Dunkardian	Lyonian	Autumian	Sakmarian
Pennsylvanian	Monongahelan			Gachelian
	Conemaughian	Virgilian Missourian	Stephanian	Kasimovian
	*	Desmoinesian	Westphalian	Moscovian
	Pottsvillian	Atokan		
		Morrowan	Namurian	Baschkirian
(Mississippian)		Chesterian		Visean

* Aproximate position of the Allegheny, put in by this writer, from Branson (1962).

Missouri (Desmoinesian or lower Allegheny) and Lesquereux (1899, Quinn and Oliver , 1962) compared the flora of the Rhode Island formation to the Monongahela of Pennsylvanian and the Lower Permian of Europe. In addition the flora from the Rhode Island formation have been compared with the Conemaugh from Nova Scotia and Missouri (Round, 1924, 1927). The fauna of the basin are scarce and both middle and late Pennsylvanian have been suggested as the age (Quinn and Oliver, 1962). There is general agreement that the sediments are middle or late Pennsylvanian (Quinn and Oliver, 1962). Branson (1962) points out that faunal and floral zones of the Pennsylvanian are generally composed of long-ranged species and that at present it is difficult to define precisely geologic ages based on these alone. He also points out the lack of certainty as to where the Lower-Middle-Upper Pennsylvanian boundries should be drawn.

Results and Discussion. Six rhyolites and three basalts from the Wamsutta volcanics were analyzed. In addition one sedimentary rock was inadvertently included in the suite of analyzed samples. The results are reported in Table V and the isochron is shown in Figure 5.1 (p.169). Inspection of the isochron plot

Table V

Volcanics from the Wamsutta Formation, South Attleboro, Massachusetts

Sample		Rb ppm.	Sr ppm.	$\frac{Rb^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$\left(\frac{Sr^{87}}{Sr^{86}}\right)_{.1194}$
R4889	Basalt	—	—	(0.12)[1]	0.1189	0.7114	0.7099
R4890	Basalt	—	—	(0.04)[1]	0.1189	0.7113	0.7098
R4896	Basalt	—	—	(0.02)[1]	0.1207	0.7063	0.7101
R4891A	Rhyolite	63.4[a]	55.3[a]	3.32	0.1205	0.7287	0.7321
R4891B	Rhyolite	98.4	49.1	5.81	0.1198	0.7384	0.7396
R4891C	Rhyolite	152.	49.8	8.87	0.1192[a]	0.7479[a]	0.7473[a]
R4893	Rhyolite	105.5[a]	87.1	3.51	0.1205	0.7263	0.7296
R4894	Rhyolite	99.3[2]	72.45[a]	3.98	0.1197	0.7331	0.7340
R4895	Rhyolite	138.	89.	4.5	0.1203	0.7328	0.7356
R4888	Shale	70.[3]	124.[a]	1.62	0.1201[a]	0.7161[a]	0.7182[a]

1. Semi-quantitative values determined by a single scan on the X-ray spectrograph on rock powders.
2. Average of two quanitative X-ray determinations and one isotope dilution analysis.
3. Average of two quantitative X-ray determinations.

a. Average of two analyses.

shows that the basalt and rhyolite points do not fit the same line. The rhyolite isochron indicates an age of 225 ± 25 M. Y. and an initial ratio of 0.721 ± 0.002. The basalts have a directly measured Sr^{87}/Sr^{86} ratio of 0.7099 ± 0.0001, and when corrected for the radiogenic strontium accumulated in 225 M. Y., yield an initial ratio of 0.708 ± 0.001. The age result for the rhyolite is not precise because of the low slope of the isochron; however, the initial ratio is clearly demonstrated to be 0.721. The difference in initial ratio between the basalts and the rhyolite indicates different genetic histories for the two rock types. The initial ratio for the basalts falls within the range for basaltic rocks reported by Faure and Hurley, and by Gast. The initial ratio for the rhyolite is higher than that of the associated basalts and basaltic rocks in general and indicates that the rhyolite is partially or wholly of crustal origin.

The Rb-Sr age for the Wamsutta rhyolite can be compared with the Rb-Sr age for the Blue Hills porphyry, the ages for the Narragansett basin reported by Hurley et al. (1960) and the lead-alpha results on zircons reported by Quinn et al. (1957). All of these ages are summarized in Table VI.

Table VI

Summary of Age Results for Narragansett Basin.

$(\lambda_{Rb^{87}} = 1.39 \times 10^{-11})$

Reference	Method and Material	Sample Localities and Number of Samples	Age M. Y.)
Quinn et al. (1957)	lead-alpha, zircons	Westerly and Narragansett Pier granites (5)	224
		Range	(208-243)
		Narragansett Pier granite, 53S-49, Quonochontaug quadrangle, Quonochontaug beach, west of Narragansett basin, (1).	274
		average as given by Quinn et al. (6).	234 ± 34
		included in the above, Q55-1, Narragansett Pier granite sills in Pennsylvanian Meta-sediments (1).	235
Hurley et al. (1960)	K-Ar, Rb-Sr biotite and whole-rock meta-sediments.	Meta-sediments, south end of Narragansett basin, whole-rock (3) and biotite K-Ar (3).	250
		Range	(230-275)

Table VI, continued

Reference	Method and Material	Sample Localities and Number of Samples	Age(M. Y.)
Hurley et al. (1960)	K-Ar, Rb-Sr biotite and whole-rock meta-sediments.	Biotite Rb-Sr (2) Average (8)	260 ± 15 255
	K-Ar biotite.	Granitic sill in Pennsylvanian meta-sediments. B3816, (1).	230 ± 11
	K-Ar biotite.	Westerly granite, B3814, Sullivan Quarry, Carolina quadrangle, Bradford, Rhode Island, west of Narragansett basin (1).	240 ± 12
Pinson et al. (1962)	Rb-Sr biotite	Westerly granite, B3042, Sullivan Quarry, Carolina quadrangle, Bradford, Rhode Island, west of Narragansett basin (1),	274 ± 10
	Rb-Sr single whole-rock using initial ratio obtained from apatite	Westerly granite, G-1 standard, Sullivan Quarry, Carolina quadrangle, Bradford, Rhode Island, west of Narragansett basin (1),	316 ± 40

Table VI, continued

Reference	Method and Material	Sample Localities and Number of Samples	Age (M. Y.)
This work	Rb-Sr whole-rock isochrons	Wamsutta rhyolite South Attleboro, Mass.. (6).	225 ± 25
		Blue Hills quartz porphyry (3) Blue Hills aporhyolite (4) Milton, Quincy, Mass..	245 ± 10 248 ± 10
		Normal Quincy granite Quincy, Mass.. (5)	325 ± 15
Hurley et al. (1960)	K-Ar, whole-rock	Normal Quincy granite, R3821 Swingle Quarry, Quincy, Mass.. (1) (minimum only, Hurley et al. (1960)).	280 ± 15

The whole-rock Rb-Sr isochron age for the Blue Hills quartz porphyry is 245 ± 10 M. Y.. The age of this rock is important because pebbles of the porphyry are found in the Pondville conglomerate at the base of the Narragansett (Norfolk) basin. Thus this age represents a maximum for the basin. The Wamsutta rhyolite age is consistent with this result. Both of these results can be compared with the published ages for the basin.

Hurley et al. (1960) reported a minimum age for the basin of 235 M. Y. (K-Ar) from the intrusive granites cutting the sediments. Actually one sample (B3816) is from an intrusive in the basin. Another sample is from the Westerly granite west of the basin and the third is from the contact zone adjacent to the granitic sample (see Table VI). This latter sample is included with the metamorphic ages; the Westerly granite will be discussed separately. The age of the intrusive sample B3816 is 230 ± 11 M. Y. which overlaps the Wamsutta rhyolite age and is consistent with the maximum age from the Blue Hills porphyry. The accord of all three ages can be interpreted to mean that the interval of time involved for sedimentation, burial and intrusion was short compared with the precision of the measurements. Quinn et al. reported one lead-alpha age of 235 M. Y. from an intrusive in the meta-sediments of the basin and this is consistent with the above group of measurements.

The 255 M. Y. age from the meta-sediments of the basin (Hurley et al.) raises an apparent anomaly since this minimum value is greater than both the maxinum (245 ± 10 M. Y.) and the volcanic (225 ± 25 M. Y.) values. This 255 M. Y. age for the meta-sediments is also greater than the 230-235 M. Y. age for the intrusives in the same area. The possibility of inherited radiogenic Ar and Sr in metamorphic sediments makes interpretation of these ages uncertain. K-Ar and Rb-Sr ages on meta-sediments are minimum ages only on the assumption that all of the argon and radiogenic strontium was driven out during metamorphism. The same pattern of slightly higher metamorphic sediment ages relative to granite intrusive ages is shown in the work on the Seboomook slate (see section on Kineo volcanics).

As indicated above the ages for the Narragansett basin show a mixed pattern. There is apparent agreement between the minimum values for the intrusives (230 ± 11 M. Y. and 235 M. Y. lead-alpha) and the maximum age (245 ± 10) for the Blue Hills porphyry. The minimum age for the intrusives and the Wamsutta volcanic age (255 ± 25) overlap. The minimum age for the meta-sediments (255 M. Y.) and both the maximum and rhyolite values apparently are contradictory. The reality of this anomaly depends on whether on not the ages for the meta-sediments are really minimum values.

The rest of the published ages are for the Westerly and Narragansett Pier granites in localities west of the Narragansett basin. Hurley et al. reported a biotite K-Ar age of 240 ± 12 M. Y. for a sample (B3814) of Westerly granite from the Sullivan Quarry, near Bradford Rhode Island.. Quinn et al. reported a zircon lead-alpha age of 243 M. Y. for a sample (S-47) from the same quarry. Pinson et al. (1962) reported a Rb-Sr biotite age of 274 ± 10 M. Y. ($\lambda = 1.39 \times 10^{-11}$ yr^{-1}), also from this quarry, which is significantly higher than the lead-alpha and K-Ar ages above. In addition a Rb-Sr whole-rock age measurement on G-1 (Westerly granite) was reported as 315 ± 40 M. Y. ($\lambda = 1.39 \times 10^{-11}$ yr^{-1}), assuming an initial ratio of 0.709 based on the measured Sr^{87}/Sr^{86} ratio of apatite from the rock. This whole-rock age has a large error of ± 40 M. Y. and may therefore not be in disagreement with the biotite age of 274 M. Y..

The Sullivan Quarry is approximately 15 miles from the nearest Pennsilvanian sediments. In this area a Westerly granite dike intrudes the Hope Valley alaskite gneiss and the Blackstone series (Moore(1959)). Both of these formations are considered pre-Pennsylvanian, probably Devonian or older (Moore (1959)). In other areas the Westerly granite intrudes the Narragansett Pier granite, for example in the Ashaway quadrangle (Quinn et al. (1957)). Around the north shore of the Quonochontaug Pond, thin dikes of fine-grained gray Westerly granite intrude the Narragansett Pier granite (Moore (1959). In this area the Narragansett Pier granite is also intruded by dikes of a granite of similar appearance and considered by Moore to be a late stage phase of the host granite. Nichols (1956) states that the Narragansett Pier granite is intruded by pegmatite dikes of similar composition in the Narragansett Pier and Boston Neck areas of the Narragansett Pier quadrangle. The fact that in some areas the Narragansett Pier granite is cut by younger dikes of similar composition suggest that all the granites correlated as Narragansett Pier granite may not be contemporaneous. It should also be noted that the single lead-alpha age measurement for the Narragansett

Pier granite along the south shore indicates an age of 274 M. Y. (Quinn et al. sample 53S-49). This value is in the range of the pre-Pennsylvanian ages as measured by the same method. Although this analysis could be in error, it could on the other hand indicate that all of the granite considered Narragansett Pier type may not be contemporaneous. This consideration is important because the geologic age of the Narragansett Pier granite primarily depends on correlation with the granite sills and pegmatites that cut the Pennsylvanian sediments of the basin.

The geologic age of the Westerly granite depends on the correlation of fine-grained granite dikes which cut the Narragansett Pier granite. In the literature it is not clear whether the Westerly granite itself intrudes the Pennsylvanian sediments. Quinn et al. (1957, p. 547) state that the Westerly is exposed mostly in the Carolina, Ashaway and Watch Hill quadrangles all of which are in the southwest corner of Rhode Island and well out of the Narragansett basin. Nichols (1956) does not mention the Westerly granite in the Narragansett Pier quadrangle. It appears that the age of the Westerly granite is established by its intrusive relations with the Narragansett Pier granite in areas outside of the Pennsylvanian basin.

If the correlations of the Westerly and Narragansett Pier granites with the granites cutting the Pennsylvanian sediments is correct then the minimum age for the sediments is at least 260 M. Y. (excluding the whole-rock age measurement on the Westerly granite). This would indicate a contradiction between the present investigation and the previous work on the granites in the area. In addition it would confirm the apparent contradiction between this report and the ages of the metasediments of the basin.

On the other hand, if one considers the minimum age of the intrusives which actually cut the Pennsylvanian sediments, then all of the results are consistent and indicate that the sequence of events involving sedimentation, burial and intrusion took place over a relatively short interval of time. This interpretation requires the Westerly granite to be pre-, rather than post- middle Pennsylvanian.

The results reported here are not in accord with the Kulp(1960), Holmes (1960) and Faul (1960) estimates for the Pennsylvanian-Permian and Pennsylvanian-Mississippian boundries. Kulp's estimate for the Pennsylvanian-Permian boundry is 270 M. Y. and for the Pennsylvanian-Mississippian boundry is 320 M. Y..

This requires an age greater than 300 M. Y. for the pre-middle Pennsylvanian. The results for the Blue Hills porphyry and the Wamsutta volcanics are approximately 50-70 M. Y. lower than Kulp's estimate for this section of the time scale.

Some of the critical samples listed by Kulp (1960, p. 20, 21) are as follows:

> (9) The igneous complex of the Oslo region is presumably late Lower Permian. One result on biotite from these rocks gives 259 ± 10 M. Y. (Faul, 1957).
> (10) For post-Middle Pennsylvanian metamorphic rocks in Rhode Island an average age of 256 ± 10 M. Y. is found by the K-Ar and Rb-Sr methods (Hurley et al., 1959).
> (11) The granites of the Cornwall region in England are definitely post-Westphalian and pre-Middle Permian. They are probably Lowermost Permian. The age obtained on repeated determinations is 270 ± 5 (Kulp et al., 1960).
> (12) Rb-Sr and K-Ar measurements on biotite in eight granites from the Vosges, Schwarzwald and Massif Central which probably are post-Dinantian but pre-Visian (i.e. late Lower Carboniferous) gave an age of about 335 ± 10 M. Y. (Faul, 1957). This valuable point probably warrents further geological study.

Faul(1960) added a U^{238}/Pb^{206} zircon age of 260 M. Y. to the K-Ar biotite age listed above for the Olso rocks. These results and the results reported here are inconsistent. It is difficult to determine to what extent they differ because of the uncertainties involved e.g. the geologic age of the Narragansett basin and the analytical uncertainty of the Wamsutta age measurement. It appears to be on the order of 10 to 20 %.

The results for the Pennsylvanian rocks from Rhode Island (Hurley et al. (1960)) have been discussed in detail. It is clear that the results reported here are consistent with data for the intrusive granite sills in the Pennsylvanian sediments but inconsistent with the results for the metamorphosed sediments.

Lambert and Mills (1961) reported a mean K-Ar and Rb-Sr age of 285 ± 8 M. Y. for the Dartmoor and Land's End granites. The Lands'End granite is only known to be post-Lower Devonian. The Dartmoor granite is known to be post-lower Westphalian. Lower Westphalian sediments of Europe are correlated with Atokan (pre-Desmoinesian) of the Mid-Continent and Middle Pottsvillian of the Appalachian mountains in North America (Branson, (1962)) (see Table IV for Pennsylvanian divisions). Therefore, Lower Westphalian is approximately equivalent to early Pennsylvanian in North America. For the Dartmoor granite itself, Lambert and Mills reported biotite K-Ar ages of 270 (Lamont) and 290 M. Y., and a biotite Rb-Sr age of 300 M. Y. ($\lambda = 1.39 \times 10^{-11}$ yr^{-1}). Comparison of these ages with those of the present investigation indicate a minimum discrepancy of approximately 15 %, based on the assumption of a maximum geologic age for the Dartmoor granite and a minimum geologic age for the Narragansett basin. If the Dartmoor granite is lowermost Permian as thought probable by Lambert and Mills, and by Kulp, then the discrepancy is greater than 15 %.

The Vosges granite (France) (Faul (1960) p. 636) is pre-Visean and post-Tournaisian. Faul reported three Rb-Sr biotite ages of 340 ($\lambda = 139. \times 10^{-11} yr^{-1}$) and four K-Ar biotite ages of 315 M. Y., giving a mean of 328 M. Y.. Comparison of these data with the results here reported is difficult owing to the extrapolations to common geologic age boundries and lack of knowledge of the length of time involved in the Carboniferous period. If the Narragansett basin sediments are as young as late Carboniferous and the total length of that period is approximately 100 M. Y. then the results are reasonably consistent.

The Age and Correlation of the Blue Hills Complex, Cape Ann granite and the Newbury Volcanics.

In this section results are reported for the Blue Hills complex, Cape Ann granite and the Newbury volcanics. Particular interest in the Blue Hills complex stems from its relation to the Pennsylvanian Norfolk-Narragansett basin south of Boston. This is discussed in the preceding section. The Cape Ann granite has been correlated with the Blue Hills complex and both are part of the extensive alkaline igneous province in New England. The Newbury volcanics are also considered a part of this igneous province.

The Blue Hills Complex. The Blue Hills complex includes the normal, or medium to coarse-grained Quincy granite, the Blue Hills granite and quartz porphyries, the Blue Hills aporhyolite and the rhombenporphyry. This complex occurs in an area approximately three by nine miles and includes all of the Blue Hills Reservation on the south, in the towns of Milton and Quincy, Massachusetts, and underlies most of the rest of Quincy to the north. Crosby (1895, 1900) first studied the area in detail. Dale (1923) described the Quincy granite from the many quarries in the area. Loughlin (1911) described the relation of the Blue Hills complex to the sediments of the Norfolk (Narragansett) basin. The most detailed study of the Blue Hills complex was done by Warren (1913). The complex as a whole is high in silica, alkalies, and iron, compared with most granitic rocks, and is low in calcium and magnesium. There is slightly more potash than soda. The granite and porphyry consist of quartz, microperthite, riebeckite and aegirite.

The normal Quincy granite occurs in the northern part of the complex, in southern Milton north of the Blue Hills, and in Quincy. The Quincy granite does not occur in the Blue Hills except at the extrene north end at Rattlesnake Hill and possibly at Chickatawbut Hill which is well within the Blue Hills. (see Figure 6, p.197). Crosby (1895) reported that the normal granite graded into fine-granite and porphyry in the area just east of Chickatawbut Hill. Warren (p. 210) states that he searched diligently in this locality and was unable to find any strictly normal Quincy granite showing these relations. Warren writes that he did observe dikes of granite cutting the porphyry, and at one outcrop, instead of dikes, he observed what he thought was granite porphyry grading into normal granite. The question of normal Quincy granite occuring around Chickatawbut Hill, as either cross cutting dikes or at graditional contacts with the porphyry, is a crucial point in the argument of the geologic age relation between the granite and the porphyry. It should be pointed out that the granite

Which occurs in this area does not exactly resemble the normal granite (Personal communication, M. P. Billings), and its true status is not yet determined. The fine-grained phase occurs in eastern and southern Quincy and in north Weymouth. It is restricted, by and large, to the northeastern edge of the normal granite. The granite porphyry with its quartz porphyry phase occupies most of the Blue Hills proper. It occurs nowhere outside of the Blue Hills except at Pine Hill just outside of the reservation. Pine Hill is another crucial locality where the porphyry, the fine granite, the coarse granite, the aporhyolite and the rhombenporphyry occur in a small area. The porphyry does not occur to the north in the Quincy area at all (Warren (1913) p. 238ff).

The rhombenporphyry occurs at Pine Hill, Pine Tree Brook and a few other areas. It occurs as xenoliths in the intrusive rocks and is frequently associated with the Braintree slate xenoliths (Warren (1913), p. 263ff).

The aporhyolite occurs in three localities restricted to the Blue Hills. The largest occurrence extends from Pine Hill just east of the park to the summit of Wampatuk Hill and south of Rattlesnake Hill south to the swamps in northern Braintree. Another occurrence is north of Fox Hill and the third and smallest exposure is at the top of Hemingway Hill. The aporhyolite, like the porphyry is restricted to the Blue Hills in the southern part of the complex. It has an aphanitic groundmass with a few feldspar and quartz phenocrysts. Spherulites and flow banding are present (Warren (1913), p. 284-291). In addition to the above there are three pegmatites, a few granite dikes cutting the granite, and a few granite dikes cutting the porphyry (Warren (1913), p. 292).

Warren's interpretation of the Blue Hills complex is as follows: A single, relatively undifferentiated magma intruded the Middle Cambrian Braintree slate. The rhyolite (aporhyolite) was extruded on the surface or intruded near the surface. A cover of porphyry formed at the top of the intrusive mass as a contact facies. This insulated the inderlying magma, and provided an opportunity for the medium to coarse-grained normal Quincy granite to form. In the northeast section of the complex a fine-grained granite is the contact phase. The magma beneath this porphyry cover broke through in a few places as granite dikes in the area east of Chickatawbut Hill. The only differentiate was the rhombenporphyry which formed adjacent to the slate contacts. This phase broke up and sunk, forming xenoliths in the parent magma. The whole complex was faulted and elevated on the north, with subsequent erosion of the porphyry cover from the northern part of the complex. The relative ages of the members of the complex based on the above interpretation are, from oldest to youngest; the aporhyolite and the rhombenporphyry, the granite porphyry and the Quincy granite. Presumably all phases were practically contemporaneous and were emplaced in a short time interval. In general, although not in every detail, the above interpretation has been accepted by geologists working in the area.

The geologic age of the complex is somewhere between post-Middle Cambrian to middle or late Pennsylvanian. This is based on the Middle Cambrian Braintree slate xenotiths, on one hand, and the Blue Hills porphyry pebbles in the middle or late Pennsylvanian Pondville conglomerate on the other. The conglomerate contains pebbles of the Blue Hills porphyry; no normal Quincy granite has ever been found.

Results and Discussion. Five samples of normal Quincy granite, three samples of Blue Hills quartz porphyry, four samples of aporhyolite and one sample of rhombenporphyry have been analyzed. All samples are whole-rocks. The results are shown in Table VII. The isochrons for the normal Quincy granite, the Blue Hills quartz porphyry and the aporhyolite are shown in Figures 6.1 (p.205), 6.2 (p.206), and 6.3 (p.207), respectively. Figure 6.4 (p. 208) shows all three isochrons for comparison. The Quincy granite isochron (Figure 6.1 (p.205)) indicates an age of 325 ± 15 M. Y. with an initial Sr^{87}/Sr^{86} ratio of 0.728 ± 0.008. The large uncertainty of the initial ratio arises from lack of samples with low Rb/Sr ratios. It is clear however that the initial ratio of the granite is well above the basaltic range of $0.708 {}^{+0.002}_{-0.003}$ (Faure and Hurley(1962)). This indicates that the material of the Quincy granite is partially or wholly of crustal origin. Hurley et al. (1960) reported a minimum K-Ar whole-rock age of 280 ± 15 M. Y. for normal Quincy granite. The results reported here for the Quincy confirm this and indicate that the age is close to 325 ± 15 M. Y.. The Blue Hills quartz porphyry isochron (Figure 6.2 (p. 206)) indicates an age of 245 ± 10 M. Y. and an initial ratio of 0.722 ± 0.002. The age of the porphyry is clearly younger than that

Table VII

Blue Hills Complex

Sample	Rb ppm.	Sr ppm.	$\frac{Rb^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$\left(\frac{Sr^{87}}{Sr^{86}}\right)_{.1194}$
R4700 Quincy granite	157.5[a]	11.1 [a]	41.7 [a]	0.1200	0.9200	0.9223
R4770 Quincy granite	164.	4.78[a]	104.	0.1204	1.1645	1.1693
R5064 Quincy granite	185.	10.0	55.0	0.1216	0.9657	0.9746
R5065 Quincy granite	157.	8.26	56.6	0.1204	0.9965	1.0007
R5067 Quincy granite	137.	15.8	25.3	0.1207	0.8348	0.8893
R4701 porphyry	200.5[a]	80.35[a]	7.24[a]	0.1186	0.7486	0.7461
R4702 porphyry	141. [a]	117. [a]	3.51[a]	0.1201	0.7327	0.7348
R4772 porphyry	164.5[a]	4.29[a]	115. [a]	0.1195	1.1122	1.1125
R5090B aporhyolite	269.	11.1	71.7	0.1198	0.9418	0.9434

Table VII, continued:

Blue Hills Complex

Sample	Rb ppm.	Sr ppm.	$\frac{Rb^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})_{.1194}$
R5090C aporhyolite	101.	12.6	23.4	0.1199	0.7903	0.7920
R5091A aporhyolite	178.	9.72	53.9	0.1210	0.8756	0.8815
R5091B aporhyolite	188.	4.44	128.	0.1200	1.1780	1.1810[1]
R5068 rhomben-porphyry	--- --	--- --	(0.9)[2]	0.1210	0.7072	0.7119

1 Incomplete analysis, only 18 sets obtained.
2 Semi-quantitative value determined by a single scan on X-ray spectrograph.
a Average of two analyses.

of the normal granite. The initial ratio is higher than that of basaltic rocks in general and equal to or less than that for the normal granite. This indicates that the material comprisind the Blue Hills porphyry is likewise partially or wholly of crustal origin. The Blue Hills aporhyolite isochron (Figure 6.3 (p207) indicates and age of 248 ± 10 M. Y. and an initial ratio of 0.708 ± 0.004. This age is analytically the same as the porphyry. The initial ratio is less than that of the porphyry and falls within the range for basaltic rocks. The measured Sr^{87}/Sr^{86} for the rhombenporphyry (R5068) is 0.712 ± 0.002. Since the rhombenporphyry is intruded by the normal Quincy granite its age must be greater than 325 M. Y.. It is younger than Middle Cambrian Braintree slate and must therefore be less than (approximately) 500 M. Y.. The initial ratio calculated on the above basis is 0.707 ± 0.003. This is within the range for basaltic rocks.

The Rb-Sr whole-rock results do not agree with Warren's (1913) interpretation for the Blue Hills complex. According to that interpretation the whole complex should be co-magmatic and essentially contemporaneous. Relatively, the normal granite should be the youngest, the porphyry and the aporhyolite the oldest members of the complex. According to the Rb-Sr whole-rock ages the normal Quincy granite is approximately 75 M. Y. older than the porphyry and aporhyolite.

On that basis not only is the age relation the reverse of Warren's interpretation but the granite is a separate intrusive.

The rhombenporphyry can not be a simple differentiation product of the granite magma because its initial ratio is less than that of the normal granite.

Although the aporhyolite and the quartz porphyry are essentially the same age their initial ratios are different. One possible explanation is simply that there were separate magmas derived from different source material. Another possibility is that the intrusive phase (the porphyry) of a single magma became contaminated with crustal strontium while the extrusive part (aporhyolite) did not, and thereby preserved the initial ratio of the magma. With the data at hand, it is not possible to prove which of these alterations is true. However, since there is nothing in the chemistry or mineralogy of the porphyry to indicate that it is contaminated relative to the porphyry, the simplier hypothesis of separate magmas is chosen as the most reasonable.

Therefore, the Rb-Sr whole-rock age results suggest that the Blue Hills complex was formed by four separate intrusions of magma. The normal Quincy granite crystallized 325 ± 15 M. Y. ago. This would be approximately late Devonian according to the results of this report. Based on field relations, the age limits of the rhombenporphyry are pre-late Devonian and post-Middle Cambrian. It is not a simple differentiation product of the granite. The aporhyolite and the quartz porphyry are essentially the same age and crystallized about 245 ± 10 M. Y. ago. This corresponds to an early or middle Pennsylvanian age according to data elsewhere in this work. Their different initial ratios indicate that these rocks were probably formed from separate magmas although the alternate possibility of a single, partly contaminated magma can not be dispoved.

It is not possible at this time to bring into accord the conflicting field interpretation of Warren and the present geochronological evidence. Billings (informal discussion) agrees that there is no incontrovertible field evidence at this moment which could be used to decide between the alternate possibilities. A new field and petrologic investigation of the complex, combined with further investigations, is certainly in order.

<u>The Cape Ann Granite</u>. The geology of Essex

County, Massachusetts was investigated by Clapp in 1921. This area includes the Cape Ann granite and the Newbury volcanics. In Clapp's work the Cape Ann granite is refrerd to as the Quincy granite from Cape Ann. This correlation of the alkaline granitic rocks of eastern Massachusetts is currently an accepted geological interpretation. The geological age of this group is given by Clapp (1921) as Carboniferous; by La Forge (1932) as pre-Lower Pennsylvanian, and probably Mississippian; and by Bell (1948) as late Silurian to early Devonian. There is no direct field evidence to date the Cape Ann granite and part of the diversity of opinion depends on the correlations involved. The alkaline rocks correlated with the Cape Ann granite intrude the sub-alkaline rocks (Salem gabbro-diorite, Dedham granodiorite etc.) in adjacent areas. This correlation requires the Cape Ann to be younger than the sub-alkaline suite. The age of the sub-alkaline suite is based on the following: At Nahant, Massachusetts, The Nahant gabbro intrudes the Lower Cambrian Weymouth formation. If the Nahant gabbro is part of the sub-alkaline suite (Emerson (1917)) then the gabbro is post-Lower Cambrian and the Cape Ann granite is younger than post-Lower Cambrian. If the Nahant gabbro is part of the alkaline suite (Clapp (1921)) then the gabbro and the Cape Ann granite are post Lower Cambrian.

At Hoppin Hill, North Attleboro, Massachusetts, 80 miles to the south, the Dedham granodiorite (sub-alkaline suite) is unconformably overlain by the Lower Cambrian Hoppin formation. If the Dedham granodiorite from Hoppin Hill is part of the sub-alkaline province from Essex County, then the sub-alkaline suite is pre-Cambrian and the Cape Ann granite is post-pre Cambrian. In summary, very little is known about the geological age of the Cape Ann granite. It is probably younger than post-Lower Cambrian.

The Cape Ann ia a massive, uniform granite consisting of microperthite, quartz, green katophorite and hedenbergite with accessory zircon, apatite, magnetite, and rarely biotite (Clapp (1921)).

<u>Results and Dicussion</u>. Five whole-rocks were collected and analyzed from Cape Ann. The results are shown in Table VIII and the isochron in Figure 6.5 (p.220). The isochron indicates an age of 415 ± 10 M. Y. and an initial Sr^{87}/Sr^{86} ratio of 0.709 ± 0.002. This initial ratio falls within the range for basaltic rocks.

Table VIII

Cape Ann Granite, Cape Ann, Massachusetts

Sample	Rb ppm.	Sr ppm.	$\frac{Rb^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})_{.1194}$
R4953	238.	13.2	53.8	0.1213	1.0217	1.0298
R4954	236.5[a]	11.2	63.3	0.1209	1.0547	1.0613
R4955	198. [a]	4.81	128.	0.1199	1.4319	1.4349
R4956	137. [a]	10.95[a]	37.1 [a]	0.1207	0.9233	0.9283
R4957	107.	53.2 [a]	5.83	0.1203	0.7401	0.7429

[a] Average of two analyses.

In the section on geology it was shown that little is known about the geologic age of the Cape Ann granite. Correlation with other igneous rocks of the area indicates only a post-pre Cambrian or post-Lower Cambrian age. The age measurements from this work indicates a late Ordovician or early Silurian age.

Hart (1951) reported a K-Ar hornblende age of 310 ± 10 M. Y. for the Cape Ann granite. Presumably this reflects partial loss of radiogenic argon from the mineral.

These results show that the Cape Ann granite, Quincy granite, and the Blue Hills porphyry and aporhyolite are not contemporaneous but represent different events.

The Newbury Volcanics. The Newbury volcanics are located in Essex County, Massachusetts, near the town of Rowley. The geology of the area has been described by Emerson (1917), Clapp (1921), La Forge (1932) and dos Santos (1960). Dos Santos (1960) divided the volcanics into four menbers: lower rhyolite, andesite, upper rhyolite and basalt. The designation "andesite" and "basalt" are for stratigraphic convenience only, since the original minerals of these basic volcanics have been completely altered. The "andesite" member contains lenses of slate and conglomerate in which fossils have been found. In 1915 Keith found some fossils in a calcareous shale in the andesite member. (Emerson, (1917)). The fossils, which were scarce and poorly preserved, could not be precisely dated and ranged in age somewhere between late Silurian and early Devonian (Emerson (1917)). There is later work which agrees with the earlier determinations (dos Santos (1960)). The Newbury volcanics are considered part of the alkaline suite of eastern Massachusetts. La Forge (1932) and Bell (1948) correlated the volcanics with the intrusion of the Quincy (Cape Ann) granite. Clapp (1921) and Emerson (1917) consider the volcanics as older than the granites.

Results and Discussion. Three rhyolite samples from the upper rhyolite member and two samples of the basic volcanics, from the andesite and basalt members, have been analyzed. The analytical results for these five whole-rock samples are reported in Table IX and the isochron is shown in Figure 6.6 (p.226). The isochron yields an age of 345 ± 10 M. Y. and an initial ratio of 0.709 ± 0.001. The single value of 0.709 ± 0.001 for the initial ratio of

Table IX

Newbury Volcanics, Rowely, Massachusetts

Sample		Rb ppm.	Sr ppm.	$\frac{Rb^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})_{.1194}$
R4308	Rhyolite	78.4	151.	5.64	0.1179	0.7414	0.7367
R4312B	Rhyolite	21.0	217.	30.3	0.1198	0.8550	0.8566
R4310	Rhyolite	22.35[a]	215.	28.2	0.1191	0.8416	0.8415[1]
R4311	"Basalt"	8.40	560.	0.04	0.1188	0.7121	0.7103
R4312	"Andesite"	25.3	903.	0.08	0.1196[a]	0.7081[a]	0.7088[a]

[1] Incomplete run, only 18 sets obtained.
[a] Average of two analyses.

both the rhyolites and the basic volcanics is compatible with a single genetic history for the two rock types and falls within the range for basaltic rocks.

The Newbury volcanics are slightly younger than the Kineo volcanics reported above. Taking into consideration the estimated errors it is concluded that the Newbury could be as old as but no older than the Kineo volcanics. Therefore, the Newbury volcanics can not be as old as the late Silurian but are early Devonian, probably somewhere between upper Lower Devonian and lower Middle Devonian. The Rb-Sr result is for the upper rhyolite only. This rhyolite is approximately 1000 feet stratigraphically above the fossils. Presumably this represents an insignificant length of time compared to the errors involved.

The Newbury volcanic activity, according to the Rb-Sr age result, was not contemporaneous with the Cape Ann granite or with the intrusives of the Blue Hills complex. The only possible exception would be the normal Quincy granite, since the error estimates for the two isochrons overlap.

Summary and Conclusions.

A summary of the results reported above is shown in Table X. The ages are internally consistent

Table X

Summary of Whole-rock Rb-Sr Ages and $\left(\frac{Sr^{87}}{Sr^{86}}\right)_0$

$(\lambda_{Rb} = 1.39 \times 10^{-11} \times yr.^{-1})$

Sample and Locality	Geologic Age	Rb-Sr Whole-rock Age (M. Y.)	$\left(\frac{Sr^{87}}{Sr^{86}}\right)_0$
Cape Ann granite. Cape Ann, Mass.. Chapter 6.	Post-Lower Cambrian	415 ± 10	0.709 ± 0.002
Arisaig volcanics. Arisaig, Nova Scotia. Chapter 4.	Basal Silurian (possibly as old as post-Lower Ordovician)	405 ± 10	0.709 ± 0.001
Kineo volcanics. Moose River synclinorium. West central, Maine. Chapter 3.	Upper Lower Devonian	360 ± 10	0.715 ± 0.001
Newbury volcanics. Rowley, Mass,. Chapter 6.	Early Devonian to late Silurian	345 ± 10	0.709 ± 0.001

Table X, continued.

Sample and Locality	Geologic Age	Rb-Sr Whole-rock Age (M. Y.)	$\left(\frac{Sr^{87}}{Sr^{86}}\right)_0$
Blue Hills complex. Quincy and Milton, Mass.. Chapter 6.	Post-Middle Cambrian to pre-middle or late Pennsylvanian		
Normal Quincy granite		325 ± 15	0.728 ± 0.008
Blue Hills aporhyolite		248 ± 10	0.708 ± 0.004
Blue Hills porphyry		245 ± 10	0.722 ± 0.002
Rhombenporphyry		--------	0.707 ± 0.003
Wamsutta volcanics. Narragansett basin. South Attleboro, Mass.. Chapter 5	Middle or late Pennsylvanian		
Rhyolite		225 ± 25	0.721 ± 0.002
Basalts		--------	0.708 ± 0.001

and do not contradict geologic facts so far as known. There are areas of disagreement with previous geological interpretation. In particular, the sequense of events in the Blue Hills complex, based on the Rb-Sr interpretation, differs from Warren's(1913)interpretation. The correlation of the Quincy and Cape Ann granites is another generally accepted interpretation with which the results reported here differ.

In Table XI the areas studied which have known geologic ages are compared with Kulp's and Holmes' 1960 time scale estimates. In addition Holmes' 1947 time scale is shown. The results reported here are approximately 8 % below the recent time scale in the Devonian-Silurian section and the discrepancy apparently increases in the Pennsylvanian. The age result for the Pennsylvanian Wamsutta volcanics is too uncertain to form a realistic estimate of the discrepancy. The result reported for the Blue Hills porphyry indicates a discrepancy of 10-20 % depending on the exact geologic age of the porphyry. This apparent discrepancy could be caused by systematic analytical error in the work reported here. However, the only reasonable source of a systematic error of this magnetude would be faulty calibration of the spikes used for Rb and Sr analyses.

Table XI

Summary of geologically well dated areas shown with time scale estimates

Holmes (1947)			Holmes (1960) Kulp (1960)	Whole-rock Rb-Sr ages ($\lambda = 1.39 \times 10^{-11}$ yr^{-1})
182			220	
		Upper	235	
	Permian	Middle	250	
203		Lower	270	
		Upper		
	Pennsylvanian	Middle		Wamsutta volcanics 225 ± 25 M. Y. Blue Hills porphyry 245 ± 10 M. Y.
		Lower	320	
		Upper		
	Mississippian	Middle		
255		Lower	350	
		Upper	365	
	Devonian	Middle	380	Newbury volcanics 345 ± 10 M. Y. Kineo volcanics 360 ± 10 M. Y.
313		Lower	400	
		Upper		
	Silurian	Middle		
350		Lower	430	Arisaig volcanics 405 ± 10 M. Y.
		Upper		
	Ordovician	Middle		
430		Lower	490	
450		Upper	510	
	Cambrian	Middle		
520		Lower	600	

In the section on analytical procedure it was shown that these spikes gave no indication of a systematic error of this magnitude.

Comparison with other radioactive age work on the areas studied indicated no such large discrepancy. In all cases the results overlap and if there is any contradiction it is on the order of a few percent. The interpretation suggested for this overlap of the minimum ages from intrusives and the direct age of the strata from volcanics is that the interval of time between sedimentation, burial, and intrusion was less than the uncertainty of the measurements.

The consistency of the results for volcanics (and related granites) of different geologic ages and different orogenic histories indicates no significant loss of radiogenic strontium from the rocks and suggests that the ages obtained are those of the source magmas themselves. This is of considerable significance, since the volcanic suites analyzed, with the exception of the Wamsutta volcanics, were regionally metamorphosed. The age results indicate that this did not effect the relative age pattern. If subsequent metamorphism had affected the primary ages there should be some correlation between increasing (older) geologic age and decreasing radioactive ages. Thus far no such trend is indicated. In fact the younger rocks studied in this investigation show ages which, if anything, are realtively too young rather than too old. Although the present data apparently do not reflect the influence of regional metamorphism, it is not implied that high temperature contact metamorphism, metasomatism, extreme faulting, etc. would not show a different pattern. A small start in this direction has been made on the Kennebec volcanics (Moose River synclinorium, Maine) which occur in a highly sheared area.

The conclusion based on internal consistency, that the whole-rock Rb-Sr ages reflect the ages of extrusion, is not the same as stating that they are the ages of extrusion, and consequently give the true ages of the strata with which they are interbedded. The proof of consistency is only the first step and the easiest. The second step requires comparison against a known standard. Since there is no <u>a priori</u> knowledge of the "true" ages of the geologic periods, results must be compared with the empirical approximations to "true" ages, which is assumed to be represented by the average of superior radioactive age measurements employing different decay schemes. The time scale is this approximation.

For the geologic periods studied in this work the time scale is based almost exclusively on K-Ar and Rb-Sr ages on biotites. In each section, Kulp's (and Faul's) critical points were reviewed and need not be repeated here in detail. It was shown that in three cases there are clearcut contradictions with the whole-rock data (Lower Permian (Norway), Lower Permian (England), post Silurian-pre Upper Devonian (Calais, Maine)) and in three cases the results overlap (post-middle or late Pennsylvanian (Rhode Island), late Lower Carboniferous, Vosges (France), post-Silurian-pre Carboniferous (Nova Scotia)). The Shap granite (England) and the Leinster granite (Erie) are only known to be Lower Devonian by correlation, and no final decision about their relation to the whole-rock results can be made.

It is believed, in summary, that these whole-rock investigations constitute a step in unravelling magmatic history. Work on volcanics which are close in geologic age to those studied here should confirm or deny the consistency thus far demonstrated. In addition, the data at hand warrant the conclusion that reliable correlations can be made using Rb-Sr whole-rock isochrons and that geologic age assignments can be made if the assignment is based on comparison with other whole-rock isochrons.

The determination of an isochron is in most cases a necessity. The content of radiogenic strontium in most rocks is low compared with minerals normally used for age work. For the few cases where the Rb-Sr ratio is high enough to calculate ages of reasonable precision, isochrons are still recommended because more information can be obtained from the data (e.g. the initial ratio) and more certainty can be attached to the age result.

The problem of correlating the alkalic granites in New England has been discussed by Toulmin (1961). He gives a summary of the recent age work and concluded that there were at least two ages of intrusion, 185 and 280 M. Y. ago. The latter is based on a whole-rock K-Ar result from the Quincy granite which is interpreted as a minimum age (Hurley et al. (1960)). The whole-rock Rb-Sr age reported here confirms that result and indicates that the age is close to 325 ± 15 M. Y.. Other whole-rock ages from this work suggest at least two and maybe three additional periods of igneous activity of the "alkalic" type. The Cape Ann granite which is correlated with the Quincy, and the Blue Hills porphyry and aporhyolite which are considered phases of the Quincy, give ages of 405 ± 10 M. Y. and 245 ± 10 M. Y., respectively. In addition, the Newbury volcanics which are generally considered an extrusive phase of this igneous activity give an age of 345 ± 10 M.Y.. Toulmin suggested that caution should be exercised in assigning geologic ages to undated alkalic intrusives in New england until reliable criteria has been established. The results reported here agree with and emphasize that suggestion. It appears, according to the age results for the Blue Hills complex, that even close field association and similar mineralogy are no guarantee that two igneous bodies are contemporaneous.

The initial ratios obtained during this investigation are tabulated in Table X and show that the initial ratios for granitic extrusives and intrusives are variable. The values reported range from 0.708 ± 0.004 to 0.728 ± 0.008. Of the eight initial ratios determined for granites and rhyolites, four fall within the range for basaltic rocks and four have higher values. All measurements on basic rocks yielded initial ratios in the basaltic range reported in the literature.

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PART II

Chapter 1

Introduction

The determination of radioactive ages for events in the geological or fossil time scale is one of the challenging problems in geochronology. Volcanic rocks are well suited for this purpose because of their conformable relation to the strata. The recent developments of Rb-Sr whole-rock age studies (Compston and Jeffery (1959), Fairbrain et al. (1960), and others) indicates that whole-rocks are less suceptible than minerals to loss of radiogenic strontium. These two factors combined suggest that whole-rock investigations of volcanic sequences should be a powerful tool for time scale studies.

The reliability of any technique must be evaluated in terms of its consistency and accuracy. The consistency of an age method can be demonstrated by analyzing suites of samples of known relative age, and then comparing the results with the relative ages. In addition, for many suites, a reasonable estimate can be made of the age spacing between suites as well as of the age sequence.

Before proceeding, a simple expression for the Rb-Sr decay scheme will be given (Faure (1961), Gast (1960)). For any radioactive nuclide,

$$(1) \quad \frac{N}{N_0} = e^{-\lambda t}$$

where

N = number of atoms at present

N_0 = number of atoms at $t = 0$

λ = decay constant

t = time elapsed since $N = N_0$.

Substituting the notation for the Rb^{87}-Sr^{87} decay scheme,

$$(2) \quad (Rb^{87})_p = (Rb^{87})_0 \, e^{-\lambda t}$$

where

$(Rb^{87})_p$ = N = number of Rb^{87} atoms at present

$(Rb^{87})_0$ = N_0 = number of Rb^{87} atoms at $t = 0$

λ = decay constant for Rb^{87}.

The number of radiogenic strontium atoms, $*Sr^{87}$, equals the difference between the number of original Rb^{87} atoms minus the number of Rb^{87} atoms at present.

$$(3) \quad *Sr^{87} = (Rb^{87})_0 - (Rb^{87})_p.$$

Rearranging eq. (2) and substituting in eq. (3) in order to eliminate $(Rb^{87})_0$,

$$*Sr^{87} = (Rb^{87})_p \, e^{\lambda t} - (Rb^{87})_p$$

$$(4)\ {}^{*}Sr^{87} = (Rb^{87})_p\ (e^{\lambda t} - 1)$$

The number of atoms of Sr^{87} present in the system is the sum of the radiogenic and non-radiogenic strontium atoms.

notation:

$(Sr^{87})_p$ = total number of Sr^{87} atoms at present

$(Sr^{87})_0$ = total number of initial or non-radiogenic Sr^{87} atoms.

and

$$(Sr^{87})_p = (Sr^{87})_0 + {}^{*}Sr^{87}$$

$$(5)\ {}^{*}Sr^{87} = (Sr^{87})_p - (Sr^{87})_0$$

Substituting eq. (5) in eq. (4) and rearranging,

$$(Sr^{87})_p = (Sr^{87})_0 + (Rb^{87})_p\ (e^{\lambda t} - 1)$$

Since the quantity measured is $(Sr^{87}/Sr^{86})_p$, it is convenient to divide through by Sr^{86} which is invariant with time.

$$(6)\ \left(\frac{Sr^{87}}{Sr^{86}}\right)_p = \left(\frac{Sr^{87}}{Sr^{86}}\right)_0 + \left(\frac{Rb^{87}}{Sr^{86}}\right)_p\ (e^{\lambda t} - 1)$$

This is a precise equation expressing the relation between the parameter in Rb-Sr geochronology. The term $(e^{\lambda t} - 1)$ can be approximated by expanding $e^{\lambda t}$ and taking the first two terms,

$$e^{\lambda t} = 1 + \lambda t + \frac{(\lambda t)^2}{2!} + \ldots\ldots$$

$$(e^{\lambda t} - 1) \cong \lambda t$$

and

$$(7)\ \left(\frac{Sr^{87}}{Sr^{86}}\right)_p = \left(\frac{Sr^{87}}{Sr^{86}}\right)_0 + \left(\frac{Rb^{87}}{Sr^{86}}\right)_p \lambda t$$

In the equation there are two measurable ratios, $(Sr^{87}/Sr^{86})_p$ and $(Rb^{87}/Sr^{86})_p$, and the decay constant for which measured values can be taken from the literature. At present, the choice of a decay constant from the available values is arbitrary. Wasserburg (1962) reviewed the laboratory determinations of the decay constant and pointed out that to date, a definitive measurement has not been made. In this thesis, the value taken is the geologically determined one, $\lambda = 1.39 \times 10^{-11}$ year $^{-1}$ (Aldrich et al. (1956)). $(Sr^{87}/Sr^{86})_0$ and t are determined from the measured values and the equation.

When the measured ratios for a suite of samples are plotted and yield a linear plot, an isochron, it means that the suite had a single value for t and $(Sr^{87}/Sr^{86})_0$. The fact that the data yielded an isochron suggests, although it does not prove, that the system was closed to Rb, Sr and radiogenic Sr. The possibility of uniform (fractional) gain or loss must be considered. It is not likely that common strontium or rubidium would be lost because these elements are stable within the mineral structures. However the diffusion of radiogenic strontium or the gain of rubidium can not be eliminated as reasonable possibilities. The best indication that the systems were closed is the demonstration that a family of isochrons, originating in suites of samples covering a wide geographical and geological range bear reasonable relation to each other and to their known or inferred geological ages. In that way, any mechanism, if one exists, which is acting to raise or lower the isochron slopes uniformly must be independent of the thermal and chemical history of the rock. Reliability must also be evaluated by comparing Rb-Sr methods with other radioactive age techniques. In the present investigation, for example, correlation is attempted with all other age data and with the recent time scale estimates of Kulp(1960), Holmes (1960), and Faul (1960).

In this investigation a series of volcanic rocks of different geologic ages from the northern Appalachians were studied. These included the basal Silurian (Arisaig, Nova Scotia), Lower Devonian (Kineo, Maine), late Silurian or early Devonian (Newbury, Massachusetts), and the Pennsylvanian (Wamsutta, Massachusetts) volcanic suites. In addition

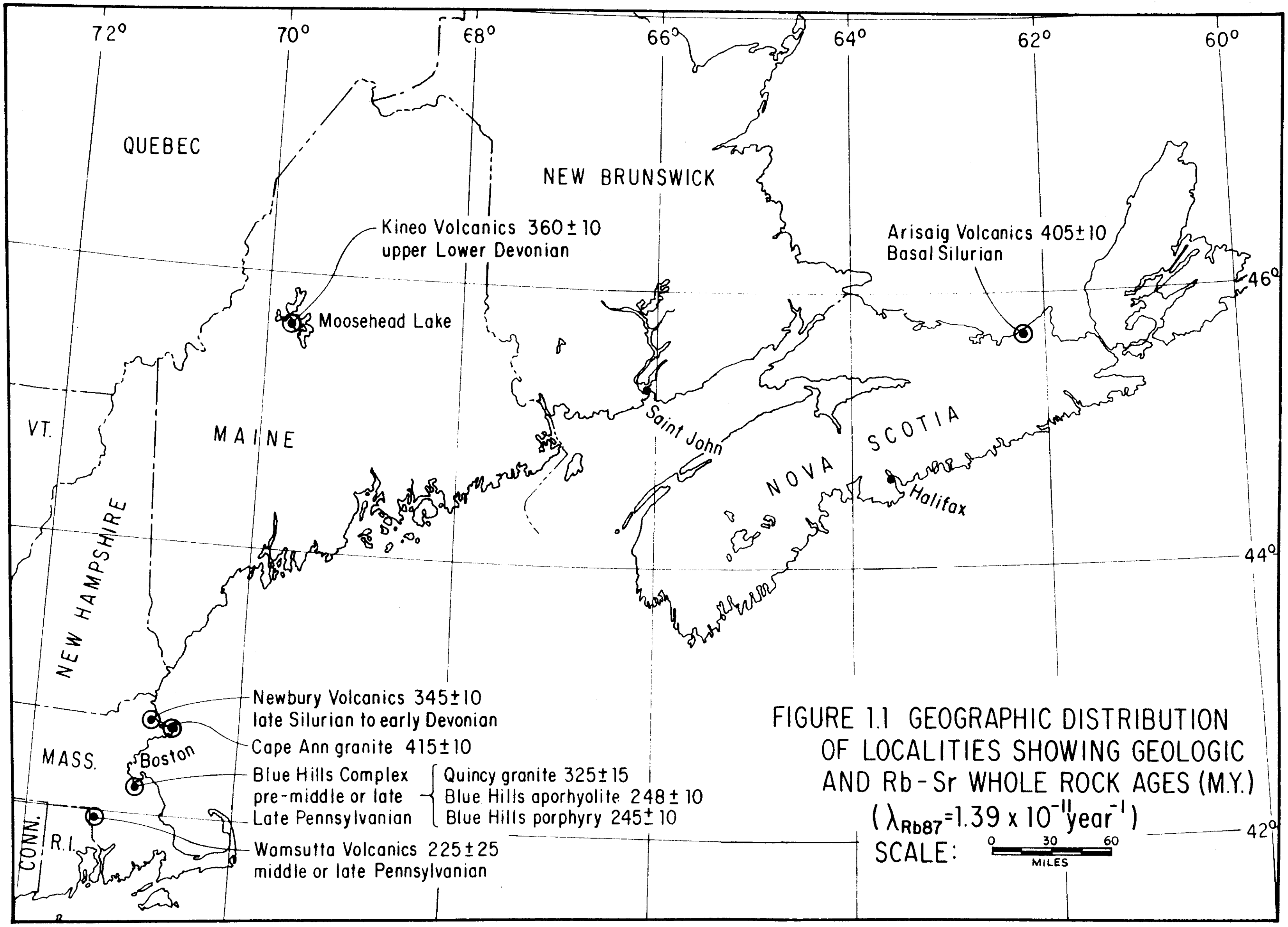


FIGURE 1.1 GEOGRAPHIC DISTRIBUTION OF LOCALITIES SHOWING GEOLOGIC AND Rb-Sr WHOLE ROCK AGES (M.Y.) ($\lambda_{Rb87} = 1.39 \times 10^{-11} year^{-1}$)

preliminary results are reported for the Middle Ordovician Kennebec volcanics from Maine and the pre Cambrian Coldbrook volcanics from New Brunswick. (see Figure 1.1). The Pennsylvanian volcanics (Wamsutta) occur in the Narragansett basin of Massachusetts and Rhode Island. The Blue Hills complex, which includes the Quincy granite and the Blue Hills porphyry and aporhyolite, stratigraphically underlie the Narragansett basin and thus defines a maximum age for the basin. Therefore it was possible to compare directly the results for the Wamsutta volcanics, interbedded with the sediments, to the maximum age for the sediments from the complex. Since the Cape Ann granite (Cape Ann, Massachusetts) has been correlated with both the Blue Hills complex and the Newbury volcanics, it was also included in the study.

Apart from the general considerations of testing a method of age dating, the individual areas studied have their intrinsic interest. In particular, the question of granite correlations in eastern Massachusetts and the origin of the Blue Hills complex are problems of interest in their own right. As mentioned above, these granites were included in the study because they define a maximum age for the Pennsylvanian volcanics of the Narragansett basin. As it developed, the results extended beyond this and some interesting information was obtained for the granites themselves both as to ages and initial ratios.

The initial Sr^{87}/Sr^{86} ratios obtained from the isochrons and from direct measurement of basic members of the suites, are compared with the Sr^{87}/Sr^{86} ratios for basaltic rocks reported by Faure and Hurley (1962) and Gast (1960). That work has shown that the distribution of Sr^{87}/Sr^{86} ratios for basaltic rocks is narrow and equal to $0.708 {}^{+0.002}_{-0.003}$. For geological reasons, the source region for basaltic rocks is considered to be the upper mantle or base of the crust and therefore the $0.708 {}^{+0.002}_{-0.003}$ value is representative of the strontium isotopic composition of that region. In addition, geochemical arguements are advanced to show that on average the crust must have a higher Sr^{87}/Sr^{86} ratio than basaltic rocks. On this basis an initial ratio higher than the basaltic value is considered to indicate that the rock was partially or wholly of crustal origin. If the initial ratio of a granite or rhyolite suite is equal to the basaltic value then the source magma for that suite may have been of sub-crustal origin. For the akaline granites from eastern Massachusetts, two of the four initial ratios were higher than that for basaltic rocks. Where there is a wide distribution of initial ratio values it is not clear whether the individual initial ratios are as significant as the distribution of the ratio values. In addition, the initial ratios of the basic and acid members of a suite are compared as a test of whether or not they are co-magmatic.

Chapter 2

Analytical Procedures

Introduction

The Laboratory procedures for the preparation of samples for isotope dilution and isotope ratio analyses have been described by Herzog and Pinson (1956) and Herzog et al. (1958) and in recent theses (Faure,(1961), Powell,(1962), and Whitney (1962)) The procedures used in this investigation were these standard procedures with a few modifications. In particular, at the suggestion of S. Moorbath, the Rb samples were isolated by precipitation as perchlorates instead of on the cation exchange column. The particular procedures followed in this investigation are described below.

Reagents

All the water used for chemical procedures was distilled and then demineralized in a commercial demineralizer.

Hydrochloric acid was distilled once in a vycor distilling flask. Acid of about 6N concentration was made from reagent grade, concentrated HCL by dilution with demineralized water. This was then distilled and the distillate diluted to 2N with demineralized water. The normality of the acid is minitored by measuring its density. For semi-automatic and hand operated columns this is sufficiently precise.

Vycor-distilled nitric acid of about 6N concentration was prepared by the same procedure as the HCl.

Reagent grade HF and $HClO_4$ were used with no further purification.

Preparation of the Sr^{85} tracer has been described by Winchester and Pinson (1962).

The Preparation of sample.

A chip or cut of fresh sample weighing approximately 25 grams was crushed in a jaw crusher and both chips and powder recovered. This was then transferred to a Pica blender mill and pulverixed. The sample holders were cleaned with tap water, distilled water and then dried with acetone before each sample was processed. Five to ten minutes in the mill was required to pulverize the sample. The sample was then transferred to a glass storage vial and no further homogenization was considered necessary.

Chemical Preparation for Strontium Isotope Ratio Analyses.

0.5 to 5 grams of powder were used for strontium isotope ratio measurements, depending on the amount of strontium in the sample. In general the samples were weighed only approximately. The large samples and small samples were for low and high strontium bearing rocks, respectively.

Both platinium and teflon dishes were used for dissolution of the samples. The dishes were cleaned by through scrubbing and rinsing with demineralized water and 2N vycor distilled HCl. If the Rb and Sr content of the previous samples were unknown, the additional precaution was taken of heating HCl in the dishes. The samples were dissolved in 25 to 100 ml of HF and 2-10 ml $HClO_4$. A Few drops of Sr^{85} tracer were added. The dishes were placed on a hot plate and evaporated to near dryness or dryness. After cooling for a few minutes (to prevent spattering) demineralized water and a minimum amount of 2N HCl were added. The dishes were returned to the hot plate. If a clear solution was obtained, the samples were evaporated to 10 to 50 ml and removed. If a satisfactory solution was not obtained, more 2N HCl was added and the sample allowed to digest again. If necessary the whole procedure was repeated. The samples were transferred to a clean 100 ml beaker or a clean polyethylene bottle. After overnight cooling the samples were filtered to remove any precipitates. The solution and residue were both checked with a counter to ensure that the strontium was not lost in the precipitates.

The filtered solution was then carefully put on a clean cation exchange column of Dower 50X, 8 % cross linked, 200-400 mesh. These are large columns, approximately 2.5 cm. in diameter and 50 cm. long with about 30 cm. of resin. The columns were cleaned between samples with 500-1000 ml. of 2N HCl. The samples were loaded by removing the column from the stand, holding it almost horizontal and carefully pouring the sample down the side of the column without disturbing the resin. The walls of the column were then washed down with demineralized water and the sample allowed to soak into the resin. It was then washed twice with approximately 25. cc of 2N HCl. The 2N HCl was put into the column by the same procedure used for loading the sample. After this second wash the feeder bottles were loaded with about 600 cc of 2N HCl and feed through the columns.

This required approximately 10 hours. The 600 cc of 2N HCl would bring the Sr sample to within an inch of the bottom of the column. The automatic feeders were disconnected and the sample was collected in 100 ml. beakers by further elution with 2N HCl. The beakers were evaporated to dryness and the strontium collected into one beaker, evaporated to dryness, and stored as $SrCl_2$.

If the sample was to be run on the mass spectrometer as a nitrate, the $SrCl_2$ was first fumed with a few drops of perchloric acid in order to destroy any resin in the sample. After fuming to dryness, the beaker was cooled, a few drops of HNO_3 were added and evaporated to dryness. This was usually done twice, in order to concentrate the strontium into one small area in the beaker.

If the sample was to be run as oxalate, demineralized water and a crystal of ammonium oxalate were added to the beaker. The beaker was put on a steam bath, evaporated to a small volume, then allowed to cool. The supernatant solution was removed using a medical syringe and a capillary tube. The precipitate was washed once or twice with demineralized water and the sample was ready for the mass spectrometer.

Chemical Preparation for Strontium and Rubidium Analyses.

0.3 to 5 grams of sample were accurately weighed out for isotope dilution analyses. The size of the sample depended principally on the Sr content of the sample. Samples were taken which were large enough to insure that the blank correction was no more than ± 1 % of the total strontium. In some cases this was not possible without excessively large samples. For samples containing in the range of 10 ppm strontium, approximately 3 grams of sample were used, Samples of this size contained so much rubidium that separate spiking on smaller samples was required in order to obtain a favorable spike to normal ratio and not use excessive amounts of spike. In the future it would probably be an improvement if this type of high Rb/Sr sample was quantitatively dissolved, diluted to volume and aliquots taken for analyses.

For samples in the 50-100 ppm. strontium and 100-200 ppm. Rb range a single weighing of approximately 1 gram sufficed for both analyses.

After spiking the samples were chemically treated as previously described for the strontium isotope ratio analyses until the last step. The final solution in this case was achieved with demineralized water and with a minimum of HCl.

This solution was evaporated to a very small volume, removed and allowed to cool. When the alkali perchlorate precipitate formed, the supernatant solution was decanted into a clean beaker. The precipitate was washed several times with demineralized water and the washings added to the beaker. The Sr^{85} tracer which was added at the beginning of the procedure was monitored with a counter to insure that most of the strontium was recovered in the solution fraction. This solution was processed on the columns as described above for the unspiked strontium. The alkali perchlorate precipitate containing the Rb was then washed into a small beaker and evaporated to dryness. Nitric acid was added and evaporated to dryness. The sample was then stored.

Strontium isotope dilution samples were all run as nitrates. The preparation is the same as described above for the unspiked samples.

Mass Spectrometry.

The mass spectrometer used in this investigation is a 60° sector, 6 inch radius, single filament, solid source, single collector instrument. With one exception (Whitney, 1962), the same spectrometer has been used for all thesis investigations over the past three years (Schnetzler (1961), Faure (1961), Powell (1962))

With a few exceptions all strontium isotope ratio analyses were done on this instrument. Another instrument, used for runs is identical in design and gives comparable results on a standard strontium carbonate (Whitney (1962)) and on duplicate runs. Isotope dilution analyses were done on these two as well as a newer, but similar solid source machine in the laboratory. All three units were built at M. I. T..

For strontium isotope dilution analyses the sample was loaded on the filament as a nitrate or oxalate. The nitrate method was used for most analyses. The nitrate sample was loaded on the filament by putting the smallest possible drop of nitric acid in the prepared sample and picking it up with a clean capillary tube attached to a syringe. This drop was evaporated on the filament and the filament was then heated to red heat for an instant.

The source was re-assembled and inserted in the mass spectrometer. As soon as a vacuum of 2×10^{-5} mm. Hg was obtained the filament current was raised to just below the Sr emission current. The sample conditioned until a vacuum of 3.5×10^{-6} Hg or better was obtained. Usually two or three hours was required to achieve this pressure. The filament current was raised until stable strontium emission began. Then the sample was checked for rubidium contamination by sweeping over the mass 85 peak. If Rb^{85} was present the filament current was reduced and the sample allowed to condition until the Rb^{85} was gone. "Gone" was defined as no visible Rb^{85} on the next most sensitive scale. In a very few instances some rubidium persisted and a correction was made. In any such case the correction was small and, where possible, all such runs were repeated. The peaks were recorded on either lined or unlined chart paper. Baseline was recorded every 6 to 18 sets depending on which sensitivity scale was used.Most of the runs were on the 30 and 300 millivolt or 100 and 1000 millivolt scales. Rarely, a run was made on the 10 and 100 millivolt scales. Runs on the strontium carbonate were usually made on both the 30 and 300 and the 100 and 1000 millivolt scales. Occasionally a standard run was partially made on the 10 and 100 millivolt scale.All scales gave the same results. A normal run consisted of 78 or more sets, usually 90. For samples highly enriched in radiogenic strontium fewer sets were required. 60 sets was the minimum. At the end of the run the filament current was raised to a maximum and the filament cleaned by monitoring with the spectrometer.

The peaks were measured to the nearest 0.01 inch, using an engineer's scale for unlined paper and by direct reading on ruled paper. The same results were obtained by either method. The peaks were measured in sets of six and ratios calculated for each set. These were averaged for the final result. The standard deviation of the mean of the unnormalized Sr^{87}/Sr^{86} ratio was calculated. This gave an instrumental precision error (%E) which was used as one indication of the quality of a run.

For strontium isotope dilution analyses the sample was handled in the same manner as described above. The vacuum required was only 2×10^{-5} mm. Hg or better, and in general no conditioning was required. Since only the Sr^{86} and Sr^{88} peaks were measured no check was made for rubidium contamination. The rest of the procedure is the same as that for isotope ratio runs except that only 42 to 60 sets were recorded.

Rubidium isotope dilution analyses were done by the same procedure as strontium isotope dilution analyses except that the filament was discarded after each run. The new filament was cleaned and checked in the mass spectrometer before mounting a new sample.

<u>Preparation of Shelf Solutions</u>.

Shelf or stock solutions are used to determine the concentration of the strontium and rubidium spikes. The accuracy of the rubidium and strontium analyses depends on the accuracy of these spikes. In addition to two strontium and one rubidium shelf solution in current use in the laboratory, the writer prepared two new shelf solutions during this investigation.

Details of the preparation of these shelf solutions are given below. For convience these will be named: Bottino's "Spec pure" $Sr(NO_3)_2$ shelf solution and Bottino's "Spec pure" RbCl shelf solution.

Matthey "Spec pure" $Sr(NO_3)_2$, laboratory no. 14436, catalogue no. J. M. 95 (Johnson, Matthey and Co., Ltd. 78/83 Hatton Garden, London) was used to prepare the shelf solution. Total cation impurities according to the manufacturer is approximately 5 ppm. (2 ppm. Ba and 1 ppm. Ca). Approximately 360 mg. were weighed out in a clean 10 ml. weighing bottle. Bottle plus salt were weighed and then placed in a drying oven at 105°c.. The bottle plus salt was weighed on three successive days until constant weight was obtained. The salt was dumped directly from the weighing bottle into a clean 1000 ml. flask and the empty vial weighed. The $Sr(NO_3)_2$ was diluted in 2N vycor distilled HCl at a temperature of 17.5°c.. The fraction of strontium in $Sr(NO_3)_2$ is 0.4140 and the salt weighed 0.3586 g., so that the resulting solution contained 148.5 ug. Sr/ml.. A clean, dry 100 ml. flask was filled with the 148.5 ug/ml. solution. This was then transferred to a clean 1000 ml. flask and diluted with 2N HCl. The temperature was 18°c. and the concentration of this dilute solution is 14.85 ug Sr/ml.. A temperature correction (Handbook of Chemistry and Physics 36th ed. p. 1957) was applied. The final concentration was calculated as 14.84 ug. Sr/ml. and 148.4 ug. Sr/ml. for the dilute and concentrated solution, respectively.

The rubidium shelf solution was prepared from Matthey "Spec pure" Rb Cl, laboratory no. 4418, catalogue number J. M. 14. Total cation impurity according to the manufacturer is approximately 35 ppm. (20 ppm. K).

The procedure was identical with that described above for the strontium shelf solution except that the salt was kept in the drying oven overnight and only one weighing was made after the initial weighing. These weighings had the same value. Dilutions were made at 22°and 23°c. for the concentrated and dilute dilutions, respectively. The temperature correction was negligible. The fraction of rubidiun in Rb Cl is 0.7068 and the weight of the salt was 0.3460 g.. The resulting solution contained 244.6 ug. Rb/ml.. 100 ml. of the concentrated solution was diluted to 1000 ml. with 2N HCl as described above. The concentration of the dilute solution is 24.46 ug. Rb/ml.. All solutions were transferred to dry clean polyethylene bottles for storage and use.

Rubidium and Strontium Spike Solutions.

The preparation and calibration of spike solutions was under the supervision of Professor H. H, Pinson. All members of the laboratory participate in the calibration of the laboratory spikes. The most recent detailed review of the spikes is given by Pinson (1962), where further details may be found. The concentration and isotopic composition of the spikes which are given below are taken from Pinson's compliation.

In this investigation two Sr^{86} spikes of the same isotopic composition and concentration were used. These spikes are labeled Sr^{86} spike solution bottle # 1 and Sr^{86} spike solution bottle # 2. The two bottles were prepared at the same time. Bottle # 1 was used from June 1960 until the beginning of July 1962. In the interval from March 1961 to July 1962 there was an increase in concentration in bottle # 1 due to evaporation. (Pinson (1962)). A correction was applied for this concentration change. Relatively few of the samples of this investigation were spiked during the preiod of rapid concentration increase of bottle # 1. The total change in concentration was about 4 %. The results for samples using the two spike bottles agreed.

The isotopic composition for the Sr^{86} spike is shown in Table 2.1. Calibration of the Sr^{86} spike bottle # 1 and bottle # 2 are shown in Table 2.2 and 2.3, respectively.

Three Rb^{87} spikes were used during this investigation. The "concentrated Rb^{87} spike solution" was used until July 1962, after that the "waste spike was used. A few analyses were made with the "dilute Rb^{87} spike II", made by dilution of the concentrated

Table 2.1

Isotopic Composition of the Sr^{86} Spike (Atomic %).

84	86	87	88	Date
< 0.05	84.1 ± 0.01	9.3 ± 0.1	6.65 ± 0.05	Oak Ridge
0.102	83 67	9.546	6.734	22 June, 1960
0.0497	83.82	0.4105	6.721	25 June, 1960
0.052	83.71	9.469	6.764	27 Feb., 1960
0.05 ± 0.006	83.73 ± 0.24	9.48 ± 0.043	6.74 ± 0.013	M. I. T. Averages

Table 2.2

Calibration of Sr^{86} Spike Solution, Bottle #1.
(22.2 ug Sr/ml, Grav. Analysis, Pinson)

Concentration ug/ml	Shelf Solution	Date
21.54	Cormier's $SrCO_3$	24 June, 1960
21.44	Cormier's $SrCO_3$	26 Feb., 1960
21.56	Cormier's $SrCO_3$	26 Feb., 1960
21.84	Pinson's $Sr(NO_3)_2$	17 March, 1961
21.86	Pinson's $Sr(NO_3)_2$	28 March, 1961
Av. 21.65		
σ =0.09		
22.28	Pinson's $Sr(NO_3)_2$	9 July, 1962
22.37	Pinson's $Sr(NO_3)_2$	6 Sept., 1962
22.10	Pinson's $Sr(NO_3)_2$	12 Sept., 1962
22.31	Bottino's "Spec. pure" $Sr(NO_3)_2$	7 Sept., 1962
22.21	Bottino's "Spec. Pure" $Sr(NO_3)_2$	12 Sept., 1962

Table 2.3

Calibration of Sr^{86} Spike Solution, Bottle #2
(22.2 ugSr/ml, Grav. analysis, Pinson)

Concentration ug/ml	Shelf Solution	Date
21.68	Pinson's $Sr(NO_3)_2$	19 July, 1962
21.87	Pinson's $Sr(NO_3)_2$	7 Sept.,1962
21.89	Pinson's $Sr(NO_3)_2$	12 Sept.,1962
21.89	Bottino's "Spec. pure" $Sr(NO_3)_2$	11 Sept.,1962
21.75	Bottino's "Spec. pure" $Sr(NO_3)_2$	7 Sept.,1962
Ave. 21.82		
$\bar{\sigma}$ =± 0.04		

spike. The rubidium spike data are given below. The isotopic composition of the concentrated and "waste" spikes are given in Table 2.4 and 2.5, respectively, and their concentrations are given in Table 2.6 and 2.7.

Calculations.

The following formulas were used to calculate Rb and Sr concentrations in samples. The Rb^{85}/Rb^{87} value for normal rubidium = 2.59 ± 0.002. Sr^{87}/Sr^{86} = 0.712 and Sr^{86}/Sr^{88} = 0.1194 for "normal" strontium. For the Rb^{87} concentrated spike solution:

$$85/87\ (\text{measured}) = \frac{0.7215(N) = 0.0175(S)}{0.2785(N) = 0.9825(S)}$$

and

$$\text{weight factor} = 0.9838 = \frac{\text{Atomic weight normal Rb}}{\text{Atomic weight spike Rb}}$$

spike concentration = 63.3 ug/ml.

The Rb^{87} "waste" spike solution has an isotopic composition and concentration different from that of the concentrated spike.

$$85/87\ (\text{measured}))= \frac{0.7215(N) + 0.0299(S)}{0.2785(N) + 0.9701(S)}$$

and

weight factor = 0.9841

spike concentration = 26.94 ug/ml.

For the Sr^{86} spikes only one formula is necessary since both bottles have the same isotopic composition.

Table 2.4

Isotopic Composition of the Concentrated Rb^{87} Spike.

	$\frac{Rb^{85}}{Rb^{87}}$	Date	Rb^{87} Atomic %	Rb^{85} Atomic %
	0.01760	20 Feb., 1960		
	0.01789	25 Feb., 1960		
	0.01787	28 Feb., 1960		
Av. =	0.01779		98.24	1.76
$\bar{\sigma}$ =	± 0.000094			

Table 2.5

Isotopic Composition of the Rb^{87} "Waste" Spike

	$\frac{Rb^{85}}{Rb^{87}}$	Date	Rb^{87} Atomic %	Rb^{85} Atomic%
	0.02976	28 July , 1962		
	0.03112	12 Aug., 1962		
	0.03145	13 Sept., 1962		
Av. =	0.03078		97.01	2.99
$\bar{\sigma}$ =	± 0.00016			

Table 2.6

Calibration of the Concentrated Rb^{87} Spike.

Concentration ug/ml	Shelf Solution	Date
63.49	Pinson's RbCl	29 Feb., 1960
64.07	Pinson's RbCl	22 March, 1960
62.30	Pinson's RbCl	26 Feb., 1961
Av. = 63.30		
σ = ± 0.52		

Table 2.7

Calibration of the "Waste" Rb^{87} Spike.

Concentration ug/ml	Shelf Solution	Date
25.85	Pinson's RbCl	2 Aug., 1962
26.95	Pinson's RbCl	6 Aug., 1962
27.53	Pinson's RbCl	14 Aug., 1962
27.43	Bottino's "Spec pure" RbCl	31 Aug., 1962
26.96	Bottino's "Spec pure" RbCl	1 Sept., 1962
Av. = 26.94		
σ = ± 0.30		

$$86/88 = \frac{0.0986(N) + 0.8373\ (S)}{0.8256(N) + 0.0674\ (S)}$$

and

weight factor = 1.0172

concentration for Sr^{86} spike bottle # 1, until summer, 1961 = 21.6 ug/ml.

concentration for Sr^{86} spike bottle # 2 = 21.8 ug/ml.

In this work some samples were highly enriched in radiogenic strontium. In these cases the atomic abundance for Sr^{86} and Sr^{88} were calculated from the isotope ratio analyses and this value used for "normal" strontium.

To convert the measured Rb/Sr weight ratio to Rb^{87}/Sr^{86} atoms the change of the atomic abundance of Sr^{86} in highly radiogenic samples must be known. The equation used was:

$$Rb^{87}/Sr^{86} = \frac{0.2855}{\text{atomic fraction } Sr^{86}}\ (Rb/Sr)_{wt.}$$

This can be justified as follows:

$$\frac{\text{Rb (wt.)}}{\text{atomic wt. Rb}} = \frac{\text{no. of Rb atoms}}{N}$$

Where, N = Avogadro's number

$$\text{no. Rb atoms} = \frac{N\ \text{Rb (wt)}}{\text{atomic wt. Rb}}$$

$$\text{no. } Rb^{87} \text{ atoms} = \frac{N\ \text{Rb (wt) atomic fraction } Rb^{87}}{\text{atomic wt. Rb}}$$

and for strontium:

$$\text{no. Sr}^{86}\text{ atoms} = \frac{\text{N Sr (wt) atomic fraction Sr}^{86}}{\text{atomic wt. Sr}}$$

then:

$$\frac{\text{Rb}^{87}}{\text{Sr}^{86}} = \left(\frac{\text{Rb}}{\text{Sr}}\right)_{\text{wt.}} \frac{\text{atomic fraction Rb}^{87}}{\text{atomic fraction Sr}^{86}} \frac{\text{atomic wt. Sr}}{\text{atomic wt. Rb}}$$

The atomic weight of Rb and the atom fraction of Rb^{87} are constant. For different $\text{Sr}^{87}/\text{Sr}^{86}$ values the atomic weight of Sr changed but it is negligible for samples in this work. For $\text{Sr}^{87}/\text{Sr}^{86} = 1.000$, the change is I part in 8700. Substituting and combining these values gives:

$$\frac{\text{Rb}^{87}}{\text{Sr}^{86}} = \frac{0.2855}{\text{atomic fraction Sr}^{86}} \left(\frac{\text{Rb}}{\text{Sr}}\right)_{\text{wt.}}$$

Rb and Sr Blanks.

In this investigation three Sr blank determinations were made and blank corrections applied to all Sr determinations. No Rb blanks were determined and no blank corrections were made for Rb. The laboratory Rb blank is < 0.1 ug. Rb and low compared to the Rb concentration of the samples in this work.

The blanks were determined by taking an aliquot of spike and carrying through the whole chemical procedure. The results are shown in Table 2.8.

Table 2.8

Date		ug. Sr
8, June 1962		0.39
21, Sept.1962		0.30
26, Sept.1962		0.21
	average	0.30 ± 0.05

Precision and Accuracy of Isotope Dilution Analyses

Introduction.

Analytical work must be evaluated from two points of view; its precision (or reproducibility) and its accuracy.

The precision of analysis is a measure of the random errors involved and can be evaluated from the results of replicate analyses of a sample.

Accuracy can be evaluated by comparing the results of different analytical techniques applied to an unknown quantity, or by analyzing a material whose true value is known. Neither of these approaches is ideal. The first assumed that the systematic errors of different analytical techniques randomly distributed about the true value and the second involves the problem of obtaining a material whose true value is known.

Precision of Rubidium-Strontium Analyses.

An estimate of reproducibilty can be formed from the results of replicate determinations. Triplicate and quadruplicate analyses on two samples are shown in Table 2.9. A series of duplicate analyses are shown in Table 2.10. Rb and Sr values on the same line were analyzed from one weighing.

The following expressions are used as estimates of precision:

Standard deviation of single analysis $\sigma = \sqrt{\frac{E\,d^2}{n-1}}$.

Relative deviation of single analysis % E = $\frac{\sigma}{x}$ x 100 .

Standard deviation of the mean $\bar{\sigma} = \frac{\sigma}{\sqrt{N}} = \sqrt{\frac{E\,d^2}{n\,(n-1)}}$.

Relative deviation of the mean $\bar{E} = \frac{\bar{\sigma}}{x}$ x 100.

The relative precision value calculated on the duplicates is averaged and the standard deviation from that average is calculated as an indication of the consistency between the duplicate analyses. The relative precision value for Rb from both Tables is in essential agreement. In Table 2.9, the relative precision is less than 2 %. The estimates for the duplicates is 2 %. Sample R4702 (Table 2.10) should probably be dropped from the average. Camparison of the spread

Table 2.9

Replicate Rb and Sr Analyses.
Single weighings shown on the same line.

Sample	Rb (ppm.)	Sr (ppm.)
R4637	231	13.2
	224	-- -
	224	13.2
	225	13.6
	226	13.3
	$\sigma = \pm 3.4$	$\sigma = \pm 0.23$
	%E = ± 1.5 %	%E = ± 1.8 %
R3061	206	67.0*
	208	62.0
	203	60.7
	---	61.8
	206	62.9
	$\sigma = \pm 2.5$	$\sigma = \pm 2.8$
	%E = ± 1.2 %	%E = ± 4.5 %
		$\sigma = \pm 1.4$
		%E = ± 2.2 %
		*Discard $\bar{x} = 61.5$
		$\sigma = \pm 0.7$
		%E = ± 1.1 %

Table 2.10

Duplicate Rb amd Sr Analyses.
Single weighings shown on same line.

Sample	Rb (ppm)	%E	Sr (ppm)	%E	$\frac{\text{Rb}}{\text{Sr}}$
R4638	--- -	- --	64.0	0.0	-- --
	--- -	- --	64.0	- -	-- --
R4569	102.	0.67	10.0	8.0	10.2
	101.	- --	11.2	- -	9.0
R4891A	63.5	0.56	55.7	1.0	1.2
	63.1	- --	54.9	- --	1.2
R4893	105.	0.67	--- --	- -	-- --
	106.	- --	--- --	- -	-- --
R4894	--- -	- --	72.5	1.0	-- --
	--- -	- --	72.4	- -	-- --
R4700	161.	3.1	11.3	2.8	14.1
	154.	-.--	10.9	-.-	14.1
R4701	200.	0.35	--- --	0.3	-- --
	--- -	- --	85.5	- -	-- --
	201.	- --	80.2	- -	-- --
R4702	135.	6.0	111.	7.4	1.22
	147.	- --	123.	- -	1.20
R4770	--- -	- --	4.52	7.2	-- --
	--- -	- --	5.04	- -	-- --
R4772	169.	3.8	4.40	3.6	-- --
	160.	- --	4.18	- -	-- --
R4954	238.	1.3	--- --	- -	-- --
	235.	- --	--- --	- -	-- --

Table 2.10, continued:

Sample	Rb (ppm)	% E	Sr (ppm)	% E	$\frac{\text{Rb}}{\text{Sr}}$
R4955	202.	2.9	--- --	- -	-- --
	194.		--- --		--- --
R4956	138.	1.0	--- --	- -	-- --
	136.		--- --		-- --
			11.5	7.1	-- --
			10.4		-- --
R4957	--- -	- --	52.9	0.8	-- --
	--- -		53.5		-- --
R4310	--- -	- --	23.0	3.9	-- --
	--- -		21.7		-- --

Av. of % E = 2.0
Delete R4702
Av. of % E = 1.6

Av. of % E = 3.6
Delete R4702
Av. of % E = 3.2

between duplicates for the Rb and Sr to the spread between the Rb/Sr ratio duplicates indicates that there was probably a weighing mistake. If R4702 is dropped, the relative precision for Rb analyses as estimated from the duplicates is 1.6 %. Thus it appears that ± 2 % is a reasonable estimate for the precision of Rb analyses. This agrees with the estimates of other workers in the laboratory, (Faure (1961), Schnetzler (1961), Whitney (1962)).

The precision of strontium analyses from Table 2.9 is less than 2 % if the 67.0 ppm. value for Sample R3061 is dropped. This can be justified by the fact that this value is 2.9 standard deviations from the mean. It is not clear that this is a good criteria when dealing with such a small set. A statistical criterion to test for rejection of measurements in small sets is difficult to establish. (Strobel (1960)). The number will therefore be discarded with reservation. The average of the spread between duplicates in Table 2.10 is 3.6 %. This is higher than that obtained from Table 2.9. The average precision value for samples with less than 15 ppm. Sr is 5.7 % and 1.2 % for duplicates with strontium greater than 15 ppm.. If the odd sample from R3061 is rejected then 2 % is a reasonable precision estimate for samples with greater than 15 ppm. Sr and ±16 % for samples with less than 15 ppm. strontium. Faure (1961) estimated ± 1 % for samples containing greater than 150 ppm. Sr but pointed out that it may be as high as ± 4 %. He estimated that the precision approached ± 15 % at the 20 ppm. level. His final estimate was ± 2 % for Rb greater than 10 ppm. and Sr greater than 150 ppm.. The results from this work agree with those conclusions except that on the average the precision for samples of less than 15 ppm. is ± 6 % but may range as high as 10 %.

The source of this apparent difference in precision for low strontium samples is difficult to assess. The most obvious source is contamination. However, most analyzed samples were large enough to keep the blank correction down to ± 1 %. In some cases (in the 4 and 5 ppm. range) this wasnot possible and the blank correction was larger. Sample inhomogeniety is another obvious possibility. Although precautions were taken to ensure a homogeneous sample it may be that in dealing with these very low strontium samples the best procedure would be to quantitatively disolve the sample and take aliquots for the analyses. Weighing, spiking and mass spectrometry should be insensitive to concentration.

Accuracy of Rubidium and Strontium Analyses

Accuracy can be estimated by inter-laboratory comparison of results with the same method of analyses, or by comparison of results obtained by multiple methods. The calibration of spikes is the most crucial part of isotope dilution analyses insofar as accuracy is concerned. One indication of accuracy is the consistency of the spike calibration with different shelf solutions. New shelf solutions were prepared and the spikes calibrated. The results are reported in Pinson's (1962) review of the laboratory spikes. Calibrations with the new shelf solutions agreed to better than 1 % with the previous ones. This can be taken as good evidence of the accuracy of the spikes used in the laboratory.

The analyses of Tilton's shelf solution (Pinson (1962), Faure (1961)) showed inter-laboratory agreement on the order of ± 1 % for Rb analyses. This is a minimum value since no chemistry is involved

Precision and Standardization of Isotope Ratio Analyses.

During the course of this work a standard strontium carbonate was analyzed periodically, and some samples were analyzed in duplicate. Following standard procedure in the laboratory, the Sr^{87}/Sr^{86} ratios were normalized to $Sr^{86}/Sr^{88} = 0.1194$.For a detailed discussion of this normalization procedure see Faure (1961).

Table 2.11 shows the results for eight analyses of the carbonate. These were done with D. Brookins. Runs (3) and (4) were discarded because they were obtained during a week when there was continual trouble with the instrument.

The results are the same within analytical precision as the previous results from this instrument (# 1) and the results given by Whitney (1962) for instrument (# 2). See Table 2.12.

Table 2.12

Previous Laboratory Results for Eimer and Amend $SrCO_3$, Lot # 492327

Reference	$\frac{86}{88}$	$\frac{87}{86}$	$(\frac{87}{86})_{.1194}$	Remarks
Powell (1962)	0.1194 ± 0.0001	0.7116 ± 0.0004	0.7116 ± 0.0004	Average of 18 analyses covering 21 months on #1.
Whitney (1962)	0.1195 ± 0.0002	0.7106 ± 0.0007	0.7108 ± 0.0003	Average of 14 analyses covering 9 months on #2.

Table 2.11

Strontium Carbonate Reagent, Eimer and Amend, Lot # 492327.

No.	Date	$\frac{86}{88}$	$\frac{87}{86}$	$(\frac{87}{86})_{.1194}$	% E[3]	No. of sets
1.	5/ 8/62	0.1191	0.7094	0.7086	0.07	90
2.	5/15/62	0.1196	0.7113	0.7118	0.10	72
3.[1]	6/15/62	0.1218	0.7035	0.7106	0.12	96
4.[1]	6/18/62	0.1185	0.7104	0.7076	0.05	42
5.	6/22/62	0.1207	0.7074	0.7113	0.09	84
6.	8/ 8/62	0.1207	0.7069	0.7107	0.07	84
7.	9/12/62	0.1195	0.7114	0.7117	0.04	84
8.	11/ 8/62	0.1199	0.7092	0.7107	0.11	90

$\bar{X} = 0.1199$	$\bar{X} = 0.7093$	$\bar{x} = 0.7108$
$\bar{\sigma} = \pm 0.0003$	$\bar{\sigma} = \pm 0.0008$	$\bar{\sigma} = \pm 0.0005$
$\% \bar{E} = \pm 0.22$	$\% \bar{E} = \pm 0.11$	$\% \bar{E} = \pm 0.07$
$\sigma = \pm 0.0007$	$\sigma = \pm 0.0019$	$\sigma = \pm 0.0012$
$\% E = \pm 0.55$	$\% E = \pm 0.27$	$\% E = \pm 0.17$

No.	Date	$\frac{86}{88}$	$\frac{87}{86}$	$(\frac{87}{86})_{.1194}$	% E	No. of sets
9.[2]	6/28/62	0.1196	0.7104	0.7110	0.05	90

---

[1] Runs number 3 and 4 are not included in the averages. Both runs were made during a week when there was continual trouble with the instrument.

[2] Strontium carbonate reagent, Eimer and Amend obtained from W. Compston, for purpose of interlaboratory comparison.

[3] This is not a true precision value but a instrumental precision value for the particular run.

The results of duplicate analyses are shown in Table 2.13. The relative deviation of a single analysis for each pair of normalized and unnormalized Sr^{87}/Sr^{86} ratios is also listed. The average relative deviation from the ten duplicates is 0.23 % for the normalized and 0.25 % for the unnormalized ratios. The relative deviation of a single analysis from the standard carbonate (Table 2.11) is 0.17 % for the normalized and 0.27 % for the unnormalized ratios. In Table 2.13, the relative deviation for the normalized 87/86 ratio for sample R4891C is abnormally high. If this is discarded the average is 0.17 % for the normalized ratio which agrees with the result from the carbonate. In this work, ± 0.25 % was taken as a reasonable precision for a single isotope ratio analysis.

Table 2.13

Duplicate Strontium Isotope Ratio Measurements.

Sample	$\frac{86}{88}$	$\frac{87}{86}$	% E	$(\frac{87}{86})_{.1194}$	% E
R3061	0.1191	0.7638	0.46	0.7628	0.32
	0.1196	0.7587		0.7593	
R4565	0.1201	0.7446	0.13	0.7468	0.05
	0.1198	0.7461		0.7473	
R4566	0.1204	0.7751	0.25	0.7783	0.15
	0.1190	0.7779		0.7766	
R4567	0.1197	0.7414	0.26	0.7423	0.38
	0.1187	0.7401		0.7380	
	0.1192	0.7376		0.7370	
R4634	0.1206	0.7061	0.40	0.7096	0.07
	0.1190	0.7101		0.7089	
R4637	0.1198	0.9782	0.38	0.9798	0.17
	0.1205	0.9730		0.9775	
R4638	0.1203	0.7793	0.31	0.7822	0.36
	0.1201	0.7759		0.7782	
R4312	0.1192	0.7085	0.09	0.7079	0.13
	0.1200	0.7076		0.7092	
R4891C	0.1199	0.7489	0.19	0.7505	0.61
	0.1185	0.7469		0.7441	
R4888	0.1201	0.7162	0.03	0.7183	0.03
	0.1201	0.7159		0.7180	
Average of % E			= $\overline{0.25}$		= $\overline{0.23}$
Average of % E deleting R4891C					= 0.17

Chapter 3

The Kineo Volcanics

Introduction

The Kineo volcanics occur in the Moose River synclinorium in west central Maine. Most of the results for this area have been previously published(Bottino, et al (1962)).

Geology

The most recent and thorough field work on the Moose River synclinorium was done by Boucot (1961). This section is taken primarily from that report. Other recent work in that area includes Woodward (1951), Hurley and Thompson (1950), and Smith(1925, 1930, 1933). Smith reported on the garnet rhyolites (Kineo) in the synclinorium.

The synclinorium contains approximately 10,000 feet of relatively unmetamorphosed upper Lower Devonian strata. The strata of Oriskany and early Onondaga age are unconformably underlain by older strata ranging in age from Helderberg through Ordivician, and possibly Cambrian and pre-Cambrian. The lower Paleozoic strata are in the chlorite zone of metamorphism. The strata of Oriskany and Onondaga age are mostly dark sandstone and slate with minor rhyolite (Kineo). Other volcanics in the section are the Ordovician Kennebec formation, the undifferentiated Ordovician or Silurian section, and the Cambrian or Ordovician section. In addition there are granitic intrusives ranging in geologic age from early Devonian to post-early Devonian.

Boucot (1960) describes the Kineo as follows (p. 163):

> Lithology- The Kineo volcanic member consists of a variety of volcanic rocks: massive conchoidally fractured felsite, massive irregularly fracturing felsite containing abundant garnet phenocrysts, dark tuff, light tuff, conglomerate consisting cheifly of volcanic materials, and flow breccia.
> The massive conchoidally fracturing felsite weathers bone white and is blue gray when fresh. Small glassy phenocrysts of quartz form about 5 percent of the rock and gray phenocrysts of feldspar about 2 percent, but garnet phenocrysts are rare. The quartz phenocrysts are usually less than 1 mm in diameter, those of feldspar about 1 to 2 mm in diameter. The feldspar phenocrysts weather out to leave rectangular voids. The gray ground mass is very fine graned. Chaotic flow banding isconspicuous in places and amygdules filled with calcite are conspicuous in others. Some specimens show vague outlines of spherulites.
> The irregularly fracturing felsite contains abundant garnet phenocrysts; the rock on fresh surfaces is blue gray and weathers greenish white. Garnet phenocrysts about 2 mm in diameter form about 5 percent of the rock, and white feldspar phenocrysts about 2 to 3 mm long form 10 to 15 percent; quartz phenocrysts are uncommon. Columnar jointing occurs in places. Vague outlines of spherulites can be cistinguished in some places and flow banding in others.

This description demonstrates the extrusive character of the Kineo volcanics.

The garnets in the Kineo are primary (Smith (1933)). Although rare, primary garnet rhyolites are known elsewhere (Cross (1886), Jung (1961)).

The geologic age of the Kineo is given by Boucot (p. 164):

> The member is probably of early Onondaga age, as indicated by its relations with the associated main body of the Tomhegan, but it may be intermediate in age between the Tarratine formation and the main part of the Tomhegan formation.

Therefore, the geologic age is early Onondaga to late Oriskany (upper Lower Devonian). This then defines precisely its geologic age.

Results

Five whole rocks and one mineral from the Kineo have been analyzed. The analyzed samples are massive conchoidally fractured felsites with the exception of R4565 and R5051 which are garnet felsites. The hornblende was separated from sample R3061. This hornblende and sample R3061 was obtained from Prof. H. W. Fairbairn who had separated the minerals in the sample as part of some earlier work.

In addition to the isotope dilution analyses for Rb and Sr, an analysis was done by X-ray spectrograph for relative intensity of the Rb/Sr weight ratio.

Nevertheless, if the relative intensity values are plotted against the Sr 87/Sr 86 ratio, extrapolation to zero Rb/ Sr gives a value for the initial strontium isotopic composition which is independent of the Rb-Sr isotope dilution analysis. All results are reported in Table 3.1. The isochron plot is shown in Figure 3.1 and the plot of relative intensity Xray Rb/Sr verus Sr^{87}/Sr^{86} is shown in Figure 3.2. The isochron is plotted showing ± 3 percent Rb^{87}/Sr^{86} and ± 0.25percent Sr^{87}/Sr^{86}.

The isochron, Figure 3.1, gives an age of 360 ± 10 M.Y. for the Kineo and initial ratio of 0.715 ± 0.001. The initial ratio by X-ray from Figure 3.2 is also 0.715 and confirms the initial ratio obtained from the isochron.

The initial Sr^{87}/Sr^{86} ratio of 0.715 ± 0.001 is higher than that of basaltic rocks which have an average Sr^{87}/Sr^{86} ratio of 0.708 and range from 0.706-o.710. (Faure & Hurley (1962); Gast (1960)). This indicates that this volcanic sequence is partially or wholly of crustial origin.

Discussion

Holmes (1960), Kulp (1960), and Faure (1960) give an estimate of 400 M.Y. for the Devonian-Silurian boundry.

Table 3.1

Kineo Rhyolite

Sample	Location	Rb ppm	Sr ppm	$\frac{Rb^{87}}{Sr^{86}}$	Intensity Xray $\frac{Rb}{Sr}$	$\frac{Sr^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\left(\frac{Sr^{87}}{Sr^{86}}\right)_{.1194}$
R3061	Moosehead				2.28			
	Lake, Kineo	206	-		2.17			
	View Hotel.	208	62.0		2.18			
	Felsite	203	60.7		2.41	0.7368	0.1191	0.7628
		-	61.8		2.33	0.7587	0.1196	0.7593
		206	61.5	9.75	2.27	0.7613	0.1194	0.7611
Hb3061	Hornblende							
	from R3061	152	527	0.83	-	0.7175	0.1195	0.7178
R4565	Garnet				1.56			
	Felsite				1.62	0.7466	0.1201	0.7468
	Misery Pond				1.55	0.7461	0.1198	0.7473
		135	64.3	6.10	1.58	0.7454	0.1200	0.7471
R4566	Felsite							
	Southeast				3.12			
	edge of				3.10	0.7751	0.1204	0.7783
	Brassua				3.09	0.7779	0.1197	0.7766
	Lake	191	44.7	12.44	3.10	0.7765	0.1194	0.7775
R4567	Felsite				1.27			
	exact				1.29	o.7414	0.1197	0.7423
	locale				1.24	0.7401	0.1187	0.7380
	unknown				1.23	0.7376	0.1192	0.7391
		143	84.8	4.91	1.26	0.7397	0.1192	0.7391

Table 3.1, continued

Sample	Location	Rb ppm	Sr ppm	$\frac{Rb^{87}}{Sr^{86}}$	Intensity Xray $\frac{Rb}{Sr}$	$\frac{Sr^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$(\frac{Sr^{87}}{SR^{86}})$ .1194
R5051	Garnet felsite, Cold Stream south of Cold Stream Pond	--	--	--	0.912 o.902 0.907	0.7297	0.1206	0.7334

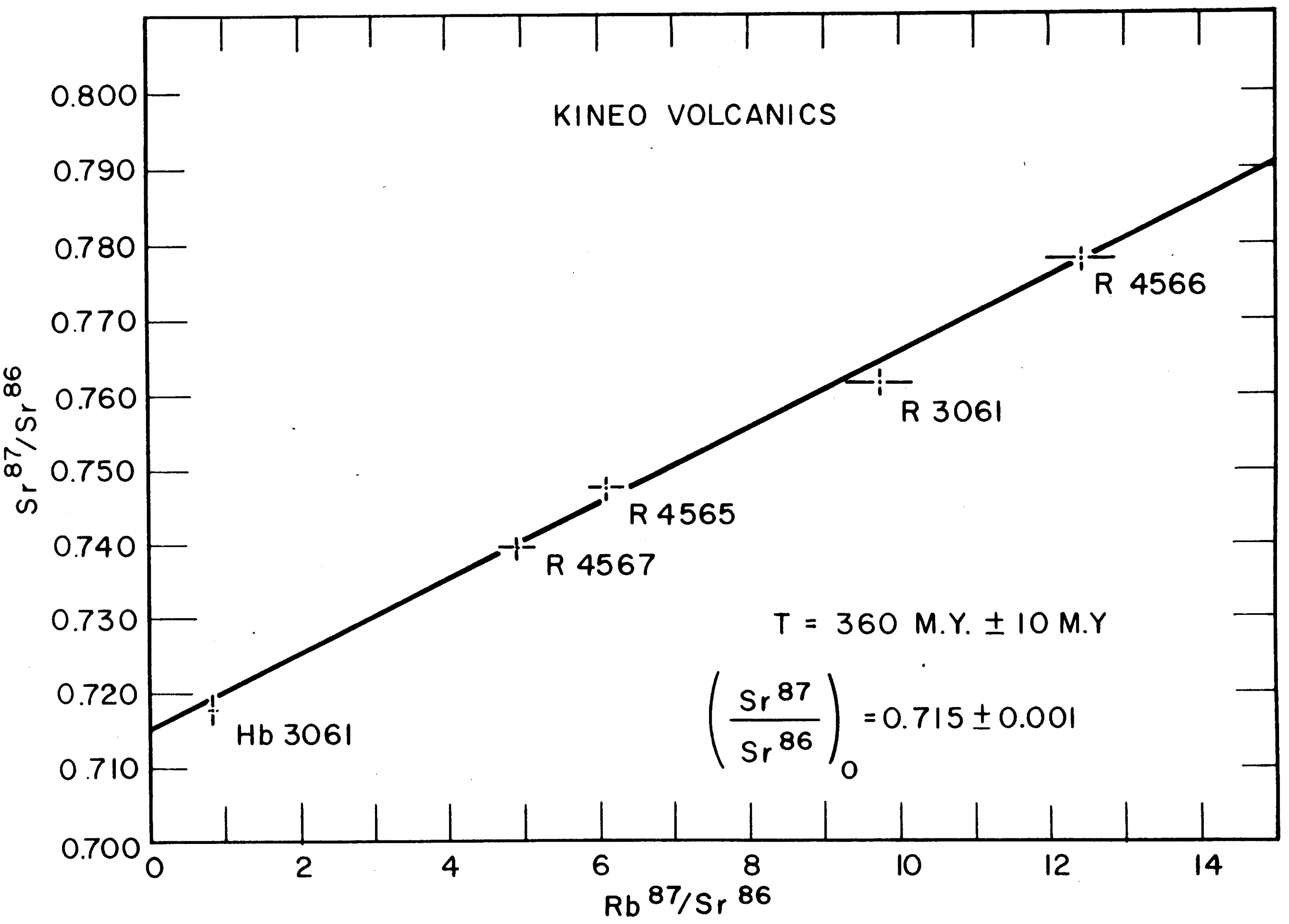

KINEO VOLCANICS
Sr^{87}/Sr^{86}
0.800
0.790
0.780
0.770
0.760
0.750
0.740
0.730
0.720
0.710
0.700
0
2
4
6
8
10
12
14
Rb^{87}/Sr^{86}
R 4566
R 3061
R 4565
R 4567
Hb 3061
T = 360 M.Y. ± 10 M.Y
$\left(\frac{Sr^{87}}{Sr^{86}}\right)_0 = 0.715 \pm 0.001$

FIGURE 3.1

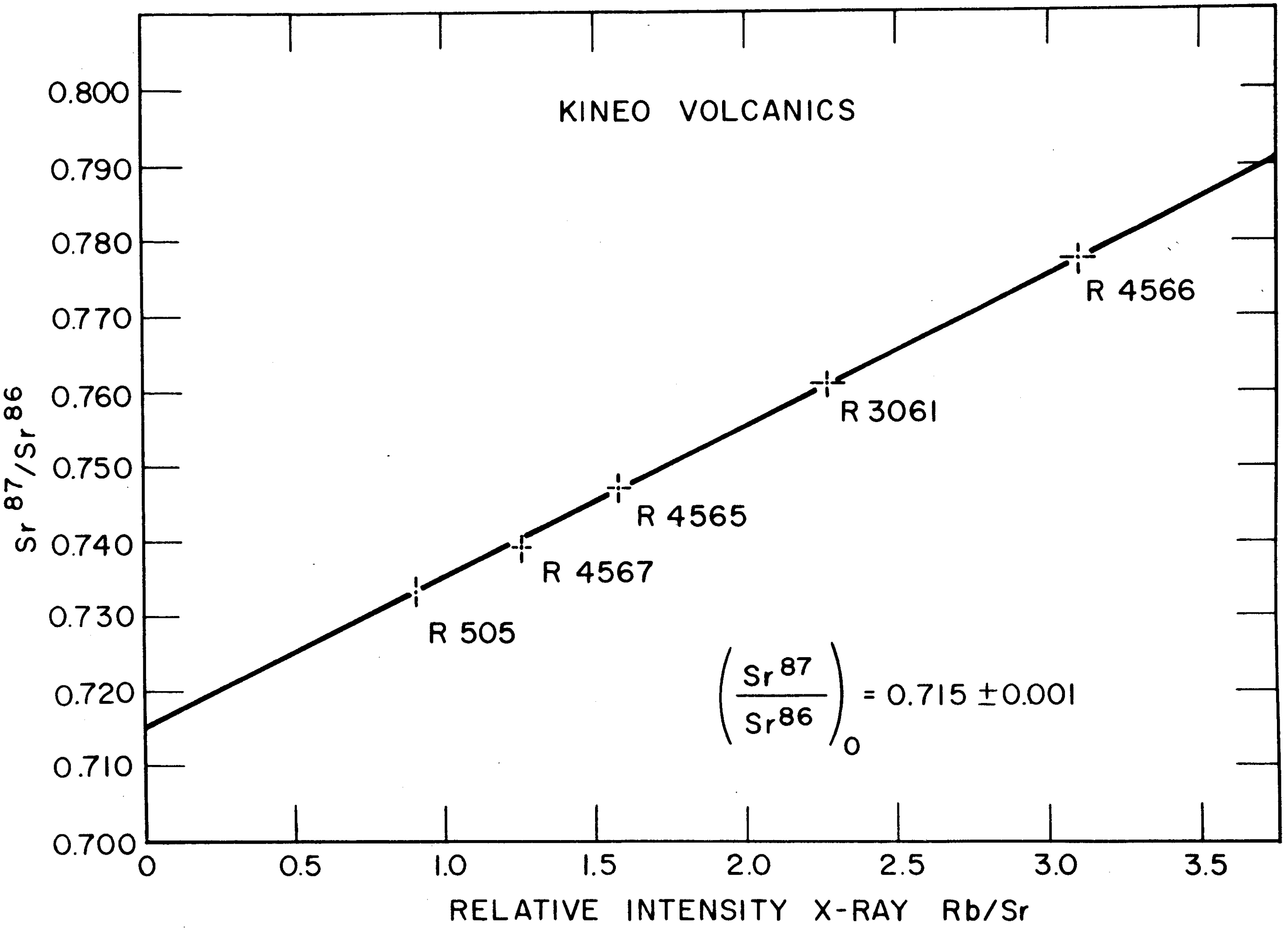

KINEO VOLCANICS
R 4566
R 3061
R 4565
R 4567
R 505
$\left(\frac{Sr^{87}}{Sr^{86}}\right)_0 = 0.715 \pm 0.001$
Sr^{87}/Sr^{86}
0.800
0.790
0.780
0.770
0.760
0.750
0.740
0.730
0.720
0.710
0.700
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
RELATIVE INTENSITY X-RAY Rb/Sr

FIGURE 3.2

Hence the age for the upper Lower Devonian would be approximately 390 M.Y..

Taken at face value, this indicates a real difference between the Kineo result and these recent time scale estimates. The Kineo result is approximately 8 percent lower than these estimates. A critical inspection of the individual values that determine this Silurian-Devonian age boundry shows that in only one case is there a clear contradication with the Kineo result. In Nova Scotia (Fairbairnet al. (1960)) two localities in the granite are close to intrusive contacts with upperLower Devonian fossiliferous strata. The results for biotites from those two localities are 391 and 410 M.Y. (Rb-Sr) and 333 and 318 M.Y. (K-Ar). As there was no analytical reason to prefer one set of ages to another the authors averaged the values. This gives a mean value of 360-365 M.Y.. The authors point out that this may not be a significant average. On the other hand this mean value is in good agreement with concordant results from several other locatities. (See Table 7, p. 411). This value (365 M.Y.) for the minimum age for the upper Lower Devonian overlaps the result for the Kineo (360 M.Y.) which is a direct age measurement of the upper Lower Devonian.

Another critical locality for comparison is in the Seboomook slate (Oriskany, middle Lower Devonian) near Jackman, Maine (Hurley et al. (1959)). The biotite K-Ar ages from the quartz monzonite range from 353-366 M.Y. with a mean of 360 M.Y.. This includes three biotites from two localities and replicate analyses from two laboratories. The whole rock K-Ar ages (four samples) on the Seboomook slate range from 350-377 M.Y.. If one assures that these sediments lost all of their inherited argon at the time of intrusion then their mean K-Ar age of 365 M.Y. is a minimum age. This assumption introduces an uncertainty into the evaluation of these whole rock ages. A single biotite Rb-Sr age of 360 ± 28 M.Y. is also reported. The strontium from this biotite is less than 2 percent radiogenic and a large uncertainty is attached to the result. This minimum value (360 M.Y. Biotite only) for the middle Lower Devonian also overlaps with the Kineo result.

Faul (1960, 1961) reports 4 biotite K-Ar ages of 405 M.Y. for a group of granites south of Calais, Maine. One of these granites intruded and metamorphosed the upper Silurian sediments (middle Ludlow to lower Gedinnian). Therefore, this value (405 M.Y.) relates to post-Upper Silurian. There is a real contradiction between the Kineo result and this result. Furthermore the contradiction is clearer when this 405 M.Y. biotite age for post-Upper Silurian is compared to the 405 M.Y. age for the basal Silurian Arisaig volcanics (this report, Chapter 4).

The Shap adamellite, in northwest England gives a biotite Rb-Sr age of 420 M.Y. ($\lambda=1.39\times10^{-11}$) (Lambert & Mills 1961). Results for the Creetown granite in Scotland and Leinster granite in Ireland also yield the same age. The mean biotite Rb-Sr age for the three granites is 423 ± 10 M.Y. ($\lambda=1.39\times10^{-11}$). The K-Ar result from these granites is 390 ± 10 M.Y.. The only question about these granites is whether or not they are really Lower Devonian intrusives.

The Creetown granite cuts Lower Silurian strata and the Leinster granite cuts Ordovician strata. The Shap adamellite intruded Ordovician strata, and metamorphosed silurian strata (presumably Lower Silurian). There are associated radial dikes which intruded Ludlovian (Upper Silurian) strata. Therefore the observed field relations only demonstrate that the Shap granite is post Lower (?) Silurian, the Creetown is post Lower Silurian and the Leister is post Ordovician.

If the radial dike swarms and the Shap adamellite are contemporaneous, then the biotite age for the Shap adamellite is a post Upper Silurian (Ludlovian) age. The further assignment of all the above granites to the lower Devonian is based on the fact that they are all members of a postorogenic calc-alkaline suite. This suite includes volcanic members of proved Lower Devonian age. Lambert and Mills (1961) state:

> A more precise assessment of stratigraphic age can be made by considering specific petrological and structural arguments. The dated intrusives are all members of the postorogenic calc-alkaline igneous suite of the Caledonides, which form a well-marked petrographic province. This suite has volcanic members of proved Lower Devonian age, and the associated intrusives are generally believed to be contemporaneous---.

It is clear then that this Lower Devonian age assignment is based on petrologic correlation and not observed intrusive relations. This is clearly recognized by Lambert and Mills. These correlations may or may not be correct. The members of a well-known alkalic suite in eastern Massachusetts, which are also correlated on petrologic grounds, range in age from 420 M.Y. to 245 M.Y. according to results from whole rock Rb-Sr studies (this report Chapter 6) (also, see Toulmin (1961)). All of this lends weight to the need for great caution in assigning geologic ages to intrusive rocks.

Summary

Comparison of the Kineo result with biotite ages from intrusives shows that the only clear contradiction is the 405 M.Y. biotite ages from around Calais, Maine (Faul (1961)).

The biotite ages from Shap, Creetown and Leinster granites in the British Isles may or may not be contradictory depending on the validity of the chronologic correlation of the Shap granite and the associated dikes.

The results for the biotite ages from Nova Scotia and Jackman, Maine are essentially the same as the Kineo. The overlap between these minimum ages from the intrusive and the directly determined age on the strata is dificult to evaluate. It appears to be contradictory but the following factors should be kept in mind:

(1) Analytical uncertainity is a possibility. All of these values have uncertainties of ± 10 M.Y. and the Kineo result is a single determination

even though based on six points. The spread between the Kineo and these intrusives could be as much as 10 M.Y. and presumably this would be enough time for sedimentation, burial and intrusion.

(2) The uncertainty in decay constants when comparing two decay schemes is a possible cause of the overlap. On the other hand the Rb-Sr ages on biotites from these intrusives are equal to or greater than the K-Ar ages.

(3) Another possible explanation is that the length of time between sedimentation, burial and intrusion is in the order of a couple of million years and would be undetectable.

(4) There is the assumption that the biotite age is the age of final emplacement and crystallization of the granite.

The 360 ± 10 result for the Kineo volcanics is consistent with the 405 ± 10 M.Y. for the basal Silurian Arisaig volcanics reported in Chapter 4 of this report.

Chapter 4

The Arisaig Volcanics

Introduction and General Geology

The Arisaig volcanics from Nova Scotia provide an opportunity to determine an age for the base of the Silurian in northeastern North America. They are located in the Arisaig-Antigonish district of northeastern Nova Scotia, and are part of the Silurian Arisaig series which outcrops along Northumberland strait from Malignant Cove to Mc Aras brook in an area approximately 6 by 1 1/2 miles.

Early workers in the area include Dawson (1891) and Honeyman (1864, 1870). Twenhofel and Schuchert (1909) and McLearn (1918, 1924) are prominent amongst those who worked on the paleontology of the Arisaig series.

The geology of the area is described by Fletcher and Fairbault (1886), and Williams (1911, 1912, 1914). Twenhofel (1909) first identified the rocks at the base of the Silurian section as volcanics.

The sediments of this Silurian section are highly fossiliferous and range in age from lower

Llandovery to Ludlow. The Fossils are correlated with European rather than North American types (Twenholel & Schuchert, 1909; Williams, 1914; MaLearn, 1924).

Williams (1914, p. 29) summarized the geologic age of the sediments as follows:

> The fauna represented in the rocks of this series is, as already shown by Twenhofel, and Schuchert, more nearly related to the Silurian faunas of Europe than to those of the corresponding period in America. It represents a period of time in Europe between the Lower Llandovery and the Ludlow, and in America between the Clinton of eastern New York and the Guelph of interior America.

The oldest sedimentary formation is the Beachill Cove formation of Llandovery age which rests on the Arisaig volcanics. Therefore the Arisaig volcanics are pre-Llandovery (pre-Lower Silurian) in age, thus defining the minimum geologic age for these volcanics.

Geological evidence of the maximum age is not so well-defined, as there are no older formations exposed in contact with the base of the Arisaig section. Williams considers the contact between the Arisaig sediments and the Arisaig volcanics to be an erosional unconformity representing a long time interval. He writes (1914, p. 89):

> The relations of the sedimentaries to the lava may be studied at the exposures west of Frenchman's barn or in Doctors brook. At the former locality the rhyolite has had portions of its surface removed along planes of flowage. The beds of shale here are flexed and have probably suffered from later movement which destroyed the original conditions. In Doctors Brook no angular unconformity was noted, but conglomerate composed for the most part of volcanic materials forms the base of the sedimentary series. The irregularities in the underlying surface and the basal conglomerate are interpreted as evidence of an unconformity which for reasons given in the description of the Malignant Cove formation (p. 87), is thought to represent a long time interval.

And on page 63 he writes:

> The contact of the sandstone with the volcanic flow is marked by a conglomerate derived from the volcanics. How much of this fragmental material is really erosion conglomerate and how much of it is the volcanic breccia which normally overlies the volcanic flow (aporhyolite), is hard to determine. The well water worn pebbles of rhyolite, however, at the base of the shale furnish good evidence that there is present at least some conglomerate that is the result of erosion.

The Maligant Cove conglomerate outcrops in a small area east of the Silurian section area. It is approximately 20 feet thick and contains fragments of purple rhyolite, pink quartz,graywacke, tuff, micropegmatite and plagioclase feldspar. The formation unconformably overlies the Lower Ordovician Browns Mountain group. (Williams (1914) p. 58-59). Williams discusses the age of the Malignant Cove conglomerate (1914), p. 59).

> Because of the lapse of time between The James River deposition and that of the Malignant Cove formation as represented by the unconformable contact along cleavage planes of James River slate, it does not seem probable that this formation was deposited during earliest Ordovician time. On the other hand, in degree of silicification the Malignant Cove conglomerates and grits resemble no other rocks of the region so clearly as those of the Browns Mountain group. Until further evidence of the age of these rocks is produced they will be classified provisionally as belonging to the middle part of the Ordovician period.

The rhyolite and micropegmatite material of the Malignant Cove conglomerate is correlated with granitic intrusives and extrusives which cut the Lower Ordovician Browns Mountain group. Therefore the geologic age of these rocks is post-Lower Ordovician and predates the Malignant Cove conglomerate. If the Malignant Cove formation is middle Ordovician then the igneous activity is post-Lower Ordovician and pre-middle Ordovician. Aside from the above consideration the minimum geologic age of the igneous activity is known only to be pre-Mississippian. (Williams (1914, p.105). Williams correlates this igneous activity associated with the Browns Mountain group and the Ariasig volcanies.

The hypothesis of a long time interval between the Arisaig volcanics and the Silurian sediments thus depends on:(1)the correlation of the Arisaig volcanics with the igneous activity cutting the Browns Mountain group; (2) the correlation of the granitic and rhyolitic material in the Malignant Cove conglomerate with the granite and rhyolite intruded in the Browns Mountain group; (3) the assignment of a middle Ovdovician age to the Malignant Cove conglomerate. The geologic age of the Arisaig volcanics can therefore be summarized as follows.

The Arisaig volcanics occur at the base of the Silurian Arisaig sediments. The oldest formation, the Beechhill Cove formation of Lower Llandovery (Lower Silurian) age was deposited on the irregular surface of the Arisaig volcanics with no apparent angular unconformity. The contact is irregular with local conglomerates composed of the underlying volcanics. Therefore the minimum geologic age for the volcanics is pre or basal Lower Silurian.

There are no field relations to directly determine the maximum geologic age because there are no pre-Silurian formations exposed in contact with the base of the Arisaig section. However, the oldest formation in the area, which unconformably underlies all the other formations, is Lower Ordovician. Therefore a post-Lower Ordovician age is a reasonable maximum age for the Arisaig volcanics, and the most probable geologic age is basal Silurian.

Results

Five rhyolite samples and one basic volcanic sample have been analyzed. these samples were collected by Professor W. H. Dennen. Analyzed samples are whole rocks.

The results are reported in Table 4.1 and the isochron is shown in Figure 4.1. The isochron is plotted showing ±3 % Rb^{87}/Sr^{86} and ± 0.25% Sr^{87}/Sr^{86} as reasonable estimates of error.

The isochron indicates an age of 405 ± 10 M.Y. and an initial ratio of 0.709 ± 0.001 for both the basic volcanics and the rhyolites.

Discussion

The single initial ratio for the acid and

Table 4.1

Arisaig Volcanics, Arisaig, Nova Scotia

Sample		Rb (ppm)	Sr (ppm)	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})_{.1194}$	$\frac{Rb^{87}}{Sr^{86}}$
R4634	Andesite			0.1206	0.7061	0.7096	
				0.1190	0.7101	0.7089	
		14.7	328	0.1198	0.7081	0.7093	0.13
R4635	Rhyolite	73.4	96.0	0.1197	0.7203	0.7212	2.02
R4636	Rhyolite	99.9	128	0.1213	0.7151	0.7208	2.26
R4637	Rhyolite	231	13.2				
		224	-				
		224	13.2	0.1198	0.9782	0.9798	
		225	13.6	0.1205	0.9730	0.9775	
		226	13.33	0.1202	0.9756	0.9787	50.4
R4638	Rhyolite	274	64.0	0.1203	0.7793	0.7822	
		-	64.0	0.1201	0.7759	0.7782	
		274	64.0	0.1202	0.7780	0.7806	12.5
R4639	Rhyolite	186	72	o.1198	0.7477	0.7490	7.5

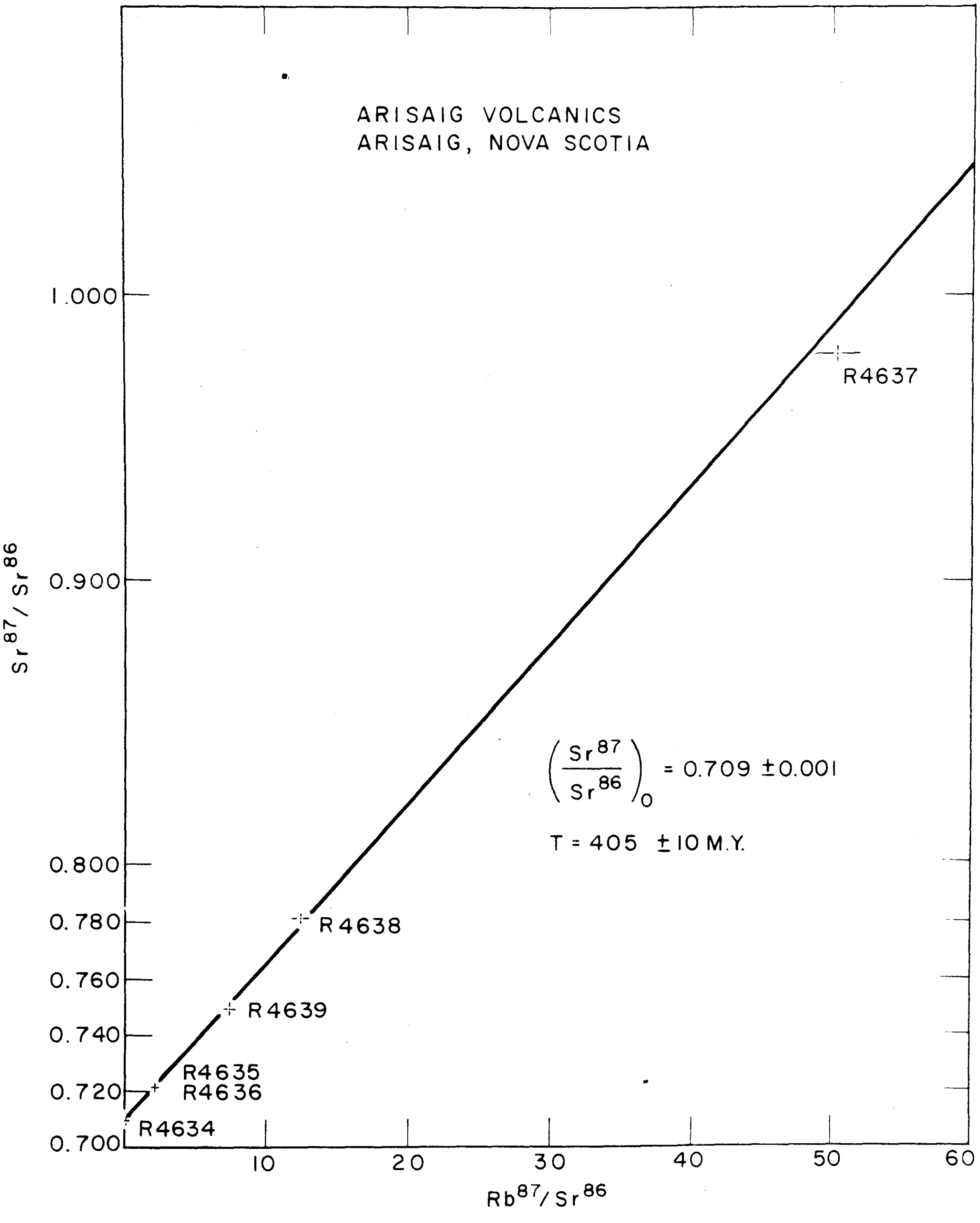

ARISAIG VOLCANICS
ARISAIG, NOVA SCOTIA
1.000
0.900
0.800
0.780
0.760
0.740
0.720
0.700
Sr^{87}/Sr^{86}
R4637
R4638
R4639
R4635
R4636
R4634
$\left(\frac{Sr^{87}}{Sr^{86}}\right)_0 = 0.709 \pm 0.001$
T = 405 ±10 M.Y.
10
20
30
40
50
60
Rb^{87}/Sr^{86}

FIGURE 4.1

basic volcanics is consistent with a single genetic history for the two rock types in this sequence. The initial ratio falls within the range for basaltic rocks reported by Faure and Hurley (1962) and Gast (1960).

The 405 ± 10 M. Y. age for the Arisaig volcanics is consistent with the 360 ± 10 M. Y. age for the upper Lower Devonian Kineo volcanics which is reported in Chapter 3 of this report. Assuming that the Devonian-Silurian boundry is about 370 M. Y. based on the Kineo age then the length of the Silurian is approximately 35 M. Y. which is not an unreasonable figure.

There are no geologically dated granitic intrusives listed by Kulp (1960) or Faul (1960) for the Silurian-Ordovician boundry. Based on interpolation, Kulp estimates 430 M. Y. and Holmes (1960) estimates 440 M. Y. for this boundry. The result for the Arisaig volcanics is approximately 8 % lower than these estimates, assuming its most probable age to be basal Silurian.

Faul (1960) reports an age of 420-450 M. Y. for the Middle Ordovician of Alabama and Tennesse. Adams and Rogers (1961) summarize much of the same data and conclude that of the 17 Rb-Sr, K-Ar and

U-Pb ages available, the 447 ± 10 M.Y. average of five U^{238}-Pb^{206} ages is the best estimate. The result for the Arisaig volcanics is reasonably consistent with these Middle Ordovician estimates. The Kulp-Holmes estimate of 430-440 M.Y. for the base of the Silurian only allows a maximum of approximately 15 M.Y. for the interval between Lower Silurian and Middle Ordovician.

Faul (1960, 1961) reports 4 biotite K-Ar ages of 405 M.Y. for a group of granites south of Calais, Maine. One of these granites intruded and metamorphosed Upper Silurian sediments (middle Ludlow to lower Gedinnian). Therefore this value of 405 M.Y. relates to post-Upper Silurian. There is a contradiction between this result for the post-Upper Silurian and the 405 M.Y. for the basal Silurian from the Arisaig volcanics.

Summary

The isochron for the Arisaig volcanics indicates an age of 405 ± 10 M.Y. and an initial ratio of 0.709 ± 0.001.

The single value for the initial ratio for the acid and basic volcanics is consistent with a single source for the rocks of the volcanic sequence. The initial ratio value falls within the range for basaltic rocks reported by Faure and Hurley (1962) and Gast (1960).

This result indicates a value of 405 ± 10 M.Y. for the base of the Silurian. This is approximately 8 % below the Kulp-Holmes estimate of 430-440 M.Y.. The result for the Arisaig volcanics is consistent with the result for the Kineo rhyolite (Chapter 3 This report) and the results for the Middle Ordovician of Tennessee and Alabama reported by Faul (1960) and Adams and Rogers (1961).

Chapter 5

The Wamsutta Volcanics

Introduction

The volcanics interbedded in the Wamsutta formation of the Narragansett basin provide an opportunity to directly determine the age of the middle or late Pennsylvanian.

Results of the Rb-Sr whole rock measurements on the Wamsutta volcanics are compared with the age of the Blue Hills porphyry of pre-middle or late Pennsylvanian age reported elsewhere in this thesis. Both of these results are then compared to the minimum ages for the Narragansett basin reported by Hurley et al. (1960) and the lead-alpha results on zircons reported by Quinn et al. (1957). In addition, comparison can be made with recent time scale estimates by Holmes(1960), Kulp (1960), and Faul (1960).

Geology

The volcanics from the Wamsutta formation (refered to as the Wamsutta volcanics for convenience in this thesis) occur south of Hoppin Hill near the town of South Attleboro in southeastern Massachusetts. The formation is part of the Narragansett basin of Massachusetts and Rhode Island.

Early workers include Woodworth et al. (1899) and Emerson (1917). Knox (1944) reported on plant fossils from this formation. Quinn and Oliver (1962) discuss the Pennsylvanian rocks of the Narragansett basin.

An unpublished map by Coomaraswamy and Ray (1954) was used for collecting samples for this investigation.

The formations of the basin in ascending order, are the Pondville, the Wamsutta, the Rhode Island and the Dighton. (See Table 5.1). These formations partly overlap (Quinn and Oliver (1962)). In particular the upper part of the Wamsutta is probably equivalent to the lower part of the Rhode Island formation. (Knox (1944)).

In the Hoppin Hill area the volcanics occur near the base of the formation and are interbedded with conglomerates. There are two basalt flows and one rhyolite flow. All three flows are separated by conglomerate beds 85 to 550 feet thick (Coomaraswamy, (1954)). The rhyolite is essentially unmetamorphosed with a red aphanitic groundmass and quartz and feldspar phenocrysts.

Table 5.1

Stratigraphy of the Narragansett Basin, Rhode Island.

After Quinn and Oliver (1962), Hurley et al. (1960), Moore (1959), Nichols (1956) and Knox (1944).

Age	Formation	Description
Late or post Pennsylvanian	Westerly granite	Light-gray, pink or tan fine grained massive granite; quartz, oligoclase, potash feldspar and biotite.
	Narragansett Pier granite	Pink, tan, gray medium-to-coarse-grained granite; chiefly massive, locally weakly foliated; quartz, oligoclase, potash feldspar and biotite.
Pennsylvanian (middle or late, Quinn and Oliver, 1962)	Dighton and Purgatory conglomerate (1000-1500 feet)	Coarse, poorly sorted, quartzite and granite roundstone conglomerates.
	Rhode Island formation (10,000')	Gray sandstone, conglomerates, shale, black shale and coal.
	Wamsutta formation (1000 feet)	Red, locally green and brown, sandstone, shale and conglomerate; interbedded rhyolite and basalts.

Table 5.1, continued

Age	Formation	Description
Pennsylvanian	Pondville conglomerate	Fine grained to coarse gray conglomerate, includes "giant" conglomerate containing Blue Hills porphyry pebbles.
(unconformity)		
Pre-middle or late Pennsylvanian Mississippian (?)	Quincy granite	Light to dark, bluish gray, medium-to-coarse grained massive granite, quartz, microperthite, riebeckite, aegirite.
	Blue Hills granite and quartz porphyries	Gray, quartz, feldspar, riebeckite, aegirite.
	Blue Hills aporhyolite	Dark red, purplish rhyolite showing flow structure.
Pre-Pennsylvanian Devonian (?) or Older	Fine-grained granite	Pinkish, gray, tan, fine-grained, partly massive, partly lineated or foliated; quartz, plagioclase, potash feldspar and biotite.
	Scituate granite gneiss	Pinkish-gray to pink medium-to-coarse granite gneiss, oval splotches of biotite, quartz, potash feldspar, plagioclase and biotite.
	Hope Valley alaskite gneiss	Pink, pinkish gray, medium-to-coarse grained alaskite gneiss, rod shaped aggregates of quartz, quartz, potash feldspar, plagioclase, biotite; other varieties.
(unconformity)		
Pre-Cambrian (?)	Blackstone series	Quartz biotite schist; gray pinkish quartz feldspar biotite gneiss.

Knox (1944) demonstrates that the age of the Wamsutta formation is probably Lower Allegheny. This is based only on correlation of fossil assembledges and not on index fossils.

Knox (1944 p. 132) describes the relation of the volcanics and the fossils as follows:

> A study of the outcrops in the vicinity revealed that the horizon at which the fossil plants were found is stratigraphically several hundred feet below the top of the formation and above the felsite flows outcropping in the vicinity about the middle of the Wamsutta series exposed in this region.

Knox (1944,p. 137) considers the relationship of the Wamsutta and Rhode Island formations to be as follows.

> Around South Attleboro the felsites in the Wamsutta came after the deposition of the Pondville conglomerate and after the red beds had begun to accumulate, but before the appearance of the Coal Measures in this section of the basin. It thus appears that the lower part of the Wamsutta may be of the same age as the lowermost beds of the Rhode Island formation or it may be somewhat older.

The age of the Wamsutta flora is determined by correlation with other fossiliferous formations and not by index fossils. Knox (1944, p. 137) writes

> Doctor Round has noted the similarity of the species of plants found in the Rhode Island Coal Measures to those of the Fern Ledges of New Brunswick and the

> Cherokee shales of Missouri (Woodworth et al. 1899, p. 116, 155). It is noted that some of the most common and widespread species on the Rhode Island formation are commonly found in the Fern Ledges. These New Brunswick beds have been considered to be Pottsville, (White, 1901), although Stopes (1914) believes they are somewhat higher and equivalent to the lowest zone of the middle Westphalian of Europe, or the Lower Alleghany in the eastern part of this country.
> On the other hand over 50 percent of the species found in the Rhode Island area are common to the Cherokee shales of Missouri of lower Pennsylvanian age. These were thought by White (1899) to be equivalent to the upper Westphalian of Europe, or the middle and upper Alleghany in eastern United States. According to the most recent data (Schuchert, 1943) the Cherokee is considered to be Lower Allegeny and late Pottsville. It thus appears that the Rhode Island Coal Measures in general are probably lower or middle Allegheny, and that the upper part of the Wamsutta red beds from which the fossil plants were obtained and which appears to be equivalent to the lower part of the Rhode Island Coal Measures, is most likely to be from the data at hand of lower Allegheny age.

Quinn and Oliver (1962) have reviewed the paleontology of the Narragansett basin sediments. They conclude that there is general agreement that the sediments are of middle or late Pennsylvanian age. They write (1962, p. 68):

> Thus there is general agreement on a middle or late Pennsylvanian age for the Narragansett basin deposits. The paleo-botanical work is out of date and modern work is needed to establish the age more precisely.

The diference between calling the maximum age of the sediments upper Lower Pennsylvanian or lower middle Pennsylvanian depends on where one places the Allegheny age division. The more specific designation, upper Lower Pennsylvanian is not warranted owing to the lack of precise fossil data for these sediments and lack of certainity about just where the Lower-Middle-Upper Pennsylvanian boundries should be drawn in general (Branson (1962)). Under the circumstances, the most reasonable designation for the maximum age is the more general one, middle Pennsylvanian after Quinn and Oliver (1962). (see Table 5.1A)

The possibility that the sediments may be as young as late Pennsylvanian must be borne in mind however, owing to the lack of precise fossil data for these sediments (Quinn and Oliver (1962)). Therefore it is probably best at this time to refer to the geologic age of the Narragansett basin as middle or late Pennsylvanian (Quinn and Oliver (1962)).

The lack of precision for the geologic age is partly due to the non-marine character of the basin which, according to Quinn and Oliver (1962), gives no indication of any marine sediments. Branson (1962) points out that faunal and floral zones of

Table 5.1A

Major Divisions of Pennsylvanian Time
from Branson (1962)

	Appalachian Mts.	Mid-continent	Western Europe	Russia
Permian	Dunkardian	Lyonian	Autumian	Sakmarian
Pennsylvanian	Monongahelan	Virgilian	Stephanian	Gschelian
	Conemaughian	Missourian		Kasimovian
	*	Desmoinesian	Westphalian	Moscovian
	Pottsvillian	Atokan		
		Morrowan	Namurian	Baschkirian
(Mississippian)		Chesterian		Visean

* Aproximate position of the Allegheny, put in by this writer, from Branson (1962).

the Pennsylvanian in general are composed of long-ranged species and that at present it is difficult to precisely determine geologic ages based on these alone. The best guide fossils are marine species such as fusulinids, certain ammonoids and brachiopods (Branson (1962)), which are, of course, absent owing to the non-marine character of the Narragansett basin.

In summary, the sediments of the Narragansett basin are middle or late Pennsylvanian in age. The unmetamorphosed volcanics of the Wamsutta formation in the Hoppin Hill area are geographically close to and stratigraphically several hundred feet below the best fossil locality in the Narragansett basin.

Results

Six rhyolite and three basalts were analyzed. In addition one sedimentary rock was inadvertently included in the suite of analyzed samples.

The results are reported in Table 5.2 and the isochron is shown in Figure 5.1. The isochron is plotted showing ± 3 % Rb^{87}/Sr^{86} and ± 0.25 % Sr^{87}/Sr^{86} as reasonable estimates of error. Inspection of the isochron plot shows that the basalts and rhyolite points do not fit the same line. The rhyolite isochron indicates an age of 225 ± 25 M.Y. and an initial ratio of 0.721 ± 0.002. The basalts

Table 5.2

Volcanics From The Wamsutta Formation, South Attleboro, Massachusetts

Sample	Rb (ppm)	Sr (ppm)	$\frac{Rb^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$\left(\frac{Sr^{87}}{Sr^{86}}\right)_{.1194}$
R4889 Basalt	-	-	(0.12)'	0.1189	0.7114	0.7099
R4890 Basalt	-	-	(0.04)'	0.1189	0.7113	0.7098
R4896 Basalt	-	--	(0.02)'	0.1207	0.7063	0.7101
R4891A Rhyolite	63.6 63.1 63.4	55.7 54.9 55.3	3.32	0.1205	0.7287	0.7321
R4891B Rhyolite	98.4	49.1	5.81	0.1198	0.7384	0.7396
R4891C Rhyolite	152	49.8	8.87	0.1199 0.1185 0.1192	0.7489 0.7469 0.7479	0.7505 0.7441 0.7473
R4893 Rhyolite	105 106 105.5	87.1 - 87.1	3.51	0.1205	0.7263	0.7296

Table 5.2, continued

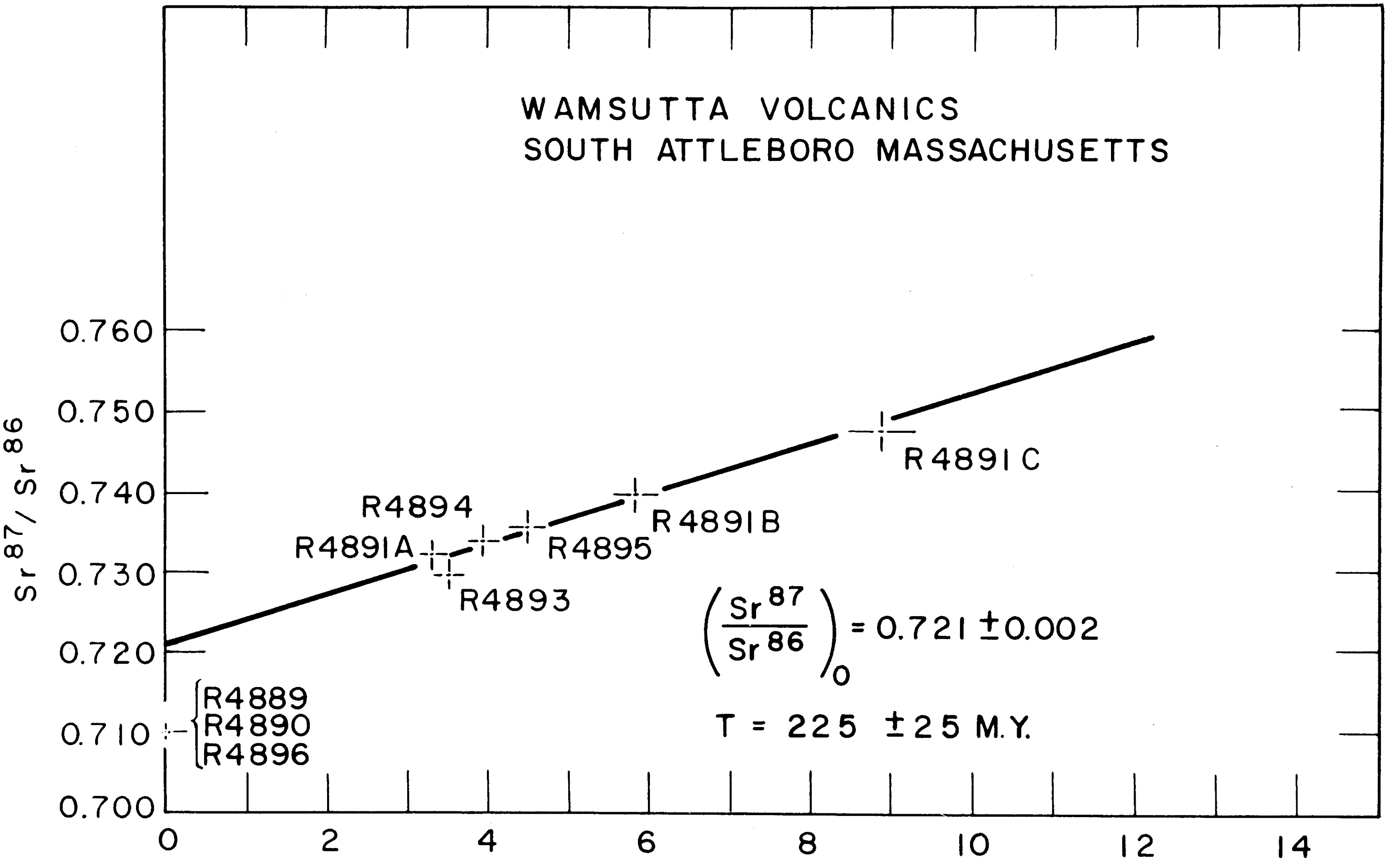
Sample	Rb (ppm)	Sr (ppm)	$\frac{Rb^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})_{.1194}$
R4894 Rhyolite	87.1[2]	-				
	99.1	72.4				
	99[3]	-				
	100[3]	-				
	-	72.5				
	99.3	72.45	3.98	0.1197	0.7331	0.7340
R4895 Rhyolite	138	89	4.5	0.1203	0.7328	0.7356
R4888 Sedimentary Rock	59.7[4]	-				
	70[3]	-				
	70[3]	-		0.1201	0.7162	0.7133
	-	124		0.1201	0.7159	0.7180
	70	124	1.62	0.1201	0.7161	0.7182

[1] Semi quantitative values determined by a single scan on the X-ray spectrograph on rock powders.

[2] The value is rejected because it is 12% low compared to the 99.1 ppm value which is confirmed by the quantitative X-ray determination of 99 and 100 ppm.

[3] These values determined by carefully standardized X-ray spectrograph analyses and are considered as reliable as the isotope dilution analyses.

[4] This value is rejected as low compared to the quantitative X-ray values.



WAMSUTTA VOLCANICS
SOUTH ATTLEBORO MASSACHUSETTS
Sr^{87}/Sr^{86}
0.760
0.750
0.740
0.730
0.720
0.710
0.700
0
2
4
6
8
10
12
14
Rb^{87}/Sr^{86}
R4894
R4891A
R4893
R4895
R4891B
R4891C
R4889
R4890
R4896
$\left(\frac{Sr^{87}}{Sr^{86}}\right)_0 = 0.721 \pm 0.002$
T = 225 ±25 M.Y.

FIGURE 5.1

have a directly measured Sr^{87}/Sr^{86} ratio of 0.7099 ±0.0001, and when corrected for the radiogenic Sr^{87} accumulated in 220 M.Y., yields an initial ratio of 0.708 ± 0.001.

The age result for the rhyolite is not precise because of the low slope of the isochron. The initial ratio of the rhyolite is clearly demonstrated.

Discussion

The difference in initial ratio between the basalts and the rhyolite indicates different genetic histories for the two rock types.

The initial ratio for the basalte falls within the range for basaltic rocks reported by Faure and Hurley (1962) and Gast (1960).

The initial ratio for the rhyolite is higher than that of the associated basalts and basaltic rocks in general. This indicates that the rhyolite is partially or wholly of crustal origin.

The Rb-Sr age for the Wamsutta can be compared to the result for the Blue Hills porphyry, the minimum ages for the Narragansett basin reported by Hurley et al. (1960), the Lead-alpha results on zircons reported by Quinn et al. (1957), and the Kulp-Holmes-Faul time scale estimates. All of these ages are summarized in Table 5.3

Table 5.3

Summary of Age Results For Narragansett Basin.

$(\lambda_{Rb^{87}} = 1.39 \times 10^{-11})$

Reference	Method and Material	Sample Locatities and Number of Samples	Age (M. Y.)
Quinn et al. (1957)	lead-alpha, zircons.	Westerly and Narragansett Pier granites (5).	224
		Range	(208-143)
		Narragansett Pier granite, 53S-49, Quonochontaug quadrangle, Quonochontaug beach, west of Narragansett basin, (1)	274
		average as given by Quinn et al. (6).	(234 ± 34)
		Included in the above, Q55-1, Narragamsett Pier granite sills in Pennsylvanian meta-sediments (1).	235
Hurley et al. (1960)	K-Ar, Rb-Sr biotite and whole-rock meta-sediments.	Meta-sediments, south end of Narragansett basin, whole-rock (3) and biotite K-Ar (3).	250
		Range	(230-275)

Table 5.3, continued

Reference	Method and Material	Sample Localities and Number of Samples	Age (M. Y.)
Hurley et al. (1960)	K-Ar,Rb-Sr biotite and whole-rock meta-sediments.	Biotite Rb-Sr (2) Average (8)	260 ± 15 255
	K-Ar biotite.	Granitic sills in Pennsylvanian meta-sediments. B3816, (1).	230 ± 11
	K-Ar biotite.	Westerly granite, B3814, Sullivan Quarry, Carolina quadrangle, Bradford, Rhode Island, west of Narragansett basin (1).	240 ± 12
Pinson et al. (1962)	Rb-Sr biotite	Westerly granite, B3042, Sullivan Quarry, Carolina quadrangle, Bradford, Rhode Island, west of Narragansett basin (1).	274 ± 10
	Rb-Sr single whole-rock using initial ratio obtained from apatite.	Westerly granite, G-1 standard Sullivan Quarry Carolina quadrangle, Bradford, Rhode Island, west of Nerragansett basin (1),	316 ± 40

Table 5.3, continued

Reference	Method and Material	Sample Localities and Number of Samples	Age (M. Y.)
This work	Rb-Sr whole-rock isochrons	Wamsutta rhyolite South Attleboro, Mass.. (6).	225 ± 25
		Blue Hills quartz porphyry (3)	245 ± 10
		Blue Hills aporhyolite (4) Milton, Quincy, Mass..	248 ± 10
		Normal Quincy granite Quincy, Mass.. (5)	325 ± 15
Hurley et al. (1960)	K-Ar whole-rock	Normal Quincy granite, R3821 Swingle Quarry, Quincy, Mass.. (1) (minimum only, Hurley et al. (1960)).	280 ± 15

The result for the Blue Hills porphyry is reported in Chapter 6 of this thesis. The Blue Hills porphyry gives a whole rock isochron age of 245 ± 10 M.Y.. This value represents a maximum age for the Narragansett basin. The direct determination of 225 ± 25 M.Y. is consistent with this result.

Hurley et al. (1960) report a minimum age for the Narragansett basin of 235 M.Y. (K-Ar) from the intrusive granites cutting the sediments and 255 M.Y. (K-Ar and Rb-Sr) from the metamorphosed sediments themselves. These samples come from the southern part of the basin which is intensely metamorphosed compared to the northern part.

The minimum age for the sediments from the intrusive granites (235 M.Y.) and the age from the Wamsutta rhyolite overlap because of the uncertainty of the rhyolite age. This uncertainty is unfortunate since it makes it very difficult to make a final decision on the relation between the minimum value and the "rhyolite value". It is clear though that the values, if not contridictory at least overlap. However the maximum value from the Blue Hills of 245 ± 10 M.Y. and the minimum value of 235 ± 5 M.Y. are at least in apparent agreement.

The fact that all three results are close together could be interpreted to mean that the interval of time involved for sedimentation, burial and intrusion is short compared to the precision of the measurements.

This is not a unique situation. Comparison of the Kineo volcanics age to the minimum age for the intrusive cutting the Seboomook slate also indicates a short time interval between sedimentation, burial and intrusion. (See Chapter 3 of this, report).

The 255 M.Y. on the meta-sediments of the basin (Hurley et al. (1960)) indicates an anomaly since this minimum value is greater than both the maximum (245 ± M.Y.) and the volcanic (225 ± 25M.Y.) values.

The 255 M.Y. value for the sediments is also greater than the 235 M.Y. value for the intrusives in the same area. K-Ar and Rb-Sr ages on sediments are minimum ages only on the assumption that all of the argon and radiogenic strontium was driven out during metamorphism. The possibility of inherited radiogenic isotopes in metamorphic sediments makes interpretation of these ages uncertain.

The same pattern of slightly higher metamorphic sediment ages relative to granitic intrusive ages is shown in the work on the Seboomook slate. (See Chapter 3, this report)

Quinn et al. (1957) report a lead-alpha age on zircons from late or post Pennsylvanian granitic intrusives of 234 ± 23 M.Y.. This value and the maximum value of 245 M.Y. from this report are in apparent agreement. It is likewise in essential agreement with the rhyolite value of 225 ± 25 M.Y. from this report.

This lead-alpha value is the average of six determinations, two from the Westerly granite and four from the Narragansett Pier granite. One sample of the latter granite gives an age of 274 M.Y. which is quite different from the other five and raises the average age value considerably. The average age for the five lower samples is 226 M.Y. with the 234 M.Y. value for all six.

The ages for the Narragansett basin result in a mixed pattern. There is at least apparent agreement between the minimum values from the intrusives (235 M.Y., Hurley et al. (1960) and 234 ± 34 Quinn et al. (1957)) and the maximum value (245 ± 10) from the Blue Hills porphyry. The intrusive minimum values and the direct value from the Wamsutta volcanics (225 ± 25 M.Y.) overlap.

The minimum value from the sediments (255M.Y. Hurley et al. (1960)) and both the maximum and direct values apparently are contradictory. The reality of this anomaly depends on whether the values for the meta-sediments are really minimum values.

It is instructive to examine these published ages more closely. Of the three granitic samples listed by Hurley et al., one (B3816) is from a granitic intrusive in the Pennsylvanian meta-sediments; one (B3814) is from the Westerly granite from the Sullivan Quarry near Bradford, Rhode Island; and one (B3815) is from the contact zone adjacent to the granitic sample.

This last sample is here included with the metamorphic sediment samples in Table 5.3.

The geologic age for the sample (B3816) is clearly post-middle or late Pennsylvanian based on its observed field relation. The K-Ar age result for this sample is 230 ± 11 M.Y..

Quinn et al. (1957) list one sample (Q55-1) which is also post middle or late Pennsylvanian based in its observed relation. The lead-alpha result on zircon from this sample gives an age of 235 M.Y.. These two samples are the only ones having field relations which directly fix their geologic age. The geologic age of the other granitic samples depend on correlation with the granitic intrusives in the basin. The rest of the granite samples analyzed by Hurley et al. and Quinn et al. are found in the area west of the Narragansett basin.

Hurley et al. reported a biotite K-Ar age of 240 ± 12 M.Y. for a sample (B3814) of Westerly granite from the Sullivan Quarry near Bradford, Rhode Island. Quinn et al. reported a zircon lead-alpha age of 234 M.Y. for a sample (S-47) from the same quarry. Pinson et al. (1962) reported a Rb-Sr biotite age of 274 ± 10 M.Y. ($\lambda = 1.39 \times 10^{-11}$) which is significantly higher than the lead-alpha and K-Ar age reported above. This is a different sample from the same quarry. In addition a whole rock age measurement on G-1 (Westerly granite) was reported as 315 ± 40 M.Y. ($\lambda = 1.39 \times 10^{-11}$, assuming an initial ratio of 0.709 based on the measured Sr^{87}/Sr^{86} ratio of apatite from the rock. This whole rock age has a large error of ± 40 M.Y. and may therefore not be in disagreement with the biotite age of 274 M.Y..

The Sullivan Quarry is approximately 15 miles from the nearest Pennsylvanian sediments. In this area a Westerly granite dike intrudes the Hope Valley alaskite gneiss and the Blackstone series (Moore,(1959), Both of these formations are considered pre-Pennsylvanian, probably Devonian or older. Moore (1959). In other areas the Westerly granite intrudes the Narragansett Pier granite. For example in the Ashaway quardrangle. (Quinn et al. (1957)).

Around the north shore of the Quonochontaug Pond thin dikes of fine-grained gray Westerly granite intrude the Narragansett Pier granite. (Moore (1959). In this area the Narragansett Pier granite is also intruded by dikes of a granite of similar appearance and is considered by Moore to be a late stage phase of the host granite. Nichols (1956) states that the Narragansett Pier granite is intruded by pegmatite dikes of similar composition in the Narragansett Pier and Boston Neck areas of the Narragansett Pier quadrangle.

The fact that in some areas the Narragansett Pier granite is cut by younger dikes of similar composition suggests the possibility that all the granites correlated as Narragansett Pier granite may not be contemporaneous. It should also be noted that the single lead-alpha age measurement for the Narragansett Pier granite along the south shore indicates an age of 274 M.Y. (Quinn et al. (1957) sample 53S-49). This value is in the range of the pre-Pennsylvanian ages as measured by the same method. Although this analysis could be in error, it could, on the other hand indicate that all of the granites considered Narragansett Pier type may not be contemporaneous. This consideration is important because the age of the Narragansett Pier granite primarily depends on correlation with the granite sills and pegmatites that cut the Pennsylvanian sediments of the basin.

The geologic age of the Westerly granite depends on the correlation of fine-grained granite dikes which cut the Narragansett Pier granite. In the literature it is not clear whether the Westerly granite itself intrudes the Pennsylvanian sediments. Quinn et al. state the following (p.547):

> The youngest of the granitic rocks are intrusive into the Pennsylvanian rocks of the Narragansett Basin. They include two main types: (1) The Narragansett Pier granite or so-called redstone, a medium-grained rock exposed near the mouth of Narragansett Bay and westward along the south shore of Rhode Island, and (2) The Westerly granite, a fine-grained rock exposed mostly in the Carolina, Ashaway, and Watch Hill quadrangles (near Westerly and Bradford).

The three quadrangles mentioned above are in the southeast corner of Rhode Island and well out of the Narragansett basin.

Quinn et al. write (p 551):

> Along the shore in the Narragansett Pier quadrangle there are numerous pegmatite dikes intrusive into the Pennsylvanian sedimentary rocks (Nichols, (1956)). Further southward, medium-grained granite is also intrusive into considerably metamorphosed Pennsylvanian rocks. At the locality of Q55-1 (south end of Tower Hill) there are several sills of granite intrusives into rocks of Pennsylvanian age. This granite is similar to the Narragansett Pier granite extensively exposed along the shore 2 miles southeast and to the so-called redstone of the quarries in the Ashaway quadrangle, except that the granite sills contain more muscivile and are not pink. At the locations of samples S-47 and Q55-3 (Bradford and Westerly) there are dikes of fine-grained granite, the Westerly granite, which are intrusive into the medium grained Narragansett Pier granite.

Nichols (1956) does not mention the Westerly granite in the Narragansett Pier quadrangle. It appears that the age of the Westerly granite is established by its intrusive relation with the Narragansett Pier granite in areas outside of the Pennsylvanian basin. If the correlation of the Westerly and Narragansett Pier granites with the granites cutting the Pennsylvanian section is correct then the minimum age for the Pennsylvanian sediments is at least 260 M.Y., excluding the whole rock age measurement on the Westerly granite. This indicates a real contradiction between the results of this thesis and the work on the granites of the area. In addition it would confirm the apparent contradiction between the results of this thesis and the ages on the meta-sediments of the basin.

On the other hand, if one considers the minimum age values for the intrusives which actually intrude the Pennsylvanian sediments then all the results are consistent and indicate that the sequence of events involving sedimentation, burial and intrusion took place over a relatively short interval of time. This interpretation requires the Westerly granite to be pre- rather than post-middle Pennsylvanian.

More age determinations should settle the question. In particular whole rock Rb-Sr work on the granites is needed for direct comparison with the results from this report. Conversely mineral ages by various methods are needed on the Wamsutta volcanics and the Blue Hills porphyry.

The results reported here are contradictory to the Kulp(1960), Holmes (1960) and Faul(1960) estimates for the Pennsylvanian-Permian and Pennsylvanian-Mississippian boundries. Kulp's estimate for the Pennsylvanian-Permian boundry is 270 M.Y. and for the Pennsylvanian-Mississippian boundry is 320 M.Y.. This requires an age greater than 300 M.Y. for the pre-middle Pennsylvanian. The results for the Blue Hills porphyry and the Wamsutta volcanics are approximately 50-70 M.Y. lower than Kulp's estimate for this section of the time scale.

Some of the critical samples listed by Kulp (1960, p, 20, 21) are as follows:

> (9) The igneous complex of the Oslo region is presumably late Lower Permian. One result on biotite from these rocks gives 259 ± 10 M.Y. (Faul, 1957).
> (10) For post-Middle Pennsylvanian metamorphic rocks in Rhode Island an average of 256 ± 10 M.Y. is found by

> the K-Ar and Rb-Sr methods (Hurley et al.,1959)
> (11) The granites of the Cornwall region in England are definitely post-Westphalian and pre-Middle Permian. They are probably lowermost Permian. The age obtained on repeated determinations is 270 ± 5 (Kulp et al., 1960).
> (12) Rb-Sr and K-Ar measurements on biotite in eight granites from the Vosges, Schwarzwald and Massif Central which probably are post-Dinantian by pre-Visian (i.e. late-Lower Carboniferous gave an age of about 335 ± 10 M.Y. (Faul,1957) This valuable point probably warrents further geological study.

Faul gives a little more detail on the Oslo rocks (1959, p. 636):

> Early Permian or later
> Granite and nordmarkite intrude rhomb porphyry lavas which are interbedded with fossiliferous lake sediments of early Permian age that are correlative with the German Rotliegends.
> K-Ar (Biotite from the Drammen granite, Faul et al. , 1959) 259 M.Y..
> U^{238}/Pb^{206} (zircon from the Oslo nordmarkite, Faul et al., 1959) 260 M.Y..

These results and the results from this report are in disagreement. Because of the uncertainties involved it is difficult to determine the extent of the disagreement (e.g. The geologic age of the Narragansett basin and the uncertainty of the Wamsutta volcanics age). It appears to be on the order of 10 to 20 %.

The results for the Pennsylvanian rocks from

Rhode Island (Hurley et al.,1960) have been discussed in detail. It is clear that the results reported here are consistent with the data for the intrusive granite sills in the Pennsylvanian sediments but inconsistent with the results for the metamorphosed sediments.

Lambert and Mills (1961) report a mean K-Ar and Rb-Sr age of 285 ± 8 M.Y. for the Dartmoor and Land's End granite. The Land's End granite is only known to be post-Lower Devonian. The Dartmoor granite is known to be post-Lower Westphalian. Lower Westphalian sediments of Europe are correlated with the Atokan (pre-Desmoinesian) of the Mid-continent and Middle Pottsvillian of the Appalachian Mountains in North America (Branson(1962)). Therefore Lower Westphalian is approximately equivalent to early Pennsylvanian in North America. Lambert and Mills reported biotite K-Ar ages of 270 and 290 M.Y. and a biotite Rb-Sr age of 300 M.Y. ($\lambda = 1.39 \times 10^{-11}$) for the Dartmoor granite.

Comparison of these ages with those of the present investigation indicate a minimum discrepancy of approximately 15 %. This is based on the assumption of a maximum geologic age for the Dartmoor granite and a minimum geologic age for the Narragansett basin. If the Dartmoor granite is lowermost Permiam as thought probable by Lambert and Mills, and by Kulp, then the discrepancy is greater than 15%.

The Vosges granites are pre-Visean. The geologic age of the Schwarzwald and Massif Central granites is not as well known as the Vosges (Faul (1960,1961).

Faul writes on the Vosges granites as follows (1960, p. 636):

> Early Carboniferous (Dinantian, pre Visean) In northeastern France, the Vosges granites intrude and metamorphosed Tournaisian sedimentary rocks. Overlaying fossiliferous rocks of early Visean age were not affected.
> Rb/Sr (biotite average of 3 samples; Carnegie Institution, 1957 recomputed 322 M.Y.) (340 M.Y.; $\lambda = 1.39 \times 10^{-11}$ author's note).
> K/Ar (biotite, average of 4 samples, Faul, Table 2) 315 M.Y..

Using $\lambda = 1.39 \times 10^{-11}$ for the Rb-Sr results gives an average K-Ar and Rb-Sr age of about 328 M.Y.. Comparison of these data with the results reported here is difficult owing to the extrapolations to common geologic age boundries and lack of knowledge of the lengths of time involved in the Carboniferous period.

If the Narragansett basin sediments are as young as late Carboniferous and the total length of the Carboniferous period is approximately 100M.Y.. Then the results are reasonably consistent.

Summary

The ages of the pre-middle or late Pennsylvanian Blue Hills porphyry and the middle or late Pennsylvanian Wamsutta volcanics from the Narragansett basin are 245 ± 10 M.Y. and 225 ± 25 M.Y. respectively. Comparison of these ages with the minimum ages for the Narragansett basin as reported by Hurley et al. (1960) indicates reasonable agreement with the 235 M.Y. value for the intrusives and disagreement with the minimum ages from the metamorphosed sediments. It is suggested that the meta-sediment ages can not be considered reliable minimum ages because of the possibility of inherited daughter products.

Kulp listed four critical points in this section of the time scale. Two of the points, the Dartmoor granite, England, and the Oslo complex, Norway, are in clear disagreement with the results of this report. Two of the points, the Narragansett basin (Rhode Island) and the Vosge granite (France) may or may not be in disagreement depending on interpretation.

The basalts have a directly measured Sr^{87}/Sr^{86} ratio of 0.7099 ±0.001 which reduces to 0.708 ± 0.001 when corrected for radiogenic strontium. The rhyolite has an initial Sr^{87}/Sr^{86} ratio of 0.721 ± 0.002. The difference in initial ratio between the basalts and the rhyolite indicates different genetic histories for the two rock types.

The initial ratio values for the basalts falls within the range for basaltic rocks reported by Faure and Hurley (1962) and Gast (1960).

The initial ratio for the rhyolite is higher than that of the associated basalts and basaltic rocks in general. This indicates that the rhyolite is partially or wholly of crustal origin.

Chapter 6

The Age and Correlation of The Blue Hills Complex, Cape Ann Granite and The Newbury Volcanics.

Introduction

In this chapter results are reported for the Blue Hills complex, Cape Ann granite and the Newbury volcanics. The problem of the age and correlation of the granites and other igneous activity of the eastern Massachusetts area is part of a continuing laboratory program. Particular interest in the Blue Hills complex stems from its relation to the Pennsylvanian sediments south of Boston. Boulders and pebbles of the Blue Hills quartz porphyry occur in the conglomerate at the base of the Pennsylvanian sediments of the Norfolk basin. Therefore the quartz porphyry defines a maximum age for the Pennsylvanian section. The Cape Ann granite has been correlated with the Blue Hills complex and both are part of the extensive alkaline igneous province in New England.The Newbury volcanics are considered a part of this igneous province.

General Geology

There are many publications on the general geology of eastern Massachusetts. Most of the work was done in the late part of the 19th century and the first thirty years of this century. The most recent general geologic map of Massachusetts and Rhode Island was published in 1917 (Emerson (1917)). The last publication on the general geology of the Boston area was by LaForge (1932). Clapp (1921) described the igneous rocks of Essex County, an area which includes the Cape Ann granite and the Newbury volcanics. Warren (1913) published a detailed and extensive study of the Blue Hills complex. Loughlin (1911) worked out the relations between the Blue Hills complex and the adjacent sediments of the Norfolk basin. Dale (1923) describes the granite quarries of New England. Unpublished reports include those of Bell (1948) and dos Santos (1960). Additional references are referred to later at appropriate places in this report; still others are listed in the bibliography

Bell (1948) divides the rocks of the Boston area into five groups based on similar lithology and supposed age.

The first group includes the older strata which occur as isolated roof pendants and inclusions in the younger intrusives. These are the Westboro, Marlboro, Weymouth, and Braintree formations, all of which Bell assigns to the Cambrain. The geologic age, based on fossil evidence shows that the Weymouth formation is Lower Cambrian; and that the Braintree formation is Middle Cambrian. The geologic age of the Westboro, Marlboro, amd Woburn formations has not been directly determined because of their discontineous and non-fossiliferous character. The Westboro is a non-fossiliferous quartzite and the Marlboro and Woburn formations are volcanics.

The second group is the sub-alkaline igneous rocks, which includes the Salem gabbro-diorite, Newburyport quartz diorite, the Dedham granodiorite and the Nahant gabbro. Clapp(1921) correlates the Nahant gabbro with the alkaline group of igneous rocks rather than with the sub- alkaline group. The Nahant Gabbro is the only member of either group which intrudes a fossiliferous section.(Lower Cambrian Weymouth formation).

The third, the alkaline group, includes all the "Quincy" granites of the area. This includes the Quincy granite and associated rocks from the Blue Hills, the Peabody granite, the Cape Ann granite, the Beverly syenite and many smaller granitic and syenitic bodies. The Lynn, Mattapan and the Newbury volcanics are generally included in this group.

The fourth group includes the stratified rocks of the Boston basin. These are the Roxbury conglomerate, the Cambridge siltstone, the Squantum tillite and the Brighton volcanics.

The fifth group consists of the diabase dikes and sills that cut most of the formations of the area. La Forge (1931) distinguishes four sets of dikes; two sets found only in certain areas of pre-Carboniferous rocks and two sets which are found throughout all the rocks of the area. These younger sets are presumably triassic in age.

In the following sections each area is described in more detail.

The Blue Hills Complex

Geology

The Blue Hills complex includes the normal, or medium to coarse grained Quincy granite, the Blue Hills granite and quartz porphyries, the Blue Hills aporhyolite and the rhombenporphyry.

The complex occurs in an area approximately 3 by 9 miles and includes all of the Blue Hills Reservation in the towns of Milton and Quincy, Massachusetts, and underlies most of the rest of Quincy. The normal granite is quarried extensively.

The first detailed work in the Blue Hills was done by Crosby (1895, 1900). Washington (1897) described and analyzed the Quincy granite. Dale (1923) described the Quincy granite from the many quarries in the area. The general geology of the area is described by Loughlin (1911), Emerson (1917), La Forge (1932) and Chute (1940). Loughlin (1911) and Billings (1929) interpreted the structural geology of the area. In particular Loughlin (1911) described the relation of the Blue Hills complex to the sediments of the Norfolk basin.

The most detailed study of the Blue Hills complex was done by Warren (1913). He divided the complex into the following rock types. Warren ((1913) p. 207);

> Rock Types - The rocks of this series are all characterized by the presence of soda-potash feldspars either in the form of a homogeneous mixture (true mixed crystal ?), cryptoperthite or microperthite: by the presence of either alkali-hornblend or pyroxenes or both, and, with the exception of one member, by the presence of abundant quartz. They may be divided into the following types:
> 1 (a) Medium to coarse grained, riebeckite-aegirite-microperthite-granite (Quincy type):
> (b) the same, but with an inconspicuous porphyritic habit. (Rattlesnake Hill type.)
> 11 Fine grained granite similar in mineral composition to 1, but predominately riebeckitic and of a little more basic composition.
> 111 The Blue Hill Porphyries: riebeckite, aegrite bearing, quartz-feldspar ar granite porphyries.
> 1V Dark, alkali-feldspar - or rhombenporphyry.
> V Cognate Xenolithes occuring in 1 and 111. These are for the most part fine grained varieties usually porphyritic and more basic than the granite.
> V1 Aporhyolite
> To these may be added, fine-granite and pegmatites, both of rare occurrence.

The complex as a whole is high in silica, alkalies, and iron, compared with most granitic rocks, and low in calcium and magnesium. There is slightly more potash than soda. (Warren (1913) p. 325).

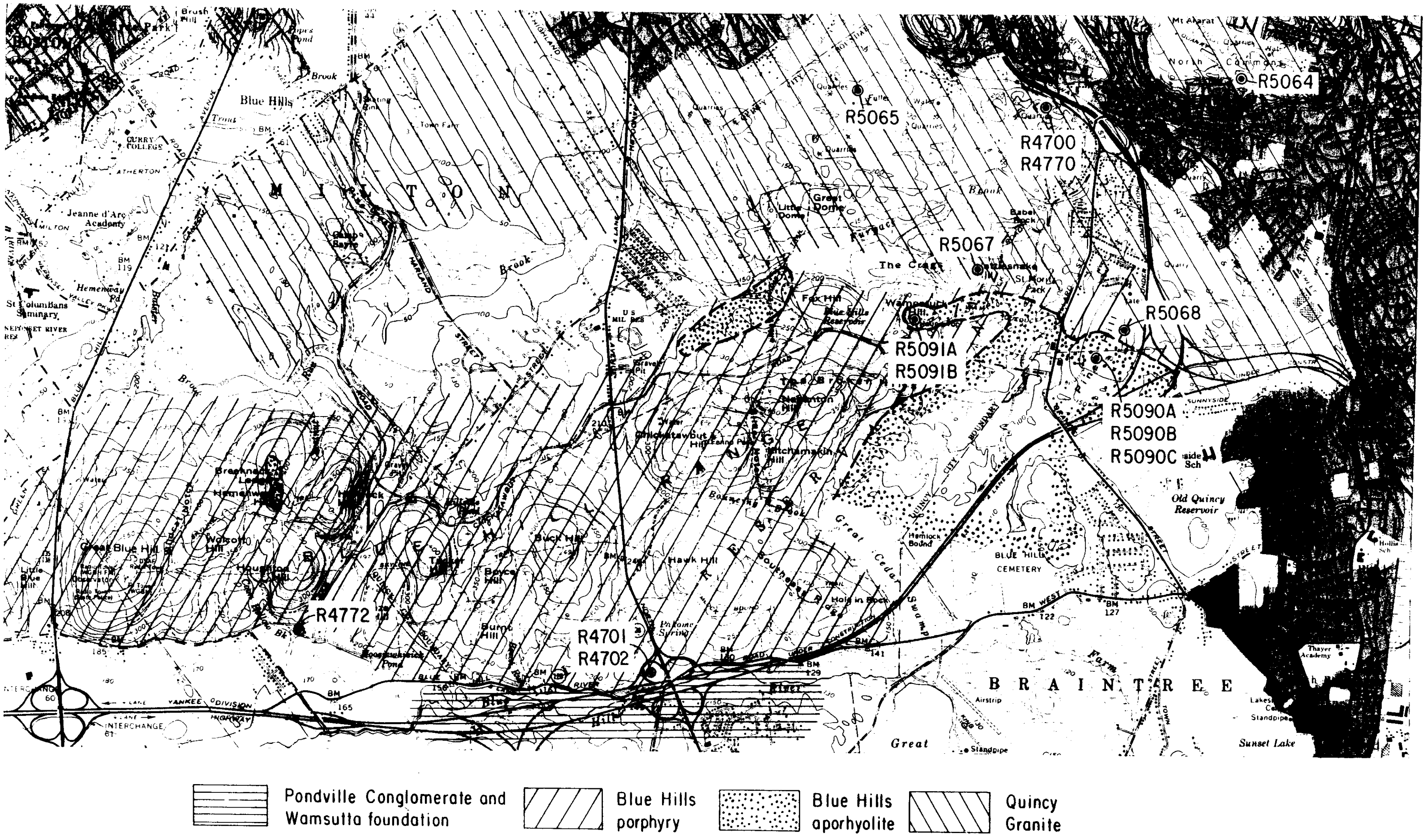
The Type 1 or normal Quincy granite occurs in the northern part of the complex, in southern Milton north of the Blue Hills and in Quincy, Warren goes on to say (p. 210),

> In fact the coarse-granite can hardly be said to occur in the Blue Hills proper except at one point (near Rattlesnake Hill), and in the form of dikes, cutting the porphyry cover in the region just east of Chickatawbut Hill.

Crosby (1895) reported that the normal granite graded into fine-granite and porphyry in the area of Slide Notch just east of Chicktatawbut Hill. Warren (p. 210) states that he searched diligently in this locality and was unable to find any strictly normal Quincy granite showing these relations. Warren did observe dikes of granite cutting the porphyry and at one place, instead of dikes, he observed what he thought was granite porphyry grading into normal granite. The question of normal Quincy granite occurring around Chicktawbut Hill, as either cross cutting dikes at gradational contacts with the granite porphyry, is a crucial point in the argument of the geologic age relation between the normal Quincy granite and the granite porphyry. It should be pointed out that the granite which occurs in this area does not exactly resemble the normal Quincy (Personal communication, M.P. Billings) and its true status is as yet undetermined.

The fine-granite faces occurs in eastern and southern Quincy, and in north Weymouth (Warren (1913), p. 210). It is restricted, by and large, to the northeastern edge of the normal granite.

The granite porphyry with its quartz porphyry phase occupies most of the Blue Hills proper. (see Fig. 6)



MAP SHOWING SAMPLE LOCALITIES AND APPROXIMATE DISTRIBUTION OF ROCK TYPES. AFTER WARREN (1913) AND CHUTE (1940)

BLUE HILLS MASSACHUSETTS

SCALE: 1 1/2 0 MILE

It occurs nowhere outside of the Blue Hills except at Pine Hill just outside of the reservation. Pine Hill is another crucial locality where the porphyry, the fine-granite, the coarse granite, the aporhyolite and the rhombenporphyry occur in a small area. The granite porphyry does not occur to the north in the Quincy area at all. (Warren (1913), p. 238 ff).

The rhombenporphyry occurs at Pine Hill, Pine Tree Brook and a few other areas. It occurs as xenoliths in the intrusive rocks and is frequently associated with the Braintree slate xenoliths. (Warren (1913) p.263 ff)

The aporhyolite occurs at three localities in the Blue Hills area. The largest occurrenceextends from Pine Hill just east of the park to the summit of Wampatuck Hill and south of Rattlesnake Hill south to the swamp in nothern Braintree. Another occurrence is north of Fox Hill and the third and smallest exposure is at the top of Hemingway Hill, The aporhyolite, like the porphyry, is restricted to the Blue Hills in the southern part of the complex. It has an aphanitic groundmass with a few feldspar and quartz phenocrysts. Spherulites and flow banding are present (Warren (1913) p.284-291).

In addition to the above there are three pegmatites, a few granite dikes cutting the granite, and a few granite dikes cutting the porphyry. (Warren (1913)p. 292)

Warren's interpretation of the Blue Hills complex is as follows. A single, relatively undifferentiated magma intruded the Middle Cambrian Braintree slate. The rhyolite (aporhyolite) was extruded on the surface or intruded near the surface. A cover of porphyry formed at the top of the intrusive mass as a contact facies. This insulated the underlying magma and provided an oportunity for the medium tocoarse-grained normal Quincy to form. In the northeast section of the complex a fine-grained granite is the contact facies. The magma beneath this porphyry cover broke through in a few places as shown by the granite dikes in the area east of Chitatawbut Hill. The only differeniate was the rhombenporphyry which formed adjacent to the slate contact. This facies broke up and sunk, forming xenoliths in the parent magma.

The whole complex was faulted and elevated on the north with subsequent erosion of the porphyry cover from the northern part of the complex.

The relative ages of the members of the complex based on the above interpretation are, from oldest to youngest: the aporhyolite and the rhombenporphyry, the granite porphyry, and normal Quincy granite. Presumably all facies were practically contemporaneous and were emplaced in a short time interval.

In general, although not in every detail, the above interpretation has been accepted by geologist working in the area.

The geologic age of the complex is somewhere between post-Middle Cambrian to pre-middle or late Pennsylvanian. This is based on the Middle Cambrian Braintree slate xenoliths, on one hand and the Blue Hills porphyry pebbles in the middle or late Pennsylvanian Pondville conglomerate on the other. The conglomerate contains only pebbles of the Blue Hills porphyry, and no normal Quincy granite has ever been found. (Loughlin (1911), Chute (1940))

The occurrence of porphyry pebbles in the Pondville conglomerate means that the age of the porphyry defines a maximum age for the middle or late Pennsylvanian.

Results

Five samples of normal Quincy granite, three samples of Blue Hills quartz porphyry, four samples of aporhyolite, one sample of rhombenporphyry and one sample of uncertain identification, have been

Table 6.1

Normal Quincy Granite, Quincy, Massachusetts.

Sample	Rb ppm.	Sr ppm.	$\frac{Rb^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})_{.1194}$
R4700	161.0 154.0 157.5	11.3 10.9 11.1	41.7	0.1200	0.9200	0.9223
R4770	164 --- - --- - 164.	-- -- 4.52 5.04 4.78	104.	0.1204	1.1645	1.1693
R5064	185. --- -	-- -- 10.0	55.0	0.1216	0.9657	0.9746
R5065	157. --- -	-- -- 8.26	56.6	0.1204	0.9965	1.0007
R5067	137. --- -	-- -- 15.8	25.3	0.1207	0.8348	0.8393

Table 6.2

Blue Hills Porphyry and Aporhyolite, Quincy and Milton, Massachusetts.

Sample	Rb ppm.	Sr ppm.	$\frac{Rb^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$\left(\frac{Sr^{87}}{Sr^{86}}\right)_{.1194}$
R4701 porphyry	--- - 200. 201. 200.5	80.5 --- - 80.2 80.35	7.24	0.1186	0.7486	0.7461
R4702 porphyry	135. 147. 141.	111. 123. 117.	3.51	0.1201	0.7327	0.7348
R4772 porphyry	169. 160. --- - --- - 164.5	--- -- --- -- 4.40 4.18 4.29	115.	0.1195	1.1122	1.1125
R5090B aporhyolite	269. ---	--- -- 11.1	71.7	0.1198	0.9418	0.9434
R5090C aporhyolite	101. ---	--- -- 12.6	23.4	0.1199	0.7903	0.7920
R5091A aporhyolite	178. ---	--- -- 9.72	53.9	0.1210	0.8756	0.8815
R5091B aporhyolite	188. ---	--- -- 4.44	128.	0.1200	1.1780	1.1810[1]

[1] Incomplete run, only 18 sets obtained.

Table 6.3

Miscellaneous Samples from the Blue Hills Complex, Quincy and Milton, Mass.

Sample	Rb ppm.	Sr ppm.	$\frac{Rb^{37}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})$ .1194
R5068 rhomben-porphyry	---	- --	(0.9)[1]	0.1210	0.7072	0.7119
R5089 porphyry	176. ?---	- -- 7.46	69.6	0.1212	0.8959	0.9027

[1] Semi-quantitative value determined by a single scan on X-ray spectrograph.

analyzed. All samples are whole rocks.

The results are shown in Tables 6.1,6.2,6.3. The isochrons for the normal Quincy granite, the Blue Hills quartz porphyry and the aporhyolite are shown in Figures 6.1, 6.2 and 6.3 respectively. Figure 6.4 shows all three isochrons for direct comparison. The isochrons (Figures 6.1, 6.2, 6.3,) are plotted showing ± 5% for Rb^{87}/Sr^{86} and ±0.25% for Sr^{87}/Sr^{86} values.

The Quincy granite isochron (Figure 6.1) indicates an age of 325 ± 15 M.Y. with an initial Sr^{87}/Sr^{86} ratio of 0.728 ± 0.008. The large uncertainty of the initial ratio arises from lack of samples with low Rb/Sr ratios. It is clear however that the initial ratio of the granite is well above the basaltic range of 0.708 ± 0.002 (Faure and Hurley (1962)). This indicates that the material of the Quincy granite is partially or wholly of crustal origin.

The Blue Hills quartz porphyry isochron (Figure 6.2) indicates an age of 245 ± 10 M.Y. and an initial ratio of 0.722 ± 0.002. The age of the porphyry is clearly younger that that of the normal granite. The initial ratio is higher that that of basaltic rocks and equal to or less than that for the normal granite. This initial ratio indicates that the material of

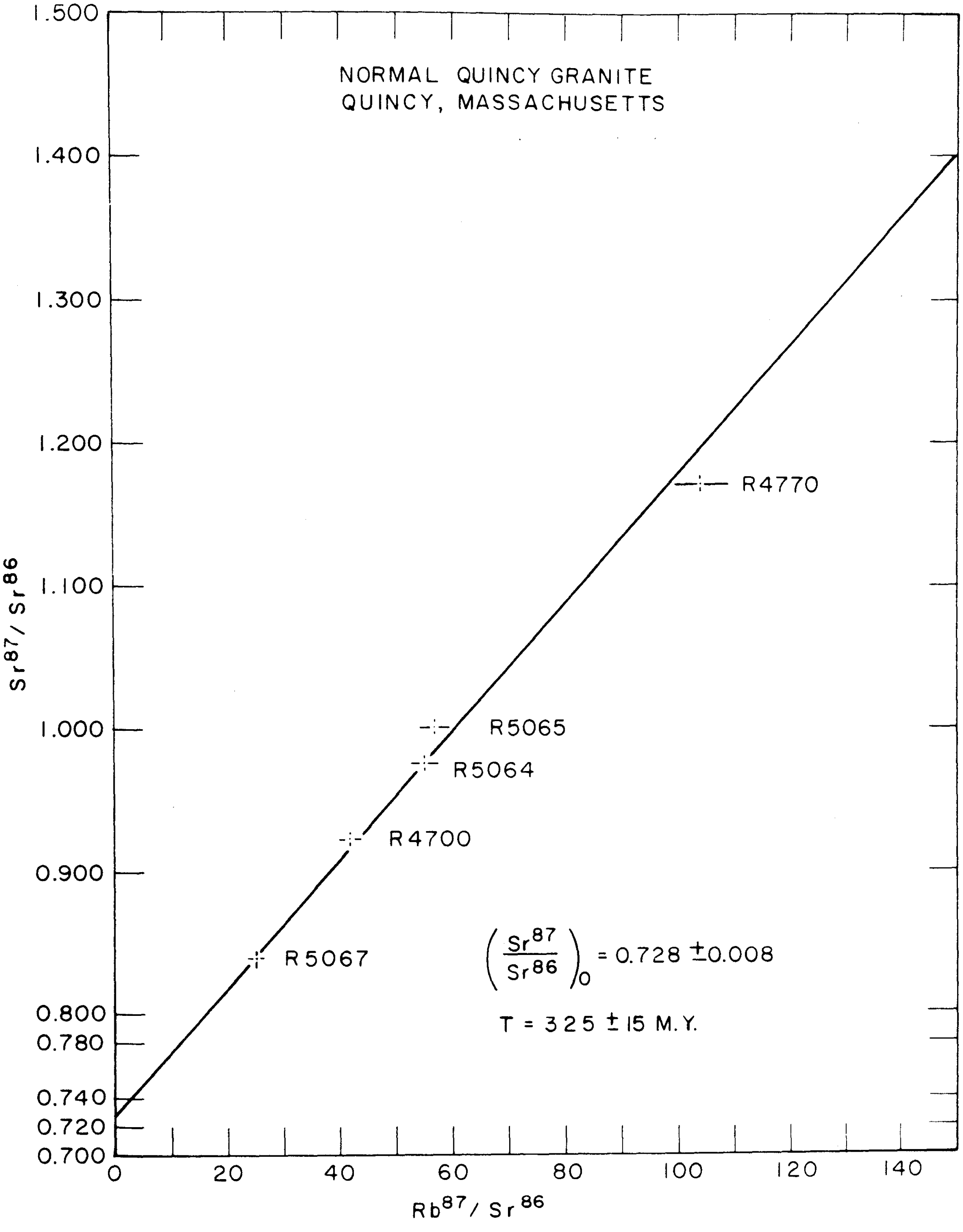

NORMAL QUINCY GRANITE
QUINCY, MASSACHUSETTS
1.500
1.400
1.300
1.200
1.100
1.000
0.900
0.800
0.780
0.740
0.720
0.700
Sr^{87}/Sr^{86}
0
20
40
60
80
100
120
140
Rb^{87}/Sr^{86}
R4770
R5065
R5064
R4700
R5067
$\left(\frac{Sr^{87}}{Sr^{86}}\right)_0 = 0.728 \pm 0.008$
T = 325 ± 15 M.Y.

FIGURE 6.1

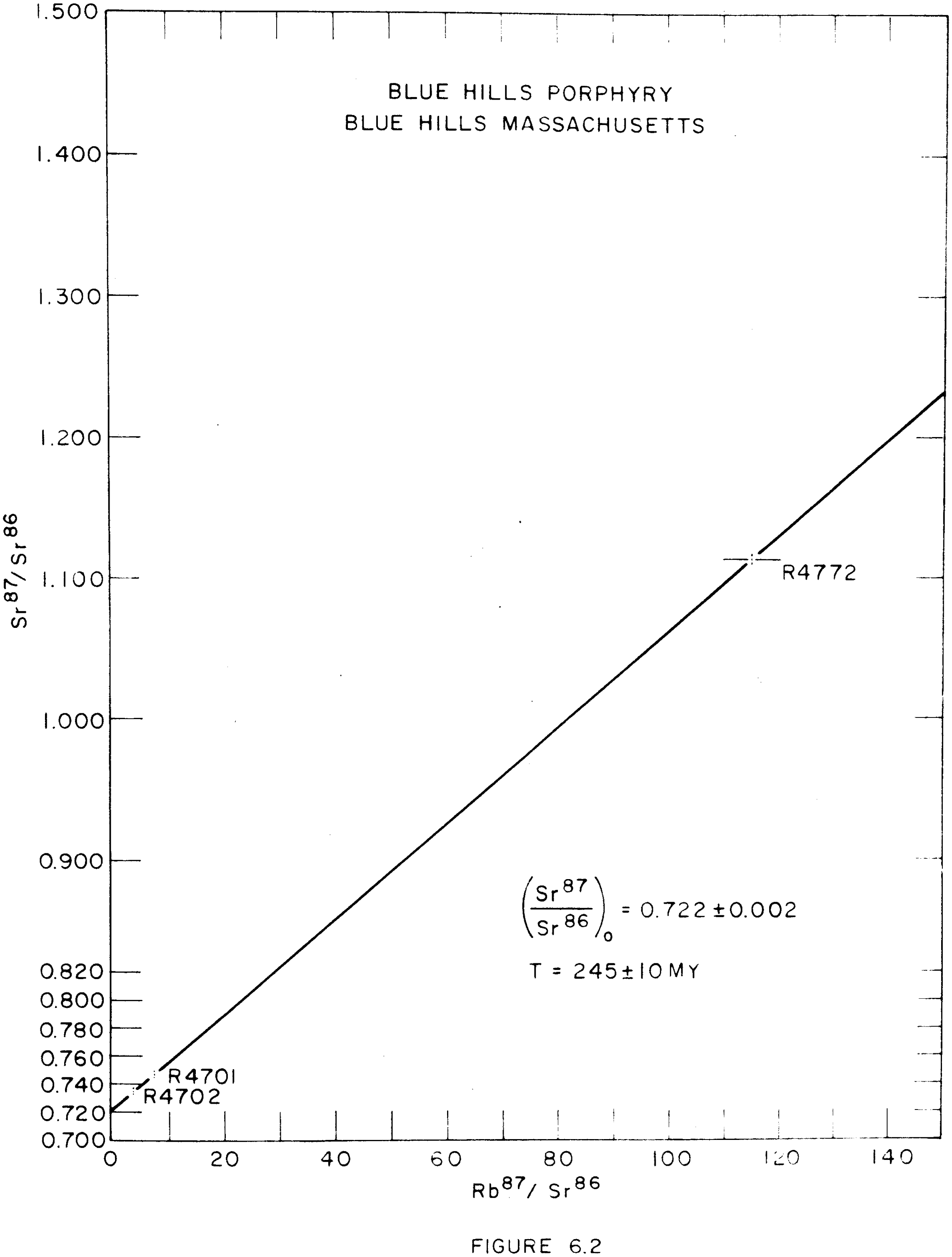

BLUE HILLS PORPHYRY
BLUE HILLS MASSACHUSETTS
Sr^{87}/Sr^{86}
1.500
1.400
1.300
1.200
1.100
1.000
0.900
0.820
0.800
0.780
0.760
0.740
0.720
0.700
R4772
R4701
R4702
$\left(\frac{Sr^{87}}{Sr^{86}}\right)_0 = 0.722 \pm 0.002$
T = 245±10 MY
0
20
40
60
80
100
120
140
Rb^{87}/Sr^{86}

FIGURE 6.2

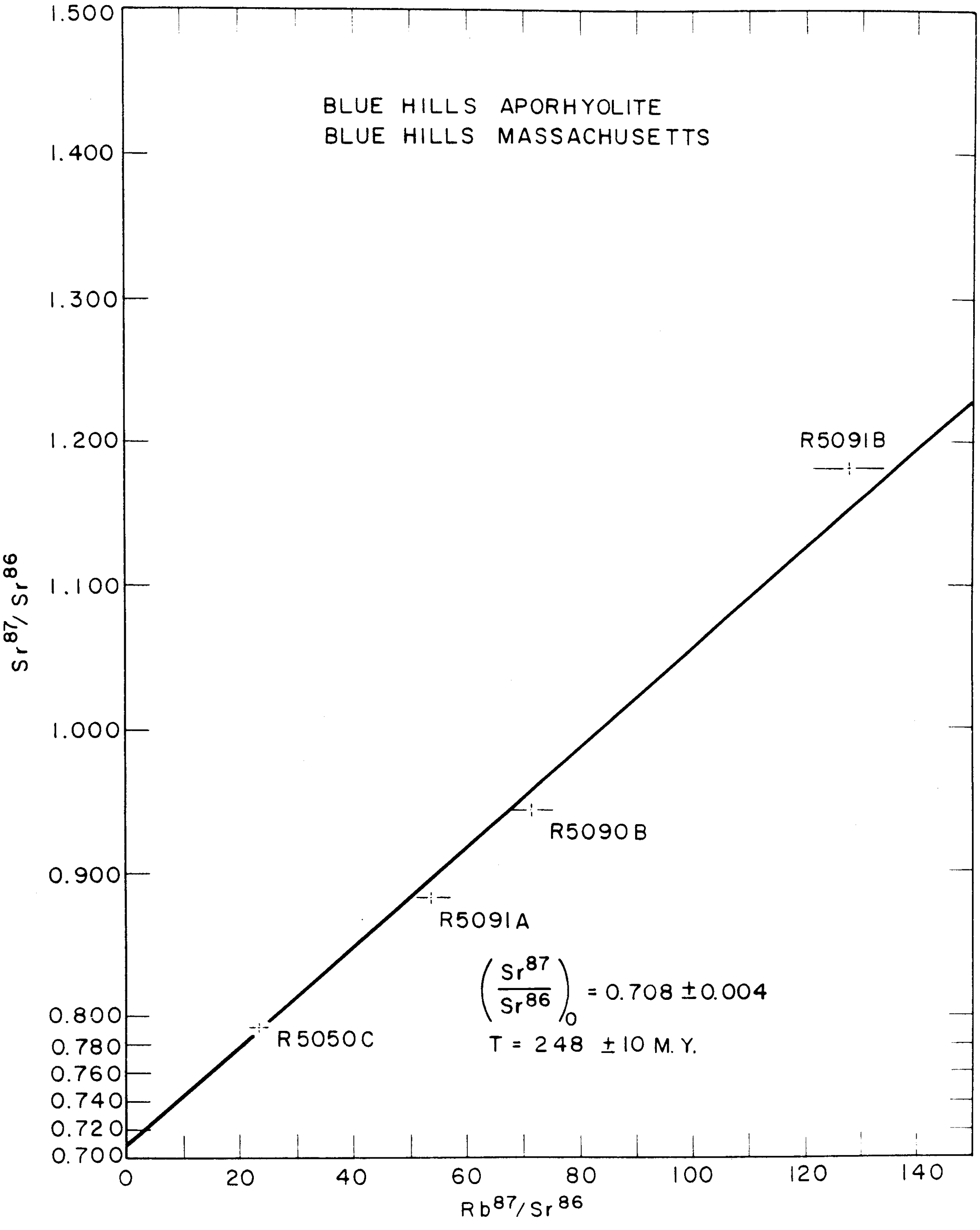

BLUE HILLS APORHYOLITE
BLUE HILLS MASSACHUSETTS
1.500
1.400
1.300
1.200
1.100
1.000
0.900
0.800
0.780
0.760
0.740
0.720
0.700
Sr87/Sr86
0
20
40
60
80
100
120
140
Rb87/Sr86
R5091B
R5090B
R5091A
R5050C
(Sr87/Sr86)0 = 0.708 ± 0.004
T = 248 ± 10 M.Y.

FIGURE 6.3

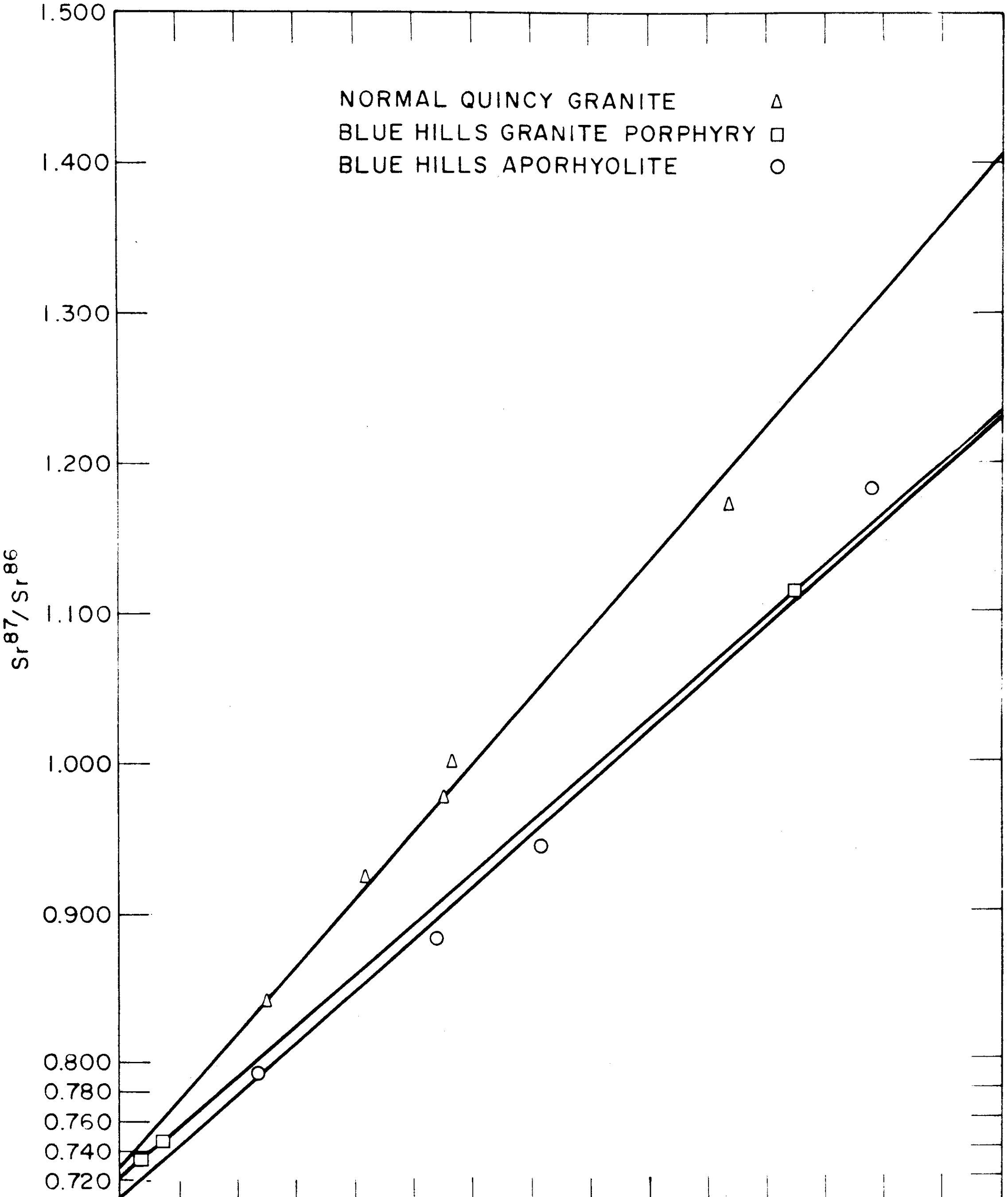

NORMAL QUINCY GRANITE △
BLUE HILLS GRANITE PORPHYRY □
BLUE HILLS APORHYOLITE ○
1.500
1.400
1.300
1.200
1.100
1.000
0.900
0.800
0.780
0.760
0.740
0.720
0.700
Sr87/Sr86
0
20
40
60
80
100
120
140
Rb87/Sr86

FIGURE 6.4

the Blue Hills porphyry is likewise partially or wholly of crustal origin.

The Blue Hills aporhyolite isochron (Figure 6.3) indicates an age of 248 ± 10 M.Y. and an initial ratio of o.708 ± 0.004. This age is analytically the same as that of the porphyry. The initial ratio is significantly less than that of the porphyry and falls within the range for basaltic rocks.

The results for the rhombenporphyry (R5068) is shown in Table 6.3. The measured Sr^{87}/Sr^{86} value is 0.712. Since the rhombenporphyry is intruded by the normal Quincy granite its age must be greater than 320 M.Y.. It is younger than the Middle Cambrian Braintree slate and must therefore be less than (approximately) 500 M.Y.. The initial ratio calculated on the above basis is 0.707 ± 0.002.

The sample R5089 (Table 6.3) **is from** a recent roadcut in Southeast Ridge, Blue Hills. It is a porphyry but different from the quartz porphyry. This single sample yields an age significantly lower than any other found in this area. Assuming 0.708 for an initial ratio, a maximum age of 200 M.Y. is indicated. If one assumes 0.725 as the initial ratio, an age of 185 M.Y. is obtained. This is a single whole rock analysis and may simply be in error. On the other hand it may indicate a period of younger igneous activity. Granites of this age do occur in New England (Toulmin (1961)).

Discussion

The Rb-Sr whole rock results do not agree with Warren's (1913) interpretation for the Blue Hills complex. According to that interpretation the whole complex should be co-magmatic and essentially contemporaneous. Relatively, the normal granite should be the youngest, the porphyry and the aporhyolite the oldest members of the complex.

According to the Rb-Sr whole rock results the coarse or normal Quincy granite is approximately 75M.Y. older than the porphyry and aporhyolite. On that basis not only is the age relation the reverse of Warren's interpretation but the granite is a separate intrusive.

The rhombenporphyry can not be a simple differentiation product of the granite magma because the initial ratio of the rhombenporphyry is less than that of the normal granite.

Although the aporhyolite and the quartz porphyry are essentially the same age their initial ratios are different. One possible explanation is simply that there were separate magmas derived from different source material. Another possibility is that the intrusive part (the porphyry) of a single magma became contaminated with crustal strontium while the extrusive part did not, and thereby preserved the initial ratio of the magma. With the data at hand, it is not possible to prove which of these alternatives is true. However, since there is nothing in the chemistry or mineralogy of the porphyry to indicate that it is contaminated relative to the aporhyolite, the simplier hypothesis of separate magmas is chosen as the most reasonable.

Therefore, the Rb-Sr whole rock age results suggest that the Blue Hills complex was formed by four separate intrusions of magma. The normal Quincy granite crystallized 325 ± 15 M.Y. ago. This would be in the late Devonian according to the results of this report.

Based on field relations, the age limits of the rhombenporphyry are pre-late Devonian and post- Middle Cambrian. It is not a simple differentiation product of the granite.

The aporhyolite and the quartz porphyry are essentially the same age and crystallized 245 ± 10 M.Y. ago. This corresponds to an early or middle Pennsylvanian age according to data elsewhere in this report (Chapter 5). Their different initial ratios indicate that these rocks were formed from separate magmas although the alternate possibility of a single, partially contaminated magma can not be disproved.

It is not possible at this time to bring into accord the conflicting field interpretation of Warren and the present geochronological evidence. Billings (informal discussion) agrees that there is no incontrovertible field evidence at this moment which could be used to decide between the alternate possibilities. A new field and petrologic investigation of the complex, combined with further age investigations, is certainly in order.

Warren's (1913) study of the complex is a detailed and extensive piece of work. It was the culmination of an earlier detailed study of the same area by Crosby (1895, 1900). Harvard students, under the supervision of Billings, have been intermittemtly mapping the complex for several years. Therefore there are probably no obvious field relations that have been missed. On the other hand, if this is a case of separate intrusions of nearly identical granitic magmas, then the field evidence become exceedingly difficult to interpret.

For example the granite in the Chickatawbut

Hill area has been accepted as normal Quincy granite, although it does not look quite like the normal granite according to Billings (personal communication). Warren points out that the normal granite is absent from the southern part of the complex except at Chickatawbut Hill and at Rattlesnake Hill. A sample from Warren's collection of the granite from Rattlesnake Hill was analyzed and it fits the normal Quincy isochron. Rattlesnake Hill is on the notheastern tip of the Blue Hills Reservation and the granite looks like the distinctive normal Quincy type. The Chickatawbut Hill area is well within the Blue Hills and the correlation of the granite in this area with normal Quincy needs more study. The occurrence and correlation of granite dikes in this and other areas is a crucial point in the geological age relations of the normal granite and porphyry. If these are dikes and if they are truly Quincy type, then Warren's interpretation is essentially correct. However, it may be impossible, based on field evidence alone, to decide this. If the interpretation of the Rb-Sr ages is correct and the complex is composed of very similar but separate intrusions, then the possibility of younger intrusions of similar material must be born in mind. The result for sample R5089 suggests that there may be yet another period of intrusion. This can be only speculation at the moment because of insufficient sampling in the age investigation.

Hurley et al. (1960) reported a minimum K-Ar whole rock age of 280 ± 15 M.Y. on normal Quincy granite. The results reported here for normal Quincy granite do not contradict this.

The 245 ± 10 M.Y. age for the Blue Hills porphyry indicates a maximum age of 245 ± 10 M.Y. for the middle or late Pennsylvanian sediments of the Norfolk-Narragansett Basin. A detailed discussion of this result is presented in the chapter on the Wamsutta volcanics (Chapter 5).

Summary

Rb-Sr whole rock analyses from the Blue Hills complex indicates that the complex was formed by separate intrusions of very similar granitic magma 325 ± 15 M.Y. and 245±10M.Y. ago. The source material for these magmas was inhomgenous with respect to its strontium isotopic composition and different from the source material for basaltic rocks. This is interpreted here to mean that these magmas were partially or wholly of crustal origin. The rhombenporphyry of the Blue Hills complex was not a simple differentiation product of the Quincy granite magma.

It's strontium isotopic composition is compatible with either a crustal or sub-crustal origin.

These results conflict with the generally accepted interpretation of the complex. However they do not conflict with any clear cut field evidence.

The maximum age for the middle or late Pennsylvanian is 245 ± 10 M.Y. based on the result from the Blue Hills porphyry.

The Cape Ann Granite

Geology

Clapp (1921) described the geology of Essex County, Massachusetts. This area includes the Cape Ann granite and the Newbury volcanics. In Clapp's work the Cape Ann granite is referred to as the Quincy granite from Cape Ann. This correlation of the alkaline granitic types of eastern Massachusetts is currently accepted geological interpretation.

The geological age of this group of alkaline igneous rocks is given by Clapp (1921) as Carboniferous; by La Forge (1932) as pre-Lower Pennsylvanian and probably Mississippian; and by Bell (1948) as late Silurian to early Devonian.

Part of this diversity of opinion depends on the correlation involved. For example, Clapp includes the two mica granite from the Andover, Massachusetts area in the alkaline group. This granite intrudes the Carboniferous sediments of the Merrimack Valley (the Merrimack quartzite), which makes it late or post-Carboniferous. Clapp also includes the Newbury (Lynn) volcanics, which are considered late Silurian to early Devonian, as the earliest phase of the alkaline igneous activity. Thus, according to Clapp, the igneous activity assigned to the alkaline group extends from the late Silurian or early Devonian to the late or post-Carboniferous.

In particular he assigns a Carboniferous age to the Cape Ann granite

There is no direct field evidence to date the Cape Ann granite. The alkaline rocks correlated with the Cape Ann granite intrude the sub-alkaline rocks (Salem gabbro-diorite etc.) in adjacent areas. Therefore based on that correlation the Cape Ann is younger than the sub-alkaline suite.

The age of the sub-alkaline suite is based on the following.

At Nahant, the Nahant gabbro intrudes the Lower Cambrian Weymouth formation. If the Nahant gabbro is part of the sub-alkaline suite (Emerson (1917)) then the gabbro is post-Lower Cambrian and the Cape Ann granite is younger than post-Lower Cambrian If the Nahant gabbro is part of the alkaline suite (Clapp (1921))then the gabbro and the Cape Ann granite are post-Lower Cambrian.

At Hoppin Hill, North Attleboro, Massachusetts, 80 miles to the south, the Dedham granodiorite (sub-alkaline group) is unconformably overlain by the Lower Cambrian Hoppin formation. If the Dedham granodiorite from Hoppin Hill is part of the sub-alkaline province from Essex County then the sub-alkaline group is pre-Cambrian. On that basis the Cape Ann is post-pre-Cambrian.

In summary, very little is known about the geologic age of the Cape Ann granite. It is probably younger than post-Lower Cambrian.

Clapp describes the Cape Ann granite as follows ((1921) p. 26):

> Lithologic character. The Quincy granite is uniform, with definite, fairly persistent characteristics. Its chief constituent is a microperthitic feldspar, which occurs in coarse, rectangular grains. Quartz is interstitial to the larger euhedral feldspars. The mafic minerals are chiefly green katophorite and hedenbergite. Biotite is significant in only a few varities. Zircon, apatite and magnetite are minor accessories.

Results

Five whole rocks were collected from Cape Ann. The results are shown in Table 6.4 and the isochron in Figure 6.5. The isochron indicates an age of 415 ± 10 M.Y.. This corresponds to Upper Ordovician according to results from this report. The initial ratio for this granite is 0.709 ± 0.002.

Discussion

In the section on the geology it was shown that little is known about the geological age of the Cape Ann granite. Correlation with other

Table 6.4

Cape Ann Granite, Cape Ann, Massachusetts.

Sample	Rb ppm.	Sr ppm.	$\frac{Rb^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$\left(\frac{Sr^{87}}{Sr^{86}}\right)_{.1194}$
R4953	238. ---	--.-- 13.2	53.8	0.1213	1.0217	1.0298
R4954	238. 235. 236.5	11.2 -- -- 11.2	63.3	0.1209	1.0547	1.0613
R4955	202. --- 194. 198.	-- -- 4.81 -- -- 4.81	128.	0.1199	1.4319	1.4349
R4956	138. 136. --- 137.	11.5 -- -- 10.4 10.95	37.1	0.1207	0.9233	0.9283
R4957	--- 107. 107.	52.9 53.5 53.2	5.83	0.1203	0.7401	0.7429

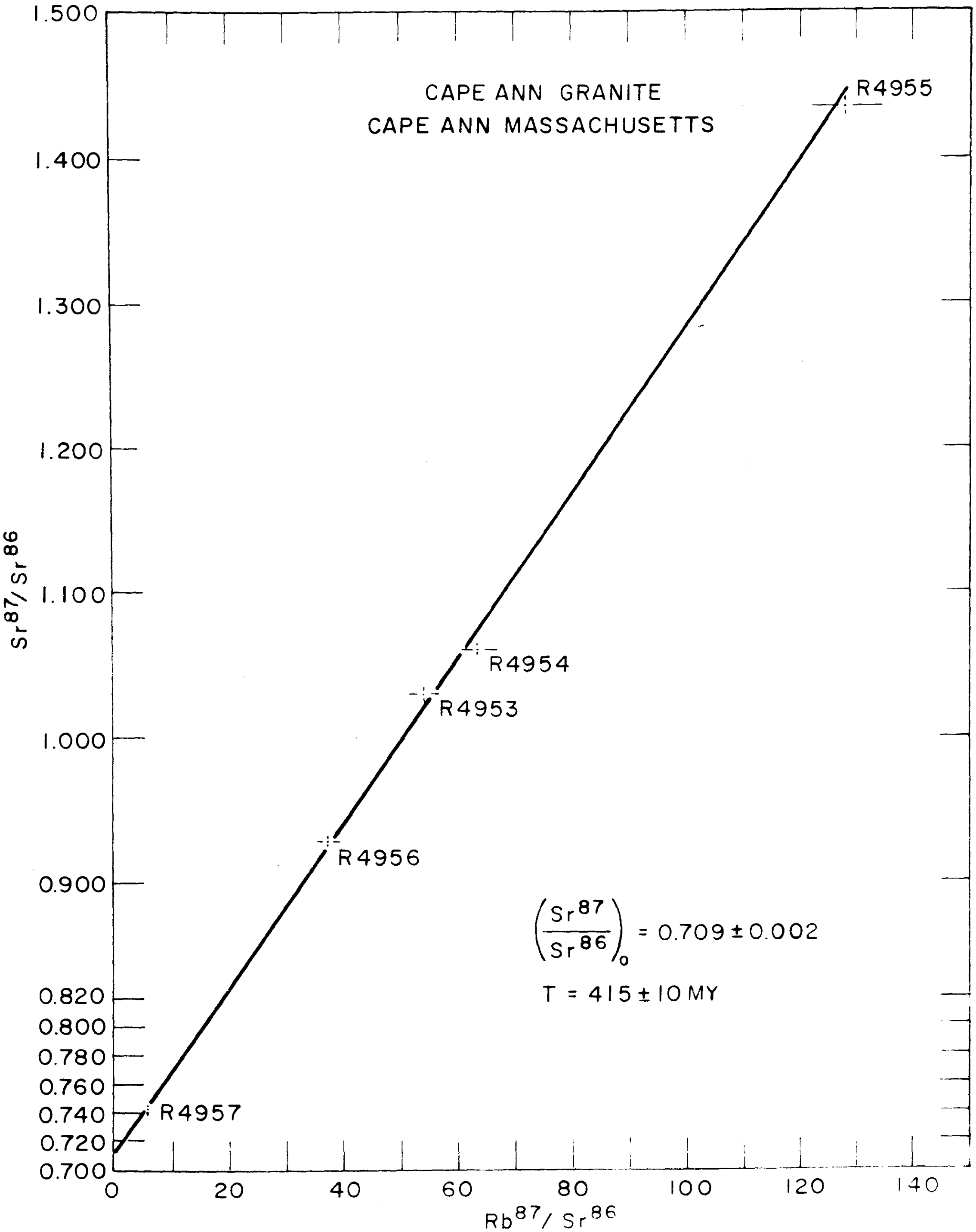

CAPE ANN GRANITE
CAPE ANN MASSACHUSETTS
Sr^{87}/Sr^{86}
Rb^{87}/Sr^{86}
1.500
1.400
1.300
1.200
1.100
1.000
0.900
0.820
0.800
0.780
0.760
0.740
0.720
0.700
0
20
40
60
80
100
120
140
R4955
R4954
R4953
R4956
R4957
$\left(\frac{Sr^{87}}{Sr^{86}}\right)_0 = 0.709 \pm 0.002$
T = 415 ± 10 MY

FIGURE 6.5

igneous rocks of the area indicates only a post-pre-Cambrian or post-Lower Cambrian age. The results from this work do not contradict this.

Hart (1961) reports an age of 310 ± 10 M.Y. for K-Ar on hornblende from the Cape Ann. Presumably this reflects partial loss of radiogenic argon from the mineral.

These results show that the Cape Ann granite, the Quincy granite and the Blue Hills porphyry and aporhyolite are not contemporaneous but represent different igneous events

The 0.709 ± 0.002 initial ratio for the Cape Ann granite falls within the range for basaltic rocks reported by Faure and Hurley (1962) and Gast (1960).

Summary

The 415 M.Y. age for the Cape Ann granite extends the alkaline igneous activity in New England back to the Ordovician. It demonstrates that age correlation based on lithologic similarity of igneous rocks is very uncertain.

The initial ratio of 0.709 ± 0.002 is compatible with but not proof of a sub-crustal origin for this granite.

The Newbury Volcanics

Geology

The Newbury volcanics are located in Essex County, Massachusetts, near the town of Rowley. The geology of the area has been described by Emerson (1917), Clapp(1921), La Forge (1932) and dos Santos (1960).

Dos Santos (1960) divides the volcanics into four members: lower rhyolite, andesite, upper rhyolite and basalt. The designations "andesite" and "basalt" are for stratigraphic convenience since the original minerals of these basic members have been completely altered.

The thickness of the formation ranges from 11,000 to 6,000 feet. The "andesite" member contains lenses of slate and conglomerate. It is in the "andesite" member that fossils have been found.

The volcanics are surrounded by the Dedham granodiorite and the Newburyport quartz diorite. The relation of the volcanics to the surrounding rocks appears to be unconformable although the actual contact is not observed (dos Santos (1960), Emerson (1970). The Lynn volcanics to the south were erupted on the erosional surface of the Dedham granodiorite (Clapp (1921), La Forge (1932)). Presumably the same is true for the Newbury volcanics. (Clapp (1921), dos Santos (1960)).

In 1915 Keith found some fossils in a calcareous shale in the andesite member. (Emerson(1917)). The fossils, which were scarce and poorly preserved, could not be precisely dated but ranged in age somewhere between late Silurian and early Devonian. (Emerson (1917)). There is later work which agrees with the earlier determination. (dos Santos (1960).

Recently more fossils were found (Personal communication. N. Cuppels). It is hoped that these will fix the geologic age of the volcanics more precisely. It should be pointed out that these fossils were not found in place, but it is believed that they are locally derived and could only come from the volcanics. (Personal communication. N. Cuppels)

With the exception of Emerson (1917) most geologist consider the Newbury, Lynn and Mattapan volcanics to be contemporaneous. Emerson believed the Newbury volcanics to be the oldest, and he correlates the Lynn and Mattapan volcanics with the Pennsylvanian volcanics of the Narragansett

Basin. La Forge (1932) and Bell (1948) correlate the Lynn, Mattapan and Newbury volcanics, and in addition, correlate this activity with the intrusion of the Quincy granite.

Results

Three rhyolite samples from the upper rhyolite member and two samples of the basic volcanics, from the andesite and basalt members, have been analyzed.

The results of the analyses on these five whole rock samples are reported on Table 6.5 and the isochron is shown in Figure 6.6 The isochron yields an age of 345 ± 10 M.Y. and an initial ratio of 0.709 ± 0.001.

Discussion

The Newbury volcanics (345 ± 10 M.Y.) are slightly younger than the Kineo Volcanics (360 ± 10 M.Y.). Taking into consideration the estimated errors it is concluded that the Newbury volcanics could be as old as but no older than the Kineo volcanics. The measured difference in ages suggests the Newbury is slightly younger than the Kineo. Therefore the Newbury volcanics can not be as old as the late Silurian but are early Devonian, probably

Table 6.5

Newbury Volcanics, Rowley, Massachusetts

Sample		Rb ppm.	Sr ppm.	$\frac{Rb^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$\left(\frac{Sr^{87}}{Sr^{86}}\right)_{.1194}$
R4308	Rhyolite	78.4	151.	5.63	0.1179	0.7414	0.7367
R4310B	Rhyolite	21.0	217.	30.3	0.1198	0.8550	0.8566
R4310	Rhyolite	23.0 21.7 22.35	215. 215	28.2	0.1191	0.8416	0.8405[1]
R4311	"Basalt"	8.40	560.	0.04	0.1188	0.7121	0.7103
R4312	"Andesite"	25.3	903	0.08	0.1192 0.1200 0.1196	0.7085 0.7076 0.7081	0.7079 0.7092 0.7086

[1] Incomplete run, only 18 sets obtained.

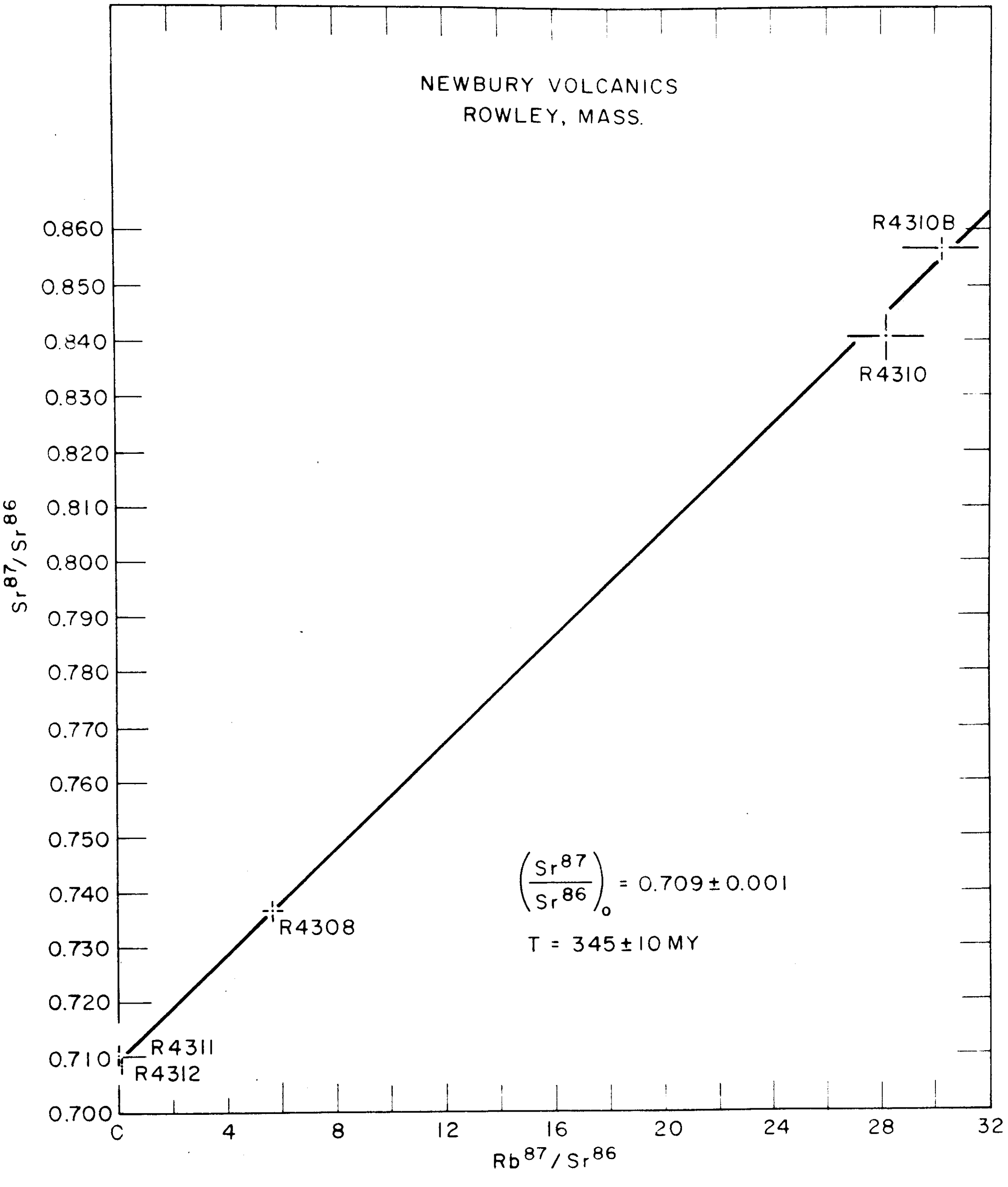

NEWBURY VOLCANICS
ROWLEY, MASS.
Sr^{87}/Sr^{86}
0.860
0.850
0.840
0.830
0.820
0.810
0.800
0.790
0.780
0.770
0.760
0.750
0.740
0.730
0.720
0.710
0.700
0
4
8
12
16
20
24
28
32
Rb^{87}/Sr^{86}
R4310B
R4310
R4308
R4311
R4312
$\left(\frac{Sr^{87}}{Sr^{86}}\right)_o = 0.709 \pm 0.001$
T = 345 ± 10 MY

FIGURE 6.6

somewhere between upper Lower Devonian and lower Middle Devonian.

The Rb-Sr age is for the upper rhyolite only. This rhyolite is approximately 1000 feet stratigraphically above the fossils. Presumably this represents an insignificant length of time compared to the errors involved.

The single value of 0.709 ± 0.001 for the initial ratio of both the rhyolites and the basic volcanics is compatible with a co-magmatic origin for these volcanics.

Summary

This early Devonian age as determined by Rb-Sr whole rock measurements falls within the age range estimated from fossil evidence (dos Santos (1960)).

The single initial ratio for both acid and basic volcanics is compatible with a co-magmatic origin for these volcanics.

The Newbury volcanic activity was not contemporaneous with the Cape Ann granite or the intrusives of the Blue Hills complex.

Chapter 7

Preliminary Results for the Coldbrook Volcanics and the Volcanics from the Kennebec Formation.

Introduction

The Coldbrook volcanics occur at the base of a Cambro-Ordovician section in southwestern New Brunswick. The analyses reported are preliminary to a more comprehensive study planned by this laboratory on the geochronology of the lowest Cambrian.

The Kennebec volcanics occur in the Moose River synclinorium in west central Maine. This formation is geologically well-dated and provides an opportunity to measure the age of the Middle Ordovician. However, this formation is badly sheared and presents more of a problem than the relatively undisturbed volcanics discussed elsewhere in this thesis. The reported results are preliminary and inconclusive.

The Coldbrook Volcanics

Geology

The Coldbrook group occurs in southwestern New Brunswick in the Saint John area. Recent workers in the area include Hayes(1914,1915,1916), Hayes and Howell (1937), Alcock (1938) and Mackenzie (1951). A summary of the geology is found in Stockwell and others (1957).

The Coldbrook volcanics comprise almost all of the Coldbrook group. Alcock (1938) included all of the pre-Cambrian volcanics of the Saint John region in this group. The group includes acid and basic volcanic flows, tuffs and breccias, plus some minor tuffaceous sediments and conglomerates. In general the volcanics are massive and dense with small phenocrysts of orthoclase, albite and quartz in the acid members. In the more basic members the ferromagnesian minerals have been altered to eoidote, zoisite, carbonate and secondary quartz (Alcock (1938)).

Estimates of the thickness of the group range from 18,000 to 33,000 feet.

The age of the Coldbrook volcanics is pre-Cambrian since it underlies the Lower Cambrian to Lower Ordovician Saint John group. Basal conglomerates of this group contain rounded pebbles of the Coldbrook volcanics. The Coldbrook volcanics overlie with angular unconformity the Green Head group (Archean). The Coldbrook is considered to be Proterozoic (Alcock(1938)), Stockwell and others (1957)).

Whether or not the Coldbrook group and the Cambro_Ordovician Saint John group are conformable is not clear. In the Proterozoic groups of Cape Breton (Nova Scotia) and Newfoundland, which are correlated with the Coldbrook, the contact with the Cambrian is generally conformable. Alcock states that the Coldbrook-Saint John contact is unconformable. Stockwell and others do not state in the text the nature of the contact but in the correlation chart for these formations they show a conformable contact. The omission is significant since in all other cases the nature of the contact is mentioned. Apparently there is disagreement with Alcock's observation of an unconformable contact.

Results

Six whole rock samples have been analyzed. The analyzed samples were collected from one area at the east end of Lilly Lake in Rockwood Park, Saint John.

In addition to the isotope dilution analyses for Rb and Sr, an analysis was done by X-ray spectrograph for relative intensity of the Rb/Sr weight ratio. These values confirm the Rb/Sr weight ratios as determined by the isotope dilution analyses. All results are reported in Table 7.1 and the isochron plot is shown in Figure 7.1. The isochron plot shows a 3 % precision error for Rb^{87}/Sr^{86} and a 0,25 % for Sr^{87}/Sr^{86}.

Inspection of Figure 7.1 shows that the points do not define a good isochron. The ages indicated from the isochron range from 400 to 500 M.Y. and the initial ratioa from 0.708 to 0.714.

Discussion

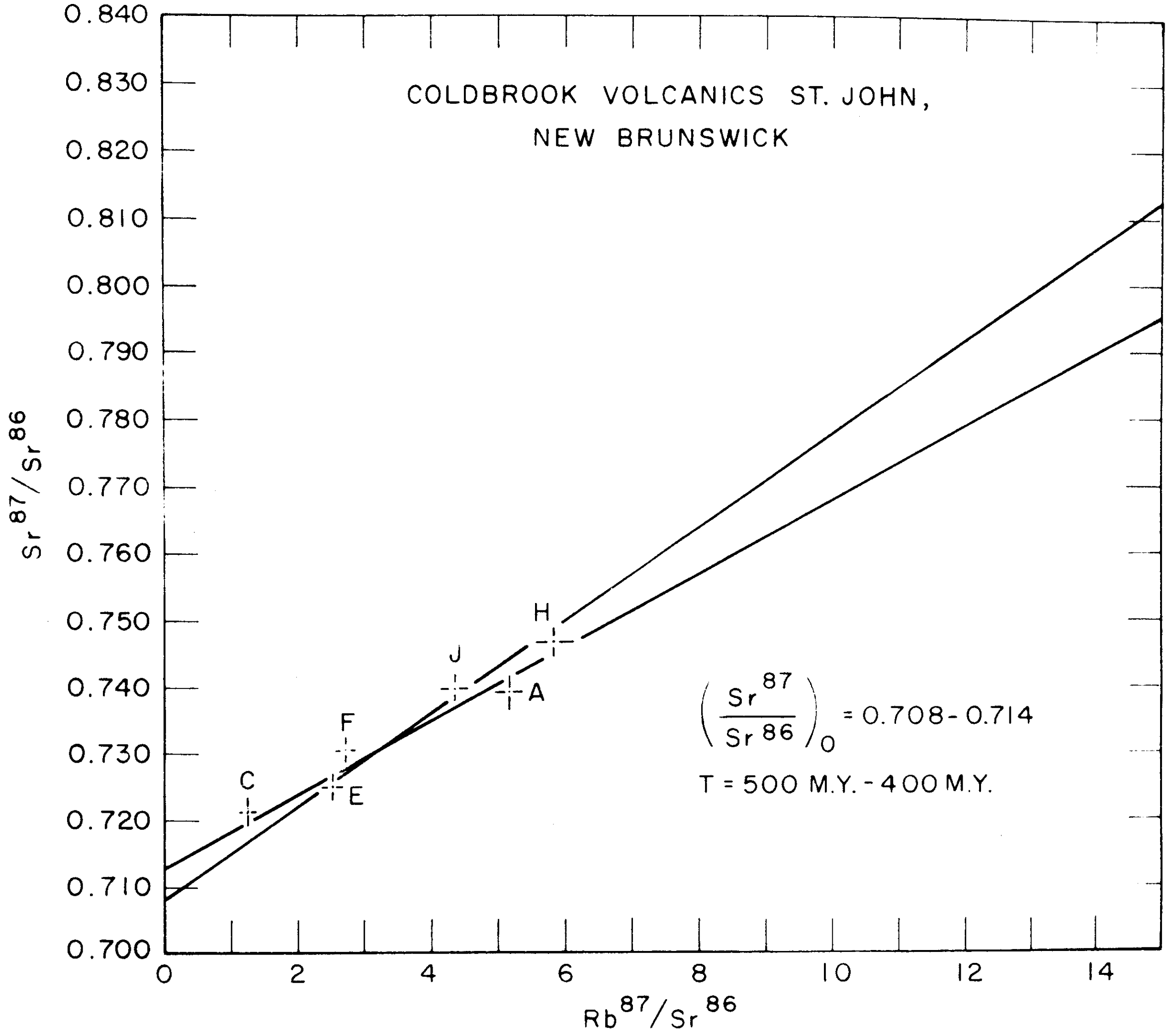
Part of the problen is analytical and part may be ascribed to the small range of the Rb/Sr ratio values. The highest Rb/Sr ratio is 2.0 and the lowest 0.43. The lack of points with higher and lower Rb/Sr ratios make the line sensitive to very small changes in the Sr^{87}/Sr^{86} ratio. For example, if the Sr^{87}/Sr^{86} ratio for R5050C is high by 0.003 , the isochron shifts from the minimum to the maximum values shown in the figure. Replicate Sr^{87}/Sr^{86} analyses of all points are required

Table 7.1

Coldbrook Volcanics, Saint John, New Brunswick.

Sample	Rb ppm.	Sr ppm.	$\frac{Rb^{87}}{Sr^{86}}$	Intensity X-ray $\frac{Rb}{Sr}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})_{.1194}$
R5050A	97.8	55.9	5.17	1.28	0.1213	0.7333	0.7391
R5050C	44.5	103.	1.25	0.33	o.1207	0.7175	0.7214
R5050E	97.0	112.	2.51	0.66	0.1201	0.7228	0.7249
R5050F	75.4	80.7	2.71	0.704	0.1198	0.7290	0.7302[1]
R5050H	114.	57.1	5.81	1.48	0.1190	0.7480	0.7467
R5050J	100.	66.8	4.36	- --	0.1201	0.7375	0.7397

[1] Only 48 sets obtained.



COLDBROOK VOLCANICS ST. JOHN,
NEW BRUNSWICK
Sr^{87}/Sr^{86}
0.840
0.830
0.820
0.810
0.800
0.790
0.780
0.770
0.760
0.750
0.740
0.730
0.720
0.710
0.700
C
F
E
J
A
H
$\left(\frac{Sr^{87}}{Sr^{86}}\right)_0 = 0.708-0.714$
T = 500 M.Y. - 400 M.Y.
0
2
4
6
8
10
12
14
Rb^{87}/Sr^{86}

FIGURE 7.1

Assuming that most of the scatter is analytical, it appears that the maximum age for these volcanics is probably 500 M.Y. and the minimum is 400 M.Y.. Even these results indicate that the age of these volcanics is probably close enough to the base of the Cambrian to provide a valuable maximum value for that boundry, warranting further pursuit of this problem...

The Kennebec Volcanics

Geology

The Kennebec formation occurs in the Moose River synclinorium in west-central Maine. The most recent and thorough field work on the area was done by Boucot (1961). A discription of the area taken from Boucot's work is presented in Chapter 3 of this report.

The Kennebec formation is volcanic and composed of massive felsite and badly sheared rhyolite tuff.

Boucot describes the Kennebec as follows (1961, P.183):

> Lithology_ Fresh surfaces of the rhyolite tuff and felsite are olive drab, and weathered surfaces and rind are white. The felsite is flinty, with a conchoidal fracture, and the more massive parts contain pyrite. Both the tuff and massive felsite contain abundant quartz phenocrysts. The tuff is poorly sorted and consists of irregular fragments of felsite, quartz phenocrysts and much silt. The fine-grained layers are metamorphosed to phyllite whose cleavage planes are coated with platy minerals.

The geologic age of the Kennebec is Middle Ordovician based on the brachiopod Valcourea (Boucot (1961)).

Results

Two whole rocks have been analyzed. These were collected by Professor W.H.Dennen near Somerset Junction (Brassua Lake quadrangle) in the type locality. Other samples were collected by the author but have not been analyzed.

The results are given in Table 7.2. Assuming an initial Sr^{87}/Sr^{86} ratio of 0.708 two "ages" can be calculated. The "age" for sample R4569A is 450 M.Y. and for sample R4569 is 325 M.Y.. The 450 M.Y. "age" is a reasonable Middle Ordovician value while the other is too low.

If one assumes that the two points define an isochron a result of 275 M.Y. and an initial ratio of 0.728 is obtained. This "age" is too low for the Middle Ordovician.

Analysis of more samples should indicate one of the three following situations: (1) a scatter of points which indicates an open system. (2) one of the samples (R4569A) is correct while the other is in error. (3) a relatively good isochron indicating an "age" around 300 M.Y. for the Middle Ordovician. This would indicate a post-Middle Ordovician event(s) which destroyed the original age pattern in the whole rock samples.

Table 7.2

Kennebec Volcanics, Moose River Synclinorium, Maine.

Sample	Rb ppm.	Sr ppm.	$\frac{Rb^{87}}{Sr^{86}}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})_{.1194}$	"Age" M. Y. $(\frac{Sr^{87}}{Sr^{86}})_0 = 0.708$
R4569	102. 100. 101.	10.0 11.2 10.6	28.2	0.1192	0.8361	0.8354	325
R4569A	52.6	19.2	7.97	0.1188	0.7601	0.7582	450

Chapter 8

General Summary of Results

A summary of the results of the preceding chapters is shown in Table 8.1. The ages are internally consistent and do not contradict geologic facts so far as known. There are areas of disagreement with previous geological interpretation. In particular, the sequence of events in the Blue Hills complex, based on the Rb-Sr interpretation, differs from Warren's (1913) interpretation. The correlation of the Quincy and Cape Ann granites is another generally accepted interpretation with which the results reported here differ.

In Table 8.2 the areas studied which have known geologic ages are compared with Kulp's and Holmes' 1960 time scale estimates. In addition Holmes' 1947 time scale is shown. The results reported here are approximately 10 % below the recent time scale in the Devonian-Silurian section and the discrepancy apparently increases in the Pennsylvanian. The age result for the Pennsylvanian Wamsutta volcanics is too uncertain to form a realistic estimate of the

Table 8.1

Summary of Whole-rock Rb-Sr Ages and $\left(\frac{Sr^{87}}{Sr^{86}}\right)_0$

($\lambda_{Rb} = 1.39 \times 10^{-11}$ yr^{-1})

Sample and Locality	Geologic Age	Rb-Sr Whole-rock Age (M. Y.)	$\left(\frac{Sr^{87}}{Sr^{86}}\right)_0$
Cape Ann granite. Cape Ann, Mass.. Chapter 6.	Post-Lower Cambrian	415 ± 10	0.709 = 0.002
Arisaig volcanics. Arisaig, Nova Scotia. Chapter 4.	Basal Silurian (possibly as old as post-Lower Ordovician)	405 ± 10	0.709 ± 0.001
Kineo volcanics. Moose River synclinorium. West central, Maine. Chapter 3.	Upper Lower Devonian	360 ± 10	0.715 ± 0.001
Newbury volcanics. Rowley, Mass.. Chapter 6.	Early Devonian to late Silurian	345 ± 10	0.709 ± 0.001

Table 8.1, continued.

Sample and Locality	Geologic Age	Rb-Sr Whole-rock Age (M. Y.)	$\left(\frac{Sr^{87}}{Sr^{86}}\right)_o$
Blue Hills complex. Quincy and Milton, Mass.. Chapter 6.	Post-Middle Cambrian to pre-middle or late Pennsylvanian		
Normal Quincy granite		325 ± 15	0.728 ± 0.008
Blue Hills aporhyolite		248 ± 10	0.708 ± 0.004
Blue Hills porphyry		245 ± 10	0.722 ± 0.002
Rhombenporphyry		--------	0.707 ± 0.003
Wamsutta volcanics. Narragansett basin. South Attleboro, Mass.. Chapter 5	Middle or late Pennsylvanian		
Rhyolite		225 ± 25	0.721 ± 0.002
Basalts		--------	0.708 ± 0.001

Table 8.2

Summary of geologically well dated areas shown with time scale estimates

Holmes (1947)			Holmes (1960) Kulp (1960)	Whole-rock Rb-Sr ages ($\lambda = 1.39 \times 10^{-11}\ yr^{-1}$)
182			220	
		Upper	235	
	Permian	Middle	250	
203		Lower	270	
		Upper		
	Pennsylvanian	Middle		Wamsutta volcanics 225 ± 25 M. Y. Blue Hills porphyry 245 ± 10 M. Y.
		Lower	320	
		Upper		
	Mississippian	Middle		
255		Lower	350	
		Upper	365	
	Devonian	Middle	380	Newbury volcanics 345 ± 10 M. Y. Kineo volcanics 360 ± 10 M. Y.
313		Lower	400	
		Upper		
	Silurian	Middle		
350		Lower	430	Arisaig volcanics 405 ± 10 M. Y.
		Upper		
	Ordovician	Middle		
430		Lower	490	
450		Upper	510	
	Cambrian	Middle		
520		Lower	600	

discrepancy. The result reported for the Blue Hills porphyry indicates a discrepancy of 10-20 % depending on the exact geological age of the porphyry. This apparent discrepancy could be caused by systematic analytical error in the work reported here. Howerer, the only reasonable source of a systematic error of this magnitude would be faulty calibration of the spikes used for Rb and Sr analyses. In the section on accuracy of isotope dilution analyses it was shown that these spikes gave no indication of a systematic error of this magnetude.

Comparison with other radioactive age work on the areas studied indicated no such large discrepancy. In all cases the results overlapped and if there is any contradiction it is on the order of a few percent. The interpretation suggested for this overlap of the minimum ages for intrusives and the direct age of the strata from the volcanics is that sedimentation, burial and intrusion occurred in a short interval of time compared to the uncertainty of the ages.

The consistency of the results for volcanics (and related granites) of different geologic ages and different orogenic histories is considered to be a good indication that radiogenic Sr has not been removed and that the ages obtained are those of the source magmas themselves. This is of considerable significance, since the volcanics suites analyzed, with the exception of the Wamsutta volcanics, were regionally metamorphosed. The age results indicate that this did not effect the relative age pattern. If subsequent metamorphism had affected the primary ages there should be some correlation between increasing (older) geologic age and decreasing radioactive ages. Thus far, no such trend is indicated, In fact the younger rocks studied in this investigation happen to show ages which, if anything, are relatively too young rather than too old. Although the present data apparently do not reflect the influence of regional metamorphism, it is not implied that high-temperature contact metamorphism, metasomatism, extreme faulting, would not show a different patten. A small start in this direction has been made on the Kennebec volcanics which occur in a highly sheared area.

The conclusion based on internal consistency, that the whole rock Rb-Sr ages reflect the age of extrusion, is not the same as stating that they are the ages of extrusion, and consequently give the true ages of the strata with which they are interbedded. The proof of consistency is only the first step and the easiest. The second step requires comparison against a known standard. Since there is no a priori knowledge of the "true" ages of geological periods, results must be compared with the empirical approximations to "true" ages, which is assumed to be represented by the average of superior radioactive age measurements employing different decay schemes. The time scale is this approximation. For the geologic periods studied in this thesis the time scale is based almost exclusively on K-Ar and Rb-Sr ages on biotites. In each chapter, Kulp's (and Faul's) critical points were reviewed and need not be repeated here in detail. It was shown that in three cases there are clearcut contradictions with the whole-rock data (Lower Permian (Norway), Lower Permian (England), post-Silurian-pre Upper Devonian (Calais, Maine)). and in three cases the results overlap (Post-middle or late Pennsylvanian (Rhode Island), late Lower Carboniferous, Vosges (France), post-Silurian-pre Carboniferous (Nova Scotia)). The Shap granite (England) and the Leister granite (Eire) are only known to be Lower Devonian by correlation and no judgement can be formed about their relation to the whole-rock results. It is believed, in summary, that these whole-rock investigations constitute a step in unravelling magmatic history. Work on volcanics which are close in geologic age to those studied here should confirm or deny the consistency thus far demonstrated. For example, age results on Helderburg age volcanics (e.g. fron the Gaspé Peninsula) should show an age equal to or slightly greater than the Kineo age. This would confirm the consistency of the work to date. If perchance, a slightly older age is obtained it will indicate a resolving power which would provide a powerful tool for both time scale and correlation studies. Other areas for future work should include the Kennebec formation (Chapter 7 this report) where there is a good chance that the age pattern in the whole-rocks has been disturbed. This is important in order to establish criteria for predicting troublesome cases.

The data at hand on volcanics warrants the conclusion that reliable correlations can be made using Rb-Sr whole-rock isochron studies. It also appears that geologic age assignments can be made if the assignment is based on comparison with other whole-rock (volcanic and granitic) studies.

The determination of an isochron is in most cases a necessity. The content of radiogenic strontium in most rocks is low compared with dateable minerals. For the few cases where the Rb/Sr ratio is high enough to calculate ages of reasonable precision, isochrons are still recommended because more information can be obtained from the data (e.g. the initial ratio) and more certainty can be attached to the age result.

The problem of correlating the alkalic granites in New England has been discussed by Toulmin (1961). He gives a summary of the recent age work and concluded that there were at least two ages of intrusion, 185 and 280 M.Y. ago. The latter age is a whole rock K-Ar result from the Quincy granite. It is interpreted as a minimum age (Hurley et al. (1960)). The whole rock Rb /Sr age reported here confirms that result and indicates that the age is close to 325 ± 15 M.Y.. Other whole rock ages from this work suggest at least two or three more periods of igneous activity of the "alkalic" type. The Cape Ann granite which is correlated with the Quincy granite, and the Blue Hills porphyry and aporhyolite which are considered phases of the Quincy granite give ages of 405 ± 10 M.Y. and 245 ± 10 M.Y., respectively. In addition, the Newbury volcanics which are generally considered an extrusive phase of this igneous activity,, give an age of 345 ± 10 M.Y.. Toulmin suggested that caution should be exercised in assigning geologic ages to undated alkalic intrusives in New England until reliable criteria has been established. The results reported here agree with and emphasize that suggestion. It appears, according to the age results for the Blue Hills complex, that even close field association and similar mineralogy are no guarantee that two igneous bodies are contemporaneous.

The initial ratios obtained during this investigation are tabulated in Table 8.1 and show that the initial ratios for granitic extrusives and intrusives are variable. The values reported range from 0.708 ± 0.004 to 0.728 ± 0.008. Of the eight initial ratios determined for granites and rhyolites, four fall within the range for basaltic rocks and four have higher values. All measurements on basic rocks yielded initial ratios in the basaltic range.

Chapter 9

Sample Descriptions

If possible, references to studies of the geology and petrology are given.

<u>Kineo Volcanics</u> (Boucot, 1961)

R3061	Kineo rhyolite. Moosehead Lake on route 15, 300 yards south of Kineoview Hotel. Collected by H. W. Fairbrain, 1954.
Hb3061	Horneblend, separated from R3061.
R4565	Kineo garnet rhyolite. Misery Pond, Brassua Lake quadrangle, Maine, Moose River synclinorium. Collected by W. H. Dennen.
R4566	Kineo rhyolite. Southeast corner, Brassua Lake, Brassua Lake quadrangle, Moose River synclinorium, Maine. Collected by W. H. Dennen.
R4567	Kineo rhyolite. From unknown part of Kineo rhyolite, Moose River synclinorium, Maine. Collected by D. Baker.
R5051	Kineo garnet rhyolite. Coldstream River just northeast of Coburn Mountain. Northeast corner of The Forks quadrangle, Moose River synclinorium, Maine.

Newbury Volcanics (dos Santos, 1960)

R4308	Newbury rhyolite. The upper rhyolite member, Red and green flow banding. Rowley, Mass.. Locality near thin section # 9. dos Santos, 1960.
R4310	Newbury rhyolite. Volcanic agglomerate from the upper rhyolite member. Rowley, Mass., on west side of Route 1, ∼ 1/3 mile south of Gov. Dummer Academy. Locality near thin section # 8, dos Santos, 1960.
R4310B	Same as R4310, second sample preparation.
R4311	Newbury basalt (?). Rowley, Mass., ∼ 1/8 mile south of Parker River on Route 1. Locality near thin section # 11, dos Santos, 1960
R4312	Newbury andesite (?). Rowley, Mass., south side of Central Street.

Kennebec Volcanics (Boucot, 1961)

R4569	Felsite. Summerset Jct., Maine; Kennebec formation; Brassua Lake quadrangle, Moose River synclinorium. Collected by W. H. Dennen.
R4569A	Same as R4569, second sample preparation.

Arisaig Volcanics (Twenhofel and Schuchert, 1909)

R4634	Andesite. Andesite unit; fine grained; non-anygdaloidal. ∼ 200 yards north of dock at Arisaig point Arisaig, Nova Scotia. Collected by W. H. Dennen.
R4635	Rhyolite. Flow banded lower pink rhyolite. ∼ 30 yards southeast of R4634. Collected by W. H. Dennen.

R4637	Rhyolite. Fine grained rhyolite from Middle Red unit (?). 20' east of R4636, Arisaig, Nova Scotia. Collected by W. H. Dennen.
R4636	Rhyolite. ~800 yards north of "Frenchman's Barn, Arisaig, Nova Scotia. Collected by W. H. Dennen.
R4638	Rhyolite. Middle Brick Red member. 100 yards north of "Frenchman's Barn, Arisaig, Nova Scotia. Collected by W. H. Dennen.
R4639	Rhyolite. Lower pink flow banded rhyolite. Northeast (?) of "Frenchman's Barn", Arisaig, Nova Scotia. Collected by W. H. Dennen.

<u>Blue Hills Complex</u> (Warren, 1913)

R4700	Quincy granite. Quarry next to Southeast Expressway, Quincy, Mass.. Collected by G. Beall.
R4701	Blue Hills quartz porphyry. Route 128 and route 28, Blue Hills Reservation. Quincy, Mass.. Collected by G. Beall.
R4702	Blue Hills quartz porphyry. Route 128 and route 28, Blue Hills Reservation. Quincy, Mass.. Collected by G. Beall.
R4770	Quincy granite. Quarry next to the Southeast Expressway Quincy, Mass..
R4772	Blue Hills quartz porphyry. Hoosicwhisick Pond and Hillside Street, Blue Hills Reservation, Milton, Mass..

R5064 Quincy granite.
Hardwick's Quarry, Quincy, Mass..
Collected by C. H. Warren, 1909
M. I. T. Petrology Collection # 887.

R5065 Quincy granite.
Gold Leaf Quarry, West Quincy, Mass..
Collected by C. H. Warren, 1909
M. I. T. Petrology Collection # 867.

R5066 Quincy granite.
First quarry on right of Granite Street off
Randolph Avenue, Milton or West Quincy, Mass..
Collected by C. H. Warren, 1909
M. I. T. Petrology Collection # 881.

R5067 Quincy granite.
Rattlesnake Hill, Blue Hills Reservation,
Quincy, Mass..
Collected by C. H. Warren, 1909
M. I. T. Petrology Collection # 908.

R5068 Rhombenporphyry.
Pine Hill, just east of the Blue Hills
Reservation, Quincy-Braintree, Mass..
Collected by C. H. Warren, 1909
M. I. T. Petrology Collection # 1159.

R5089 Porphyry.
Southeast ridge 1 mile west of Jct. 37 and
128 on route 128, ~ 1/10 mile west of Braintree-
Quincy line, Quincy, Mass., new road cut.

R5090A Aporhyolite.
R5090B Pine Hill opposite Chickatawbut Road just
R5090C outside Blue Hills Reservation, Braintree, Mass..

R5091A Aporhyolite.
R5091B Wampatuck Hill aporhyolite in Blue Hills
Reservation off of Chickatawbut Road, Quincy, Mass..

<u>Cape Ann Granite</u> (Clapp, 1921)

R4953 Cape Ann granite.
Route 128, just past Annisquam Bridge,
Cape Ann, Mass..

R4954	Cape Ann granite. Route 128 just past Annisquam Bridge 25 feet from R4953. Red phase. Cape Ann, Mass..
R4955	Cape Ann granite. Route 128 extension 0.4 miles past the second rotary. Fine grained phase. Cape Ann, Mass..
R4956	Cape Ann granite. Route 128 extension 0.4 miles past the second rotary. Coarse grained phase. Cape Ann, Mass..
R4957	Cape Ann granite. Route 123 just north of Jct. 128, eastern slope of Mount Ann. Cape Ann, Mass.. Collected by W. H. Dennen.

Wamsutta Volcanics (Coomaraswany, 1954)

R4888	Green shale. Newport Avenue just off route 123 South Attleboro, Mass..
R4889	Basalt ∼ 0.1 mile north of Jct. Newport Avenue and route 123 South Attleboro, Mass..
R4890	Basalt ∼ 0.1 mile north of Jct. Newport Avenue and route 123 South Attleboro, Mass..
R4891A R4891B R4891C	Rhyolite. ∼ 0.3 mile north of Jct. Newport Avenue and route 123 South Attleboro, Mass..
R4893	Rhyolite. Cumberland Avenue 0.1 mile south of Jct. Cumberland Avenue and route 1 South Attleboro, Mass..

R4894 Rhyolite.
R4895 Route 1 0.1 mile south of Jct. Cumberland
Avenue and Route 1.
South Attleboro, Mass..

R4896 Basalt.
1/4 mile south of Jct. of Cumberland Avenue
and route 1 on route 1.
South Attleboro, Mass..

Coldbrook Volcanics (Alcock, 1938)

R5050A Coldbrook volcanics.
R5050C East end of Lilly Lake in Rockwood Park
R5050E St. John, New Brunswick.
R5050F All samples from one large outcrop.
R5050H
R5050J

Newbury volcanics collected by Bottino and W. H. Pinson. Jr.

Wamsutta volcanics collected by M. Bottino and S. Moorbath.

Unless noted, samples were collected by the author.

Chapter 10

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Biography

The author was born December 2, 1935 in Brooklyn, New York, and raised in Norfolk, Virginia. He is the son of Louis E. Bottino and Grace V. Cogliandro.

The author completed his secondary education at Augusta Military Academy, Fort Defiance, Virginia in June, 1954, and entered M. I. T. in September, 1954. The year, 1956, he spent in the field for McPhar Geophysics Ltd. of Toronto, Ontario. The degree of Bachelor of Science in Humanities and Science, was conferred on him in June, 1959 and in September, 1959 he was enrolled in the graduate school, Department of Geology and Geophysycs at M. I. T..

During the academic year 1959-1960, he held a half-time research assistantship in the Geochemistry Laboratory. For the academic years 1960-1961 and 1961-1962, and the summer and fall semesters of 1962, the author held a half-time research assistantship in the Geochronology Laboratory. The summers of 1959 and 1960 were spent at A. F. Cambridge Research Center, Geoghysics Research Directorate in the Spectroscopic Studies Section under Dr. Y. Tanaka.

In 1960, the author was elected to the Society of Sigma Xi and in 1961, became a student member of the American Geophysical Union.

In June of 1958, the author was married to Miss. Carroll Ann Sheridan of Arlington, Massachusetts. He has two children, Sanford W. L., born May, 1959 and Michael Louis, born May, 1962.