RUBIDIUM - STRONTIUM AGE INVESTIGATIONS
IN THE MIDDLE HADDAM AND GLASTONBURY
QUADRANGLES, CONNECTICUT

by

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SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF
PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF
TECHNOLOGY

January, 1963

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Submitted to the Department of Geology and Geophysics on February 20, 1963, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

The Pre-Triassic rocks of the Middle Haddam and Glastonbury quadrangles in Connecticut have been studied by the Rb-Sr method of age determination. The pegmatite, Maromas Granite Gneiss, Glastonbury Gneiss, Collins Hill Formation, Monson Gneiss, Middletown Formation have all been studied from this area; and the Ammonoosuc Volcanics of New Hampshire have been studied to test correlation of the Bronson Hill anticline from New Hampshire to Southern Connecticut. In addition, granitic dikes which cut the Monson Gneiss in the Killingworth dome have also been studied. Minerals from the Strickland and Spinelli Quarries and whole-rocks from the Hale Quarry were used in the pegmatite study, and whole-rocks for the remaining formations. The following ages and initial Sr(87/86) ratios were obtained:

Type	Rb-Sr Age		Initial Ratio
pegmatite minerals	250 ± 10		0.737 ± 0.002
Maromas Granite Gneiss	287 ± 10		0.714 ± 0.002
Glastonbury Gneiss	360 ± 10		0.710 ± 0.002
Granite dikes in Monson	418 ± 10	assumed	0.708
Middletown Formation	450 ± 15		0.707 ± 0.001
Ammonoosuc Volcanics	460 ± 15		0.708 ± 0.001
Monson Gneiss	550 ± 80		0.708 ± 0.001

In addition, a possible age of 395 $\pm$ 20 m.y. has been indicated for
the Collins Hill Formation, which is a metasediment and thus the
resultant age is open to question. The initial ratio for the Collins
Hill Formation is 0.719 $\pm$ 0.002, which confirms theories that it was
derived in large part from detrital constituents; but the age is too
low as it has been correlated to Middle Ordovician (?) strata in
New Hampshire. The proximity in age between the Ammonoosuc and the
Middletown confirms their correlation, and the low initial ratios sug-
gest confirmation of derivation from basic volcanics. The pegmatites
have not been derived in situ, nor are they directly related genetically
to the Maromas Granite Gneiss despite their closeness in age. The
Maromas Granite Gneiss has an initial ratio of 0.714, which indicates
a crustal pre-history before emplacement, and the 287 $\pm$ m.y. age suggests
intrusion into the other basement formations in the area. That the
Maromas, Glastonbury, and granitic dikes in the Monson show significantly
different ages suggests at least three periods of emplacement or re-
mobilization of granitic material within the area. The Glastonbury
Gneiss is probably intrusive into the Collins Hill, but later meta-
morphism(s) has obscured the contact relations.

All isotopic ratios have been determined mass spectrometrically,
but Rb/Sr ratios have been determined by both mass spectrometric isotope
dilution and by X-Ray Spectrographic techniques. The precision and

accuracy of these techniques are discussed.

A major revision of the stratigraphic column in the Middle Haddam and Glastonbury quadrangles is proposed, as well as limits on various parameters for the genesis of pegmatites and mantled gneiss domes.

The emphasis of this thesis is on geologic application of the absolute ages determined; and while the usefulness of the whole-rock method has been confirmed in this thesis, the necessity of rigid geologic control is obvious.

Thesis Supervisor: P. M. Hurley

Title: Professor of Geology

Acknowledgements

The possibility of applying whole-rock Rb-Sr ages to problems of complex geology in an area where field interpretations are in conflict was suggested by Professor P. M. Hurley, thesis supervisor. His suggestions have been invaluable during the course of this investigation. Thanks are also due to Professors H. W. Fairbairn and W. H. Pinson for their help during the course of the work.

Particular thanks are due to Dr. Gunter Faure and Mr. M. L. Bottino for analytical advice and discussion of the problem. Thanks are also due to Dr. C. C. Schnetzler for spiking of some of the samples, and to Messrs. R. H. McNutt and E. C. Perry for aid in the X-Ray Spectrography. Some aspects of the problem have been discussed with Drs. Stephen Moorbath, P.R. Whitney, and G. C. Czamanske, and with Mr. T. E. Krogh. Laboratory assistance by Mr. Richard Reesman, Miss Erna Beiser, and Mrs. Martha Godchaux is gratefully acknowledged.

It would have been impossible to obtain meaningful results without the cooperation and suggestions of geologists more familiar with Connecticut geology. Special thanks are due to Drs. R. L. Goldsmith, L. R. Page, and Roberta Dixon of the U.S. G.S.; Dr. John Rosenfeld of U.C.L.A.; Dr. Gordon Eaton of the University of California (Riverside); Dr. Lawrence Lundgren, Jr., of Rochester University; Dr. R. H. Jahns of the Pennsylvania

State University; Dr. John Rodgers, and students, of Yale University; Dr. J. B. Thompson and Mr. Peter Robinson of Harvard University; and many others.

This writer gratefully acknowledges the beneficial discussion with Dr. M.P. Billings of Harvard University and Dr. J. W. Peoples of Wesleyan University on the thesis subject, and the donation of samples of the Maromas Granite Gneiss by Dr. Peoples and samples of the Ammonoosuc Volcanics by Dr. Billings. Dr. G. J. Wasserburg of the California Institute of Technology has discussed many aspects of the problem with the writer, and his suggestions are gratefully acknowledged.

The encouragement and assistance of my wife, Barbara, throughout the course of the investigation has made this thesis possible.

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Part I

(intended for publication)

Rb-Sr Geochronological Investigations in the Middle Haddam and Glastonbury
Quadrangles, Eastern Connecticut

by

D. G. Brookins and P. M. Hurley

Abstract

The Pre-Triassic rocks of the Middle Haddam and Glastonbury quadrangles in Eastern Connecticut have been investigated by the Rb-Sr method of age determination, with the emphasis on application of the measured ages to aid interpretation of the complex problems of stratigraphy and correlation within the area. Whole-rock ages have been determined for the Maromas Granite Gneiss, the Glastonbury Gneiss, and the Middletown Formation within the area; and for the Ammonoosuc Volcanics from New Hampshire. Also from within the Connecticut area, the Collins Hill Formation and the Monson Gneiss have been studied, as well as granitic dikes which cut the Monson Gneiss. Pegmatite minerals from the Strickland Quarry have also been investigated. Using the decay constant $\lambda = 1.39 \times 10^{-11}$ yr^{-1}, the following ages and initial Sr(87/86) ratios have been determined:

Formation	Rb-Sr Age (m.y.)	Initial Sr(87/86)
Pegmatites	250 ± 10	0.737 ± 0.002
Maromas Granite Gneiss	287 ± 10	0.714 ± 0.002
Glastonbury Gneiss	360 ± 10	0.710 ± 0.002
Middletown Formation	450 ± 15	0.707 ± 0.001
Ammonoosuc Volcanics	460 ± 15	0.708 ± 0.001
Granite Dikes (in Monson)	418 ± 15	--------------
Monson Gneiss	550 ± 80	0.708 ± 0.001

The Collins Hill Formation yields a possible age of 395 ± 20 m.y., but the isochron method (Nicolaysen, 1961) is questionable when applied to such a metasedimentary unit. The pegmatite age is in good agreement with earlier work, and the proximity in age between the Middletown Formation and the Ammonoosuc Volcanics confirms their correlation. The different ages for the Maromas Granite Gneiss, the Glastonbury Gneiss, and the Granite dikes in the Monson indicate at least three different episodes of emplacement of granitic material. The high initial ratio of the Maromas indicates a lengthy crustal pre-history before emplacement; but, despite the narrow time span between the Maromas and the pegmatites, the great difference between the initial ratios of the Maromas and the pegmatites indicates that they are not genetically related.

The investigation confirms the usefulness of the Rb-Sr whole-rock method as a geologic tool, and emphasizes the necessity of rigid geologic control during such an investigation.

Introduction

The Rb-Sr whole-rock method of absolute age determination has been used to study the Pre-Triassic basement formations of the Middle Haddam and Glastonbury Quadrangles in Eastern Connecticut with the emphasis being placed on application to problems of stratigraphy and correlation. Minerals from the Strickland Quarry Pegmatite and the Spinelli Prospect Pegmatite have also been studied. The Ammonoosuc Volcanics of New Hampshire have been investigated to test the proposed correlation of the Bronson Hill Anticline sequence in New Hampshire to the equivalent sequence in Connecticut.

All of the rocks studied are Paleozoic in age, and thus the approximate age formula discussed by Compston and Jeffery (1961) may be used, in which the age, t, is given by:

$$t = \frac{Sr(87/86)_{now} - Sr(87/86)_{initial}}{Rb(87)/Sr(86) \times \lambda} .$$

The graphical method using the coordinates proposed by Nicolaysen (1961) have been used in this work, and the decay constant $\lambda = 1.39 \times 10^{-11} \ yr^{-1}$ proposed by Aldrich and Wetherill (1958) has also been applied.

Experimental Procedure

Faure (1961) has described the general analytical procedure in great detail, and these techniques have been only slightly modified during the course of this work. All dissolutions were made in clean Platinum dishes by adding a mixture of hydrofluoric acid and per-chloric acid. For isotope dilutions, the spike solution was added prior to the dissolution; and Rb was separated from Sr after the dissolution as Rubidium perchlorate. For both isotope dilution and isotope ratio analyses Sr was separated and purified on a cation ex-change column using vycor distilled 2N HCl as eluant; the position of the Sr on the column was monitored by a radioactive Sr^{85} tracer. The mass spectrometer used for the isotopic analyses was a solid source, 6" radius, $60°$ sector, single collector model which has been described previously by Herzog and Pinson (1956) and Faure (1961). Rb samples were mounted as nitrates on the filament; and Sr as either nitrate or oxalate, as both methods give a stable emission. Some of the $(Rb/Sr)_{wt}$ ratios were determined by X-Ray Spectrographic techniques, using fluoride-converted samples and standards to minimize matrix effects.

Precision and Accuracy

The precision of the isotopic ratios was checked by replicate analyses of most samples, the majority of which fell within $\pm$ 0.001 of the mean. For single analyses, the standard deviation has been shown

by Faure (1961) to be $\pm$ 0.002; and this value was used in
construction of figures. Absolute accuracy was monitored by
periodically analyzing a standard sample which has been analyzed
by other laboratories. Eimer and Amend $SrCO_3$ (lot #492327) was used
for this purpose, with an average value for eleven analyses of
$Sr(87/86)$ = 0.7093; and a corrected value of $Sr(87/86)$ = 0.7106. The
corrected value is more accurate and in good agreement with other work
(see Aldrich, 1953, Faure, 1961, and Whitney, 1962).

Normalization Correction

It is assumed that the $Sr(86/88)$ ratio is constant in nature;
and, although the exact value of this constant is not known, it is
commonly given as 0.1194 (after Nier, 1938). The measured $Sr(87/86)$
ratio is adjusted by an amount proportional to one-half of the
departure of the measured $Sr(86/88)$ ratio from 0.1194. The cause of
this departure from 0.1194 (or any constant value) is not known, but
it is probably not due to fractionation within the mass spectrometer.

General Geology

Rosenfeld and Eaton (in Rodgers and Rosenfeld, 1959) have shown
that the Siluro-Devonian rocks of the Bronson Hill Anticline (see
Billings 1956) of New Hampshire can be traced with certainty into the
area of study, and thus allows some degree of stratigraphic control.
In brief, they have found that the so-called Bolton Schist can be di-
vided into four formations, the upper three of which can definitely

be correlated with the New Hampshire sequence. Because of similar
positions relative to these rocks, the underlying rocks may then also
be correlated between the two areas. Eaton and Rosenfeld (1960) pro-
pose the following stratigraphic column:

FIGURE A-1

Connecticut Formation	New Hampshire Formation	Probable Age (N.H. rocks)
Camp Jenkins	Littleton	Early Devonian
Mine Brook	Fitch	Middle Silurian
Great Hill	Clough	Early Silurian
- - - - - - - - angular unconformity - - - - - - - -		
Collins Hill	Partridge	M. to L. Ordovician(?)
- - - - - - - - - - - unconformity - - - - - - - -		
Glastonbury and Maromas	Oliverian (?)	Pre-M. Ordovician (?)
Middletown	Ammonoosuc	do.
Monson (including Haddam)	(?)	do.

The Bronson Hill Anticline is a well-defined structural belt
which runs on a nearly N-S trend from Maine to Long Island Sound,
and is basically a complex anticlinorium consisting of elongated
gneiss-cored anticlines in metamorphosed stratified rocks. In the
Middle Haddam and Glastonbury Quadrangles, the Bronson Hill Anticline
is bordered on the west by a border fault dividing the Triassic from

the Pre-Triassic rocks, and on the east by undifferentiated gneisses and schists, generally correlated as part of the Merrimac Syncline (Billings 1956). Some Triassic diabase dikes cut the Pre-Triassic rocks near the border fault on a parallel trend. In addition, pegmatites cut all the other Pre-Triassic rocks, but are especially common in the Collins Hill Formation. The area has been subjected to several metamorphisms, and relationships between the various formations are therefore often obscure.

The principal problem in the area is the proper positioning of the gneiss-cored anticlines relative to the stratified rocks, and to each other. Billings (1956) has suggested that the Oliverian domes in New Hampshire are intrusive into both the Clough (Silurian) and the Ammonoosuc (Ordovician?), and has further suggested that the Oliverian domes are contemporaneous and related in origin based on mineralogic and textural similarities, equivalence of structural position, and other evidences (p. 52). Lundgren (1962) has described the similarities of the Oliverian domes to the Southern Connecticut domes, and a striking similarity is obvious. Billings (1956) favors an intrusive history of the Oliverian domes into the other basement rocks; but Lundgren (1962) and Eaton and Rosenfeld (1960), following part of the theory of Eskola (1949), do not believe that the doming was caused by intrusion, but took place much later than the ortho-gneissic genesis. Eaton and Rosenfeld (1960), Fig. A-1, have

proposed that the Maromas and Glastonbury are pre-Collins Hill but post-Middletown, and that the Monson is pre-Middletown. It is clear that the only certain correlations shown in Fig. A-1 are: Camp Jenkins-Mine Brook-Great Hill with Littleton-Fitch-Clough, Collins Hill with Partridge, and Middletown with Ammonoosuc.

Brief Lithologic Description

For description of the Camp Jenkins, Mine Brook, and Great Hill Formations, the reader is referred to Eaton and Rosenfeld (1960) because these formations have not been studied during the present investigation.

The Collins Hill Formation is a rusty-weathering two-mica schist with subordinate garnet, pyrite, kyanite and/or sillimanite. Basal members are apparently conglomeratic in part, commonly occurring immediately under an irregular sequence of garnetiferous and calc-silicate beds. Pegmatites are also very common. The Collins Hill occupies narrow synclines between the gneiss-cored anticlines within the area.

The Glastonbury Gneiss can be roughly divided into three main facies; an Eastern Granitic Facies, composed in main of quartz, microcline, perthite, and minor biotite (or muscovite near the contacts with schist), and oligoclase; a Central Facies of a darker,

augen gneiss with K-feldspar augen in a matrix of biotite, quartz,
minor oligoclase, and locally abundant hornblende and/or epidote;
and a Western Schistose Facies, which is predominantly a
biotite-quartz-microcline schist, with minor oligoclase. The
Central Facies constitutes the bulk of the formation, and may be
divided into a Western Porphyroblastic Facies and an Eastern Flaser
Gneiss Facies with a gradational contact between the two. Herz (1955)
has described the Glastonbury Gneiss in great detail, and Stugard
(1958) has also discussed it. Aplites and mafic schlieren are present
in parts of the Glastonbury, and pegmatites commonly occur near the
aplitic parts.

The Glastonbury occurs as a major anticlinal dome which can be
traced into Massachusetts.

The Maromas Granite Gneiss occurs as a pronounced major semi-
elliptical dome in the Middle Haddam Quadrangle, and also as two
elongated lenses between the Collins Hill and the Middletown
Formations. It also occurs as intimate injections into the
Middletown Formation in other spots. The rock is predominantly a
granitic gneiss showing microcline augen, with some biotite and/or
hornblende, and minor garnet. Stugard (1958) lists some of the
salient structural and mineralogic features of the gneiss.

The Middletown Gneiss mantles the Monson Gneiss both in the
Killingworth Dome and on the elongated anticlinal structure to the
northeast, but is not in contact with the Monson along the border
fault. The Middletown Formation is a well foliated, medium grained,
gneiss with some schistose members. Hornblende and plagioclase are
the most predominant minerals in the formation, with subordinate
biotite, and quartz is usually present. Cummingtonite, antho-
phyllite, and sometimes garnet are locally abundant. The striking
feature of the Middletown in all occurrences is the preponderance of
amphibole and plagioclase, and in some places biotite and quartz, over
K-feldspar. The plagioclase varies from An_{20} to An_{70} within the
formation.

The Ammonoosuc Volcanics are discussed here because they have
been studied to test the proposed Middletown-Ammonoosuc correlation.
The Ammonoosuc Volcanics occur in four distinct belts in New
Hampshire according to Billings (1956); and only ten to fifteen
per cent of the formation is considered to be of sedimentary origin,
including black slate, gray arenaceous slate, and impure quartzite.
The metavolcanics are represented by chlorite and chlorite-epidote
schists, with or without conglomerate; and by soda rhyolite, with
some volcanic conglomerate. The volcanic nature of the formation
is indisputable, and even the chlorite and chlorite-epidote schists
have the chemical composition of andesites and basalts. Various

grades of metamorphism, up to staurolite-sillimanite rocks, are present in the formation.

The Monson Gneiss occupies the principal mass of the Killingworth Dome and also occurs as an elongated anticlinal structure which can be traced into Massachusetts. These two occurrences are thought to be continuous (see Digman, in Rodgers, Gates, and Rosenfeld, 1959, p. 50). Mikami and Digman (1957) have studied the Monson (called Haddam) Gneiss in the Killingworth Dome, and have called it a tonalite. The rock has a salt and pepper appearance caused by hornblende and/or biotite speckled in a matrix of plagioclase and quartz, and garnets and minor opaques are sometimes present. The biotite is usually chloritized, and epidote is common in cracks in the plagioclase. Microcline is a rare accessory and usually, but not always, occurs near granitic dikes and sills which cut the more basic gneiss in several places. Mafics never exceed fifteen per cent in the gneiss, plagioclase varies from fifty to seventy per cent, and quartz from twenty to thirty-five per cent. The Killingworth Dome has a central core, and a peripheral zone which takes in (and may exceed) a so-called mixed zone adjacent to the mantling Middletown Formation. The fabric changes from granoblastic in the outer portions to hypidiomorphic in the core; plagioclase varies from An(25-03) in the outer zones to An(40-42) in the central core. Hornblende decreases inwards and biotite increases. The Monson Gneiss in the elongated anticlinal structure

is a coarse grained plagioclase-quartz-biotite gneiss with a pronounced foliation. Stugard (1958, p. 636) has presented modes from the area.

Pegmatites cut all of the above mentioned formations in the area, but are particularly common in the Collins Hill Formation, less common in the Glastonbury and Middletown, still less common in the Monson, and only one pegmatite has been shown to cut the Maromas. Two distinct varieties of pegmatites are present, narrow lenses and stringers of quartzo-feldspathic composition which are conformable to the regional structure of their host rocks; and large, semi-elliptical granitic masses which show a roughly parallel orientation to the regional structure; but which are often locally discordant to, and cross-cutting to, their host rocks. This latter variety has a diversified mineralogy and is usually characterized by microcline-perthite and/or plagioclase, with subordinate quartz, muscovite, tourmaline, biotite, garnet and rare element bearing phases. Internal zoning in these larger pegmatites is common, usually in the sequence from walls inward, by a border zone, wall zone, intermediate zone(s), and a core. Stugard (1958) estimates that at least sixteen per cent of the pegmatites are zoned, and even those in which no clear sequence of zones is noted exhibit at least a border zone. For this investigation, minerals from the Strickland and Spinelli Quarries have been studied; and these quarries are described in Cameron et al.(1954).

Previous Age Determinations

Previous age determinations in the area have been predominantly devoted to pegmatite minerals, and thus do not aid the interpretation of the surrounding basement rocks other than to place a minimum age on them. Rodgers (1952) has summarized most of the early work (including the classic work of Nier, 1939, a, b) and has proposed an average age of emplacement of 260 $\pm$ 50 m.y. for the pegmatites. Most of these ages were determined by the U-Pb and Th-Pb methods, and Brookins (1963) has summarized some of these earlier U-Pb and Th-Pb dates plus more recent determinations by Wasserburg et al. (1955) and Wasserburg and Hayden (1955) with a resultant average of 259 $\pm$ 15 m.y. Previous K-Ar and Rb-Sr ages on pegmatite minerals from the Massachusetts Institute of Technology, and K-Ar ages from other laboratories have been summarized in the Ninth Annual Progress Report, U.S. A.E.C., N.Y.O.-3942, 1961. The K-Ar ages average 250 m.y., and the Rb-Sr ages average 240 m.y. using $\lambda = 1.47 \times 10^{-11}$ yr^{-1}. Recalculated for $\lambda = 1.39 \times 10^{-11}$yr^{-1}, the Rb-Sr age becomes 250 m.y. K-Ar ages on micas from the Collins Hill Formation and the Glastonbury Gneiss give 230 m.y., which may mark the end of metamorphism in the area.

Analytical Results

The data are presented in Table A-1, and the isochrons for the various formations are shown in Figs. A-2 to A-9. The error limits on the various isochrons have been determined by constructing maximum and minimum isochrons through the error limits of all the points, and are not shown here for clarity of presentation.

Samples

R4717 - Collins Hill Formation, Biotite-quartz-(plagioclase) schist. 150 feet from the HW contact of the Strickland Pegmatite.

R4719 - Biotite-quartz-(plagioclase)-(garnet) schist, 5 inches from the FW contact of the Strickland Pegmatite.

R4720 - Biotite-muscovite($\pm$)-sericite-(garnet) schist, slightly mylonized. Contact facies, FW side of Strickland Pegmatite.

R4721 - Biotite-quartz-(garnet)-(plagioclase) schist, 15 from FW contact of Strickland Pegmatite.

R4788 - Biotite-quartz-plagioclase schist, near the Maromas contact.

A4774 - Massive plagioclase, Strickland Quarry Pegmatite.

A4992 - Cleavandite, with minor quartz and light blue tourmaline. Strickland Quarry Pegmatite.

R4791 - Maromas Granite Gneiss. Microcline-plagioclase (An-14)-(biotite) gneiss. West side of Collins Hill.

R5059 - do. Microcline-quartz-plagioclase (An-15)-biotite gneiss, near main Maromas Dome, donated by Dr. J. W. Peoples of Wesleyan University.

R5052 - Middletown Formation, amphibolite (hornblende 70 per cent, quartz 10 per cent, plagioclase (An-33) 20 per cent). West side of State Highway 17 just south of intersection with Isinglass Hill Road.

TABLE A-1

ANALYTICAL DATA

Sample	Formation Symbol	$(Rb/Sr)_{wt}$	$(Rb^{87}/Sr^{86})_{at}$	$(Sr^{86}/Sr^{88})_{av}$	$(Sr^{87}/Sr^{86})_{N}$
R4717	ch	0.57'	1.65	0.1198	0.7291
R4719	ch	0.99'	2.87	0.1204*	0.7370*
R4720b	ch	1.62'	4.71	0.1199*	0.7439*
R4721	ch	0.51'	1.48	0.1192*	0.7264*
R4788	ch	0.42'	1.22	0.1189*	0.7283*
A4774	p	0.50"	1.45	0.1212	0.7411
A4992	p	2.10"	6.18	0.1204	0.8855
R4791a	mr	2.01'	5.84	0.1195*	0.7370*
R4791b	mr	1.62'	4.70	0.1204**	0.7334**
R4791d	mr	1.35"	3.92	0.1190*.	0.7299*
R5059a	mr	12.50'	36.70	0.1198.	0.8560
R5059b	mr	9.63'	28.20	0.1188	0.8285
R4792a	gl	4.55'	13.26	0.1198	0.7763
R4792b	gl	5.97"	17.44	0.1196**	0.7995**
R4792c	gl	2.33"	6.77	0.1203*	0.7460*
R3372#	gl	9.51'	27.85	-	0.8478
R4998	gl	0.45"	1.30	0.1197**	0.7194**
R4999	gl	0.15"	0.43	0.1196*.	0.7109*
R5052	mi	0.04"	0.12	0.1192*	0.7070*
R5053a	mi	0.82'	2.38	0.1192*	0.7230*
R5053b	mi	0.95'	2.75	0.1190.	0.7254
R5053c	mi	1.62'	4.67	0.1191*	0.7350*
R5056b	mo	0.17"	0.49	0.1192*	0.7120*
R5056c	mo	0.37'	1.07	0.1182*	0.7171*
R5058d	mo	0.61"	1.77	0.1192.	0.7208.
R5058e	mo	0.01"	0.03	0.1187*	0.7081*
R5058a	g	17.40'	51.84	0.1197*	1.0090*
R5058f	g	15.10"	44.77	0.1185	0.9587
R5069	am	1.80"	5.24	0.1189	0.7415
R5070	am	0.63"	1.83	0.1196	0.7217
R5071	am	0.12"	0.35	0.1190	0.7120
R5072	am	0.03"	0.09	0.1194	0.7081

' = Isotope Dilution Determination
" = X-Ray Spectographic Determination
* = Mean of Duplicate Analyses
** = Mean of Triplicate Analyses
# = Data from NYO-3942, USAEC, 1961
ch = Collins Hill Formation
p = Pegmatite Minerals
mr = Maromas Granite Gneiss
gl = Glastonbury Gneiss
mi = Middletown Formation
mo = Monson Gneiss
g = Granite Cutting Monson
am = Ammonoosuc Volcanics

R5053 - Biotite-quartz-microcline-plagioclase-(minor epidote) gneiss, road cut on Highway 15 near Vernon turnoff.

R5069 - Ammonoosuc Volcanics, donated by Dr. M. P. Billings of Harvard University. Rhyolite porphyry, Harvard No. L-70.

R5070 - do., Quartz bearing soda rhyolite, H. No. L-H56.

R5071 - do., Biotite gneiss, H. No. L-H48.

R5072 - do., Chlorite-epidote schist, H. No. L-H48.

R4792 - Glastonbury Gneiss, Granite gneiss, from border facies near contact with Collins Hill, east of Strickland Quarry.

R4998 - do., Chloritized biotite-quartz-plagioclase gneiss, from outcrop south of Spinelli Prospect showing no microcline in hand specimens.

R4999 - do., Chloritized biotite-quartz-plagioclase gneiss, from east of Hale Quarry.

R5056 - Monson Gneiss, plagioclase-quartz-hornblende gneiss, two miles northwest of Marlborough from road cut on State Highway 2.

R5058 - Monson gneiss, and granitic dikes in Monson Gneiss, all from localities south of Higganum.
R5058e = plagioclase-quartz-hornblende gneiss
R5058d = plagioclase-quartz-biotite gneiss
R5058a,f = microcline-perthite-biotite granite dike in Monson.
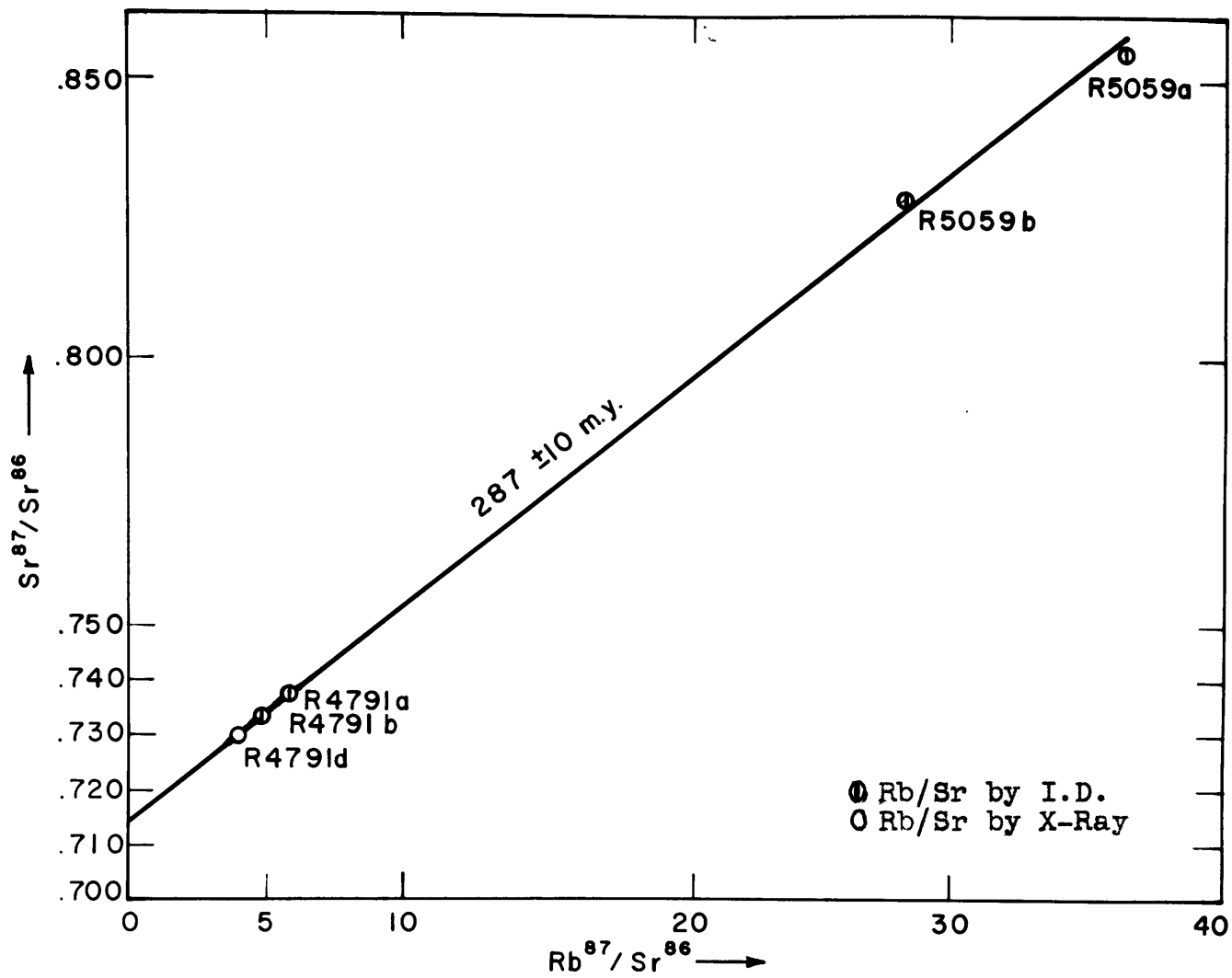
FIG. A-2 MAROMAS GRANITE GNEISS WHOLE-ROCK ISOCHRON
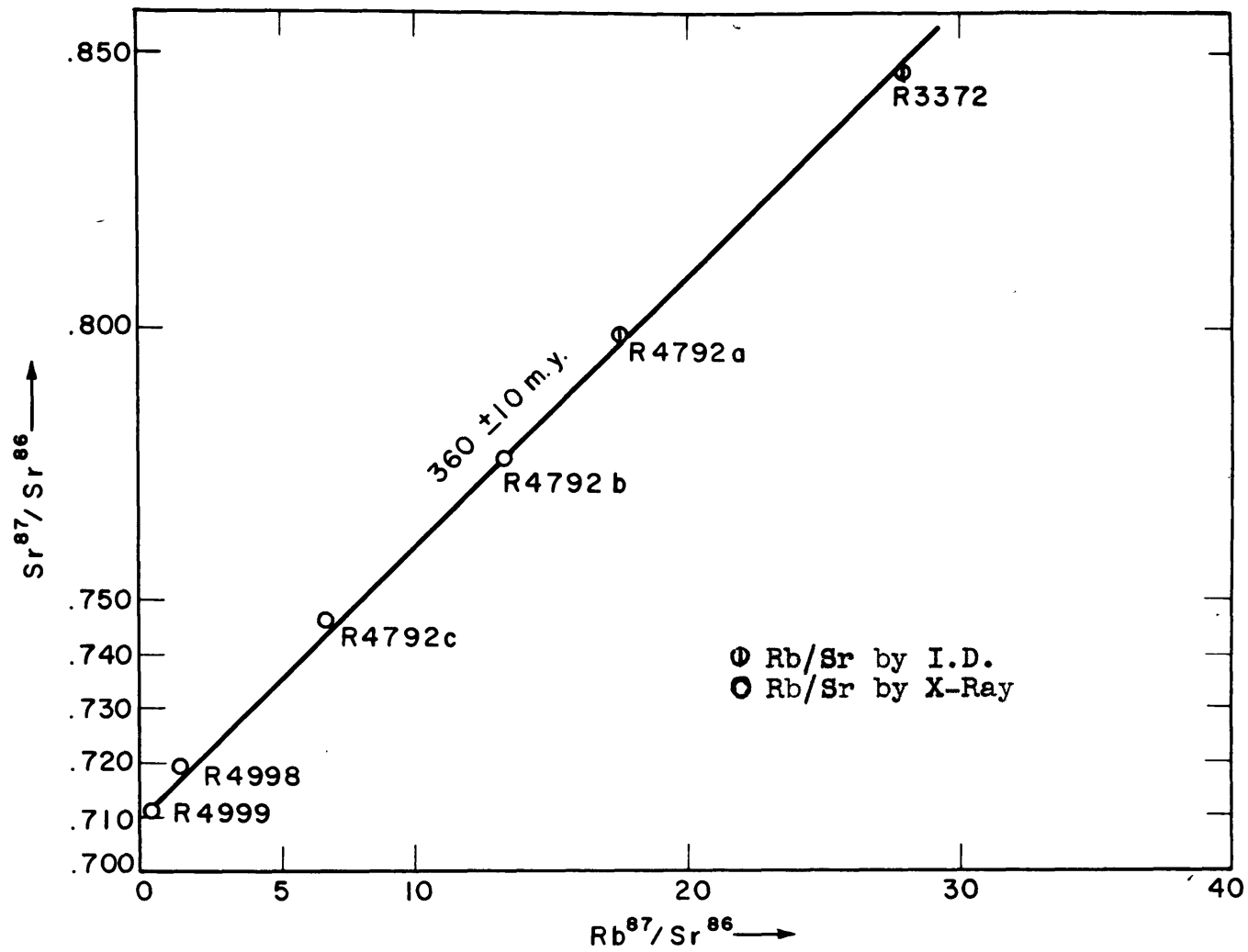
FIG. A-3 GLASTONBURY GNEISS   WHOLE-ROCK ISOCHRON
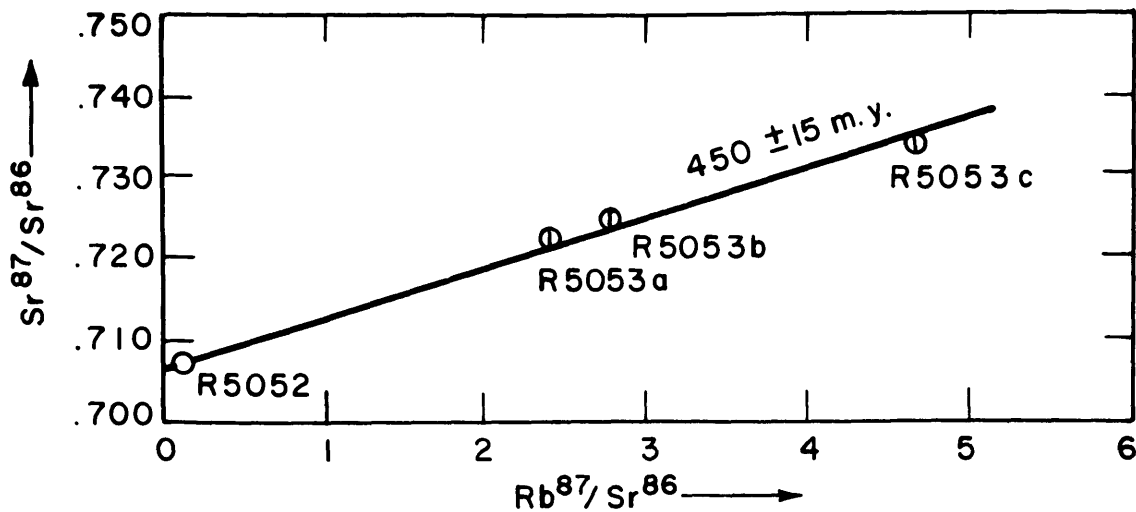
FIG. A-4 MIDDLETOWN FORMATION
WHOLE-ROCK ISOCHRON
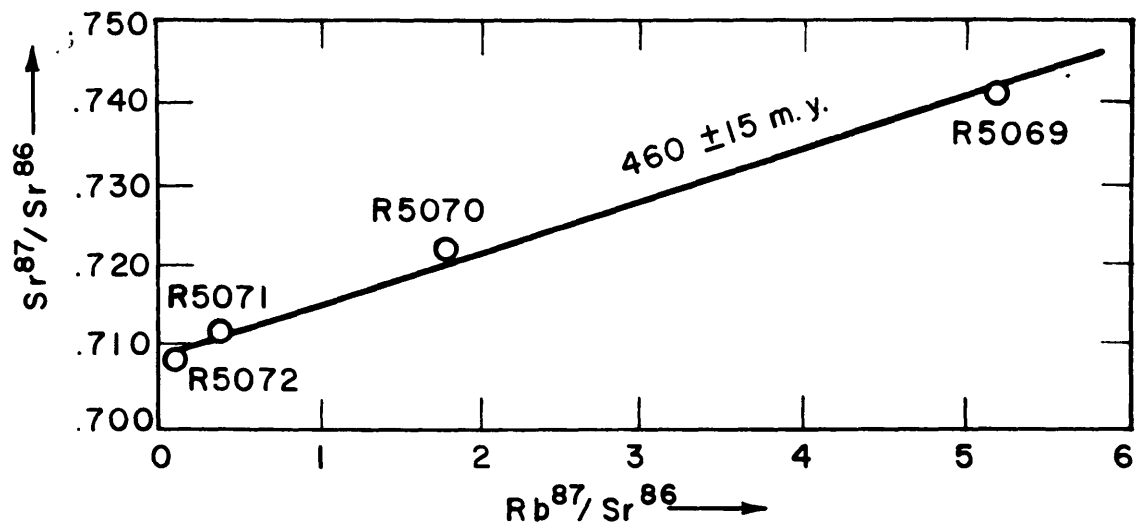
FIG. A-5 AMMONOOSUC VOLCANICS
WHOLE-ROCK ISOCHRON

⊕ Rb/Sr by I.D.
o Rb/Sr by X-Ray
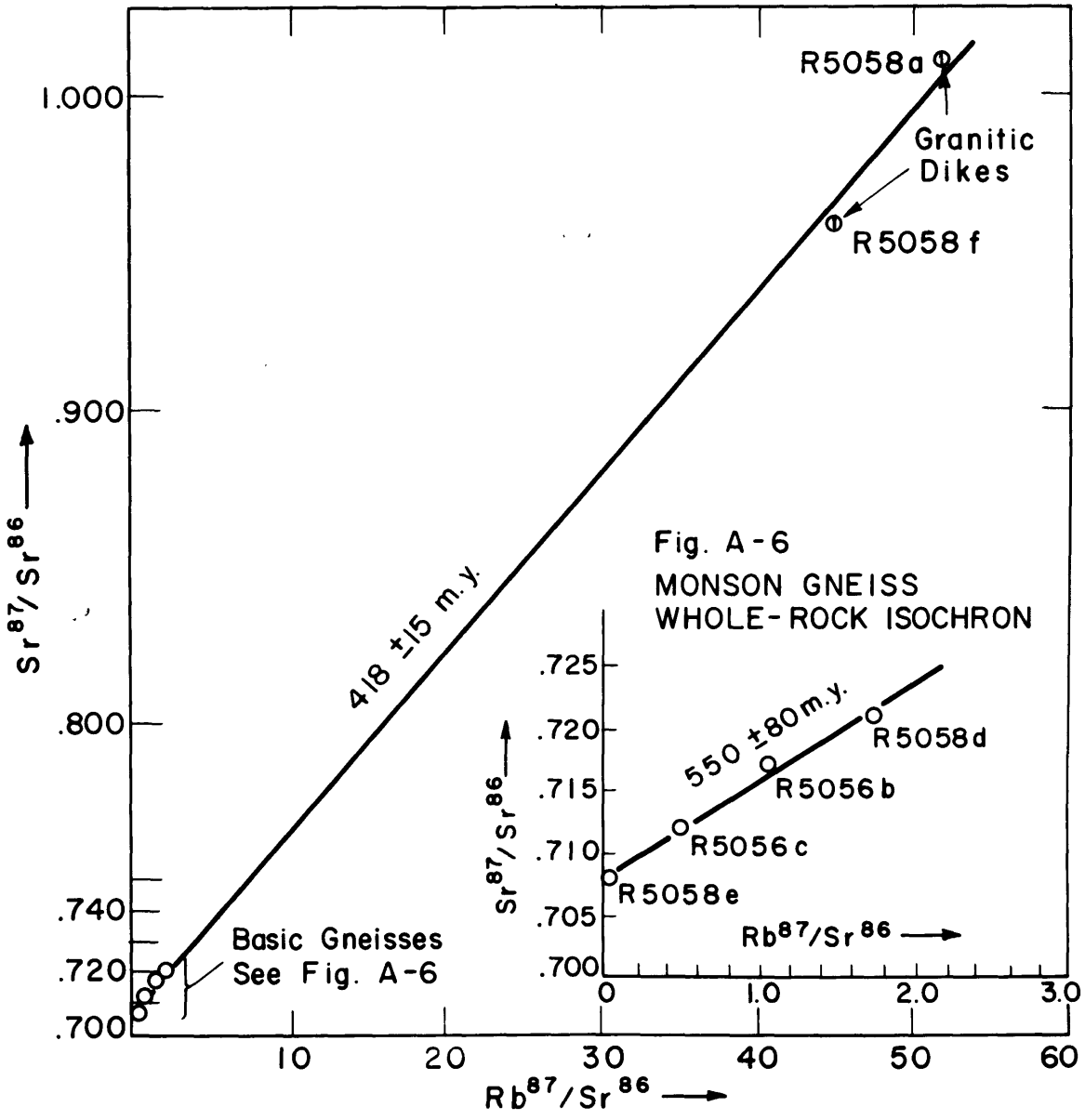
FIG. A-7   GRANITIC DIKES — MONSON GNEISS
POSSIBLE WHOLE-ROCK ISOCHRON
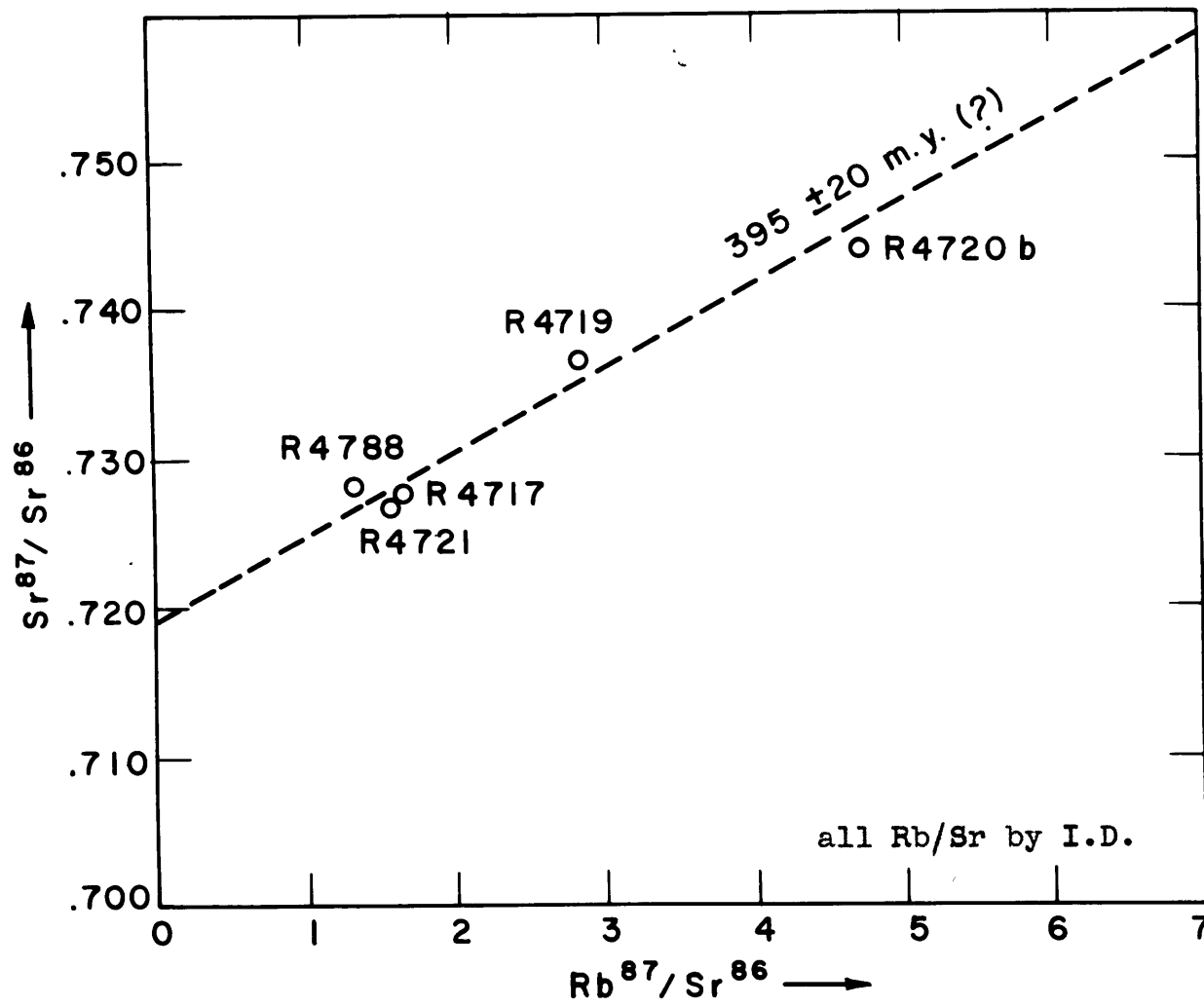
FIG. A-8   COLLINS HILL FORMATION
POSSIBLE WHOLE -ROCK ISOCHRON
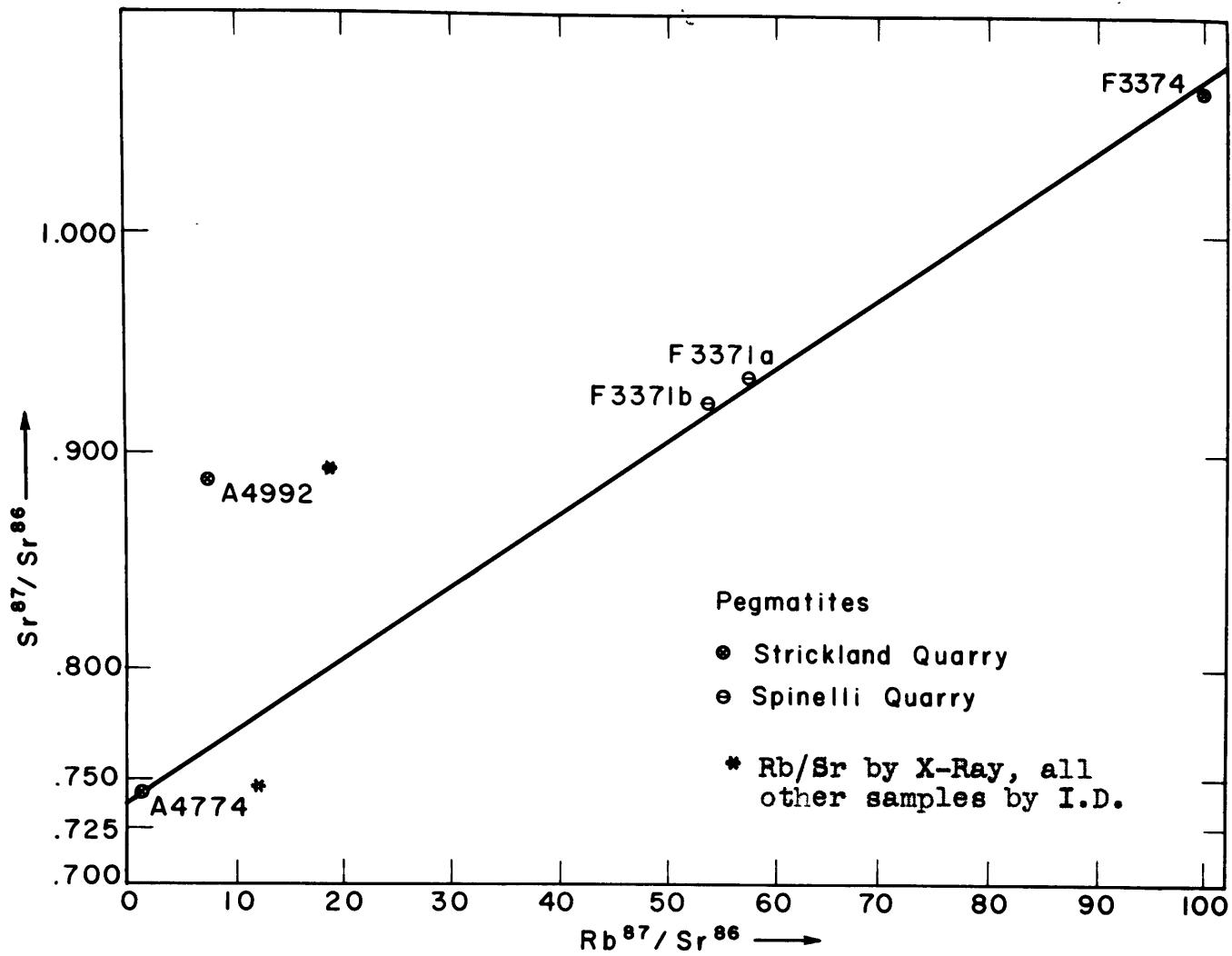
FIG. A-9 PEGMATITES MINERAL ISOCHRON

Discussion and Conclusions

The pegmatites show an age of 250 $\pm$ 10 m.y., which is in agreement with previous age determinations by other age determination methods from the area. The pegmatite minerals define an isochron which indicates an initial Sr(87/86) ratio of 0.737 $\pm$ 0.002. Sample A4992, a late-stage cleavandite, shows anomalous enrichment in Sr-87. The source of this excess Sr-87 may have been from an early crystallizing Rb-rich phase within the pegmatite system, such as lepidolite. As both geochronological and geologic evidence show that there have been no major metamorphic events since the emplacement of the pegmatites, the initial ratio is therefore representative of the source material from which the pegmatites were derived. Hence the pegmatitic material must have undergone a previous crustal history before final emplacement into its present sites. The Collins Hill Formation, the country rock for the Strickland Quarry Pegmatite, shows, in Figure A-8, a possible isochron, defined by samples both near and well removed from the pegmatite contact, which indicates that the local systems in the country rocks are too restrictive to have allowed any significant amount of mobile material to have migrated into the present pegmatite site. That the pegmatite has not been formed by any in situ process is consistent with field relations, which indicate forceful injection of the pegmatite into the Collins Hill Formation.

There is no direct genetic relationship between the Maromas
Granite Gneiss and the pegmatites despite their proximity in age.
The Maromas Granite Gneiss yields an initial $Sr(87/86)$ ratio of
0.714 ± 0.002, which indicates derivation from material which has
spent previous time in a sialic reservoir prior to emplacement; but
it is improbable, assuming the same parent magma for both the Maromas
and the pegmatites, that the parent magma could re-homogenize in a
span of only approximately 30 m.y. to yield an increase in the ini-
tial $Sr(87/86)$ ratio of 0.023. It is easier to envisage a process by
which various alkali-rich portions of country rock at depth have
undergone anatexis, and have been subsequently injected into their
present sites. That the pegmatite mineral isochron, Figure A-9, is
defined by samples from both the Strickland Quarry Pegmatite and the
Spinelli Prospect Pegmatite suggests cogenesis, and possibly the same
parental source, but more statistics are needed on other pegmatites
in the area to test this hypothesis.

The Maromas Granite Gneiss was emplaced $287 \pm$ m.y. ago and has
remained a closed system since that time. This age indicates that
the Maromas Granite Gneiss is intrusive into the other basement forma-
tions in the area. The $250 \pm$ m.y. pegmatite emplacement age is
generally taken to indicate the end of the Appalachian Orogeny in the

area, and therefore the lack of strong metamorphic features within the Maromas Granite Gneiss relative to the other granitic gneisses (e.g. Glastonbury Gneiss, etc.) and the paucity of pegmatites within the Maromas Granite Gneiss are explained by its 287 $\pm$ 10 m.y. age of emplacement. The contact between the Collins Hill Formation and the Maromas Granite Gneiss is obscure; but schlieren of the Collins Hill Schist are found within the Maromas Granite Gneiss near the contact and aplites related to the Maromas show the same type of intrusive effects at the Collins Hill contact as do the aplites related to the pegmatites which cut the Collins Hill. Because the Collins Hill Formation generally occupies narrow synclines between gneissic anticlines, and due to the obscurity of the contact relations between the two, Rodgers and Rosenfeld (1959) have placed the Maromas Granite Gneiss below the Collins Hill Formation on the stratigraphic column. G. P. Eaton (written communication), however, believes that the Maromas Granite Gneiss cuts even the Collins Hill Formation, a view which is substantiated by the Rb-Sr age measurements of this report.

The relation of the Glastonbury Gneiss to the Collins Hill Formation is more tenuous, but the 360 $\pm$ 10 m.y. age on the Glastonbury suggest that it has been intruded into the Collins Hill Formation. Although the possible isochron in Figure A-8 suggests an

"age" of 395 ± 20 m.y. for the Collins Hill Formation, it must be remembered that the formation is metasedimentary; and, as mentioed by Whitney (1962) and Compston and Pidgeon (1962), the apparent age is probably erroneous. That the possible absolute age is wrong is suggested by its probable geologic age of Late to Middle Ordovician (?), because the Silurian-Ordovician boundary is probably greater than 410 m.y. (M.L. Bottino, personal communication). The apparent isochron does, however, confirm derivation from material of a previous history because of the high initial $Sr(87/86)$ ratio of 0.719. The Glastonbury Gneiss, on the other hand, yields an initial $Sr(87/86)$ ratio of 0.710 ± 0.002, which strongly suggests original derivation from material of some crustal prehistory prior to emplacement; but caution must be used in implying intrusion (because of the 367 ± 10 m.y. age) because the samples were taken from the porphyroblastic facies (see Herz, 1955), and may thus not be representative of the whole formation. The Glastonbury-Collins Hill contact is more obscure than the Maromas-Collins Hill contact, but this may be due to the greater exposure to metamorphism(s) of the Glastonbury-Collins Hill contact because of its greater age. Schlieren of schist in the Glastonbury near the Collins Hill contact, and the local development of diopside (indicating intrusion ?) near the contact, and a possible chilled zone (now covered) have been cited by Stugard (1958) as evidence for intrusion;

but, as pointed out by Herz (1955), these features can be explained without recourse to igneous processes. The Great Hill Formation exhibits a basal conglomerate near the Glastonbury Gneiss and is probably post-Glastonbury; but as an angular unconformity exists between the Great Hill and the Collins Hill and the time span represented by the hiatus is not known, the Glastonbury may well be post-Collins Hill. From the above-mentioned evidence, it is plausible to suggest intrusion of the Collins Hill Formation by both the Glastonbury and Maromas Gneisses.

The Middletown Gneiss has been correlated with the Ammonoosuc Volcanics of New Hampshire, and the 450 ± 15 m.y. Middletown Age and the 460 ± 15 Ammonoosuc Age tentatively confirm this correlation; and suggest a mean age of 455 ± 10 m.y. for both formations. The initial $Sr(87/86)$ ratios of the Middletown Gneiss and of the Ammonoosuc Volcanics are 0.707 ± 0.001 and 0.708 ± 0.001, respectively. These values are equal within the limits of error and suggest a derivation of at least part of the formations from basic volcanics. This is consistent with discussion by Mikami and Digman (1957) for the Middletown Formation, and by Billings (1956) for the Ammonoosuc Volcanics.

Figure A-6 shows a possible isochron for the Monson Gneiss based on four low Rb/Sr samples; and despite the large error, the

550 $\pm$ 80 m.y. age suggests that the Monson Gneiss is older than the
Middletown Formation. This is consistent with the current field work
of Rosenfeld and Eaton (1959), Lundgren (1962), and Peter Robinson
(personal communication). Figure A-7 shows another isochron which
yields an age of 418 $\pm$ 15 m.y. but is anchored by the two granitic
dike samples, R5058a and R5058f. Mikami and Digman (1957) have sug-
gested that these dikes may represent late stage differentiation pro-
ducts of the original "tonalitic magma" which was intruded into the
Middletown Formation. Eaton and Rosenfeld (1960) and others have
suggested that the doming is not igneous in origin and that the
mantling strata is younger. This latter interpretation is more
feasible based on both field work and the possible isochron of
Figure A-6; and the granitic dikes must therefore either represent
later intrusions into the Monson or remobilized (and rehomogenized)
granitic facies of the Monson. The first of these two possibilities
is more likely. The contact between the Middletown and the Monson
is obscure, and Lundgren (1962) has proposed a gradational contact
between the two formations; but Eaton and Rosenfeld (1960) have in-
dicated that an unconformity exists. As the Middletown Formation is
probably Early to Middle Ordovician (?), the Monson Gneiss is there-
fore pre-Middle Ordovician, but how far back in geologic time past
the Middle Ordovician is not known. The 418 $\pm$ 15 m.y. age for the
granitic dikes is significant in that it indicates a distinct period

of emplacement of granitic material not related to the 360 ± 10 m.y. Glastonbury gneiss nor the 287 ± 10 m.y. Maromas gneiss. Further work may possibly correlate the 418 m.y. event to some of the granitic rocks further south in the section.

Although the area studied is rather restricted in size, the difference in ages between the Maromas Gneiss, Glastonbury Gneiss, Granitic Dikes, and the Monson Gneiss indicate that (1) there have probably been several generations of gneissic material along the entire Bronson Hill Anticline and that the Oliverian domes of New Hampshire probably represent more than one age of emplacement, (2) the initial Sr(87/86) ratios of the different gneiss domes studied indicates different crustal prehistories before emplacement for the different gneisses, and (3) contact effects have been largely obliterated by subsequent metamorphisms.

This study is far from complete but definitely shows the power of the Rb-Sr whole-rock method in dealing with complex geologic problems in a regionally metamorphosed area, and also emphasizes the need for careful geologic control within the area.

Acknowledgements

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Part II

CHAPTER ONE - DESCRIPTIVE GEOLOGY

Introduction

This chapter will attempt to introduce the reader to the main
features of stratigraphy and structure within the area of study, and
to discuss the correlation of the area to other areas.

The work of Rosenfeld and Eaton (1959) has confirmed the
earliest work in the area by Percival (1842), which was largely ig-
nored or forgotten by later workers until Rosenfeld and Eaton (op. cit.).
This has caused a major revision of stratigraphy in the area, and al-
lowed correlation with an area in New Hampshire which is fairly well
understood. Most of the stratified metasediments and metavolcanics
can be readily correlated, but the gneissic rocks are more difficult to
interpret. This chapter will review the main theories of stratigraphy
within the area based on geological evidence alone, and will not in-
clude any previous or current age determinations as these will be
covered later in this thesis.

Figure 1.1

Geologic map of east-central Connecticut
and central Massachusetts

Explanation

☐ Triassic rocks

▨ Paleozoic metasedimentary
        rocks

▧ Feldspathic gneisses

▨ Granitic rocks

Foliation dome
        or anticline

1. Killingworth Dome
2. Maromas Dome
3. Glastonbury Dome

Scale in miles

10   0   10
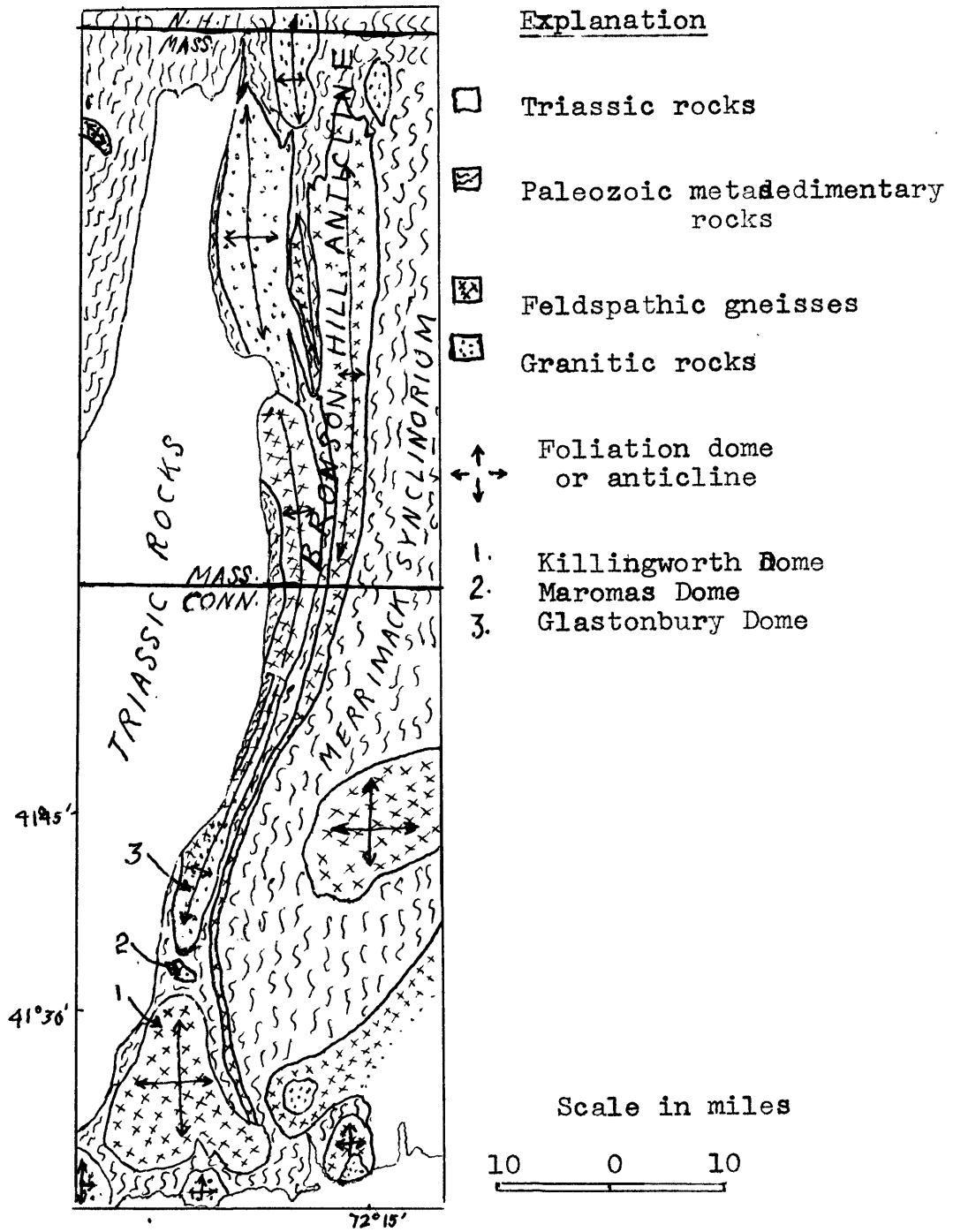
Modified from Lundgren (1962)

Geology

The following descriptive material is modified from recent work
reported in Rodgers and Rosenfeld (1959) and Eaton and Rosenfeld
(1960).

The Pre-Triassic basement formations which occur within the
Middle Haddam and Glastonbury Quadrangles are part of a well-
differentiated structural belt of formations that have been more or
less mapped continuously from the Maine - New Hampshire border west
of the Rangley Lakes southwest and south along the east side of the
Connecticut River to Central Connecticut, and then across the river
southwest to Long Island Sound. This belt is basically a complex
anticlinorium composed of elongate dome-shaped gneiss-cored anti-
clines in metamorphosed stratified rocks. It is referred to as the
Bronson Hill Anticline (Billings, 1956). North - south trends are
common for the anticlines, and they show an en echelon pattern to
the overall trend of the anticlinorium due to the slight counter-
clockwise rotation of their long axes relative to the regional trend
of the anticlinorium. This en echelon pattern is clear in Southern
Connecticut and in New Hampshire, but less obvious in Northern
Connecticut and Massachusetts. Some of these features are shown in
Figure 1-1.

The Bronson Hill Anticline in Connecticut is bordered on the
east by broad, gentle, largely undifferentiated gneisses and schists

with some intrusive masses; generally correlated as part of the
Merrimac Syncline (Billings, 1956). The western boundary is marked
by a border fault dividing the Triassic and Pre-Triassic rocks, ex-
cept for occasional Triassic diabasic dikes which cut the basement
rocks parallel to the border fault.

The formations present in the Middle Haddam and Glastonbury
Quadrangles are the Bolton Group, consisting of the Camp Jenkins,
Mine Brook, and Great Hill Formations; the Collins Hill Formation;
the Glastonbury Gneiss; the Maromas Granite Gneiss; the Middletown
Gneiss; and the Monson Gneiss. The distribution of these formations
is shown in Figures 1-2 and 1-3. In addition, pegmatites cut the
above formations but are especially common in the Collins Hill
Formation. The area has been subjected to several metamorphisms,
and relations between formations are therefore often obscure.

Lithology

Bolton Group

The three formations constituting the Bolton Group, the
Camp Jenkins, Mine Brook, and Great Hill Formations, were formerly
grouped along with the Collins Hill Formation into the now dis-
carded Bolton Schist Formation. The work of Rosenfeld and Eaton
(in Rodgers and Rosenfeld, 1959) has confirmed the original work of

Figure 1.2   Glastonbury Quadrangle

after Herz (1955)

0 ——————— 1
scale in miles
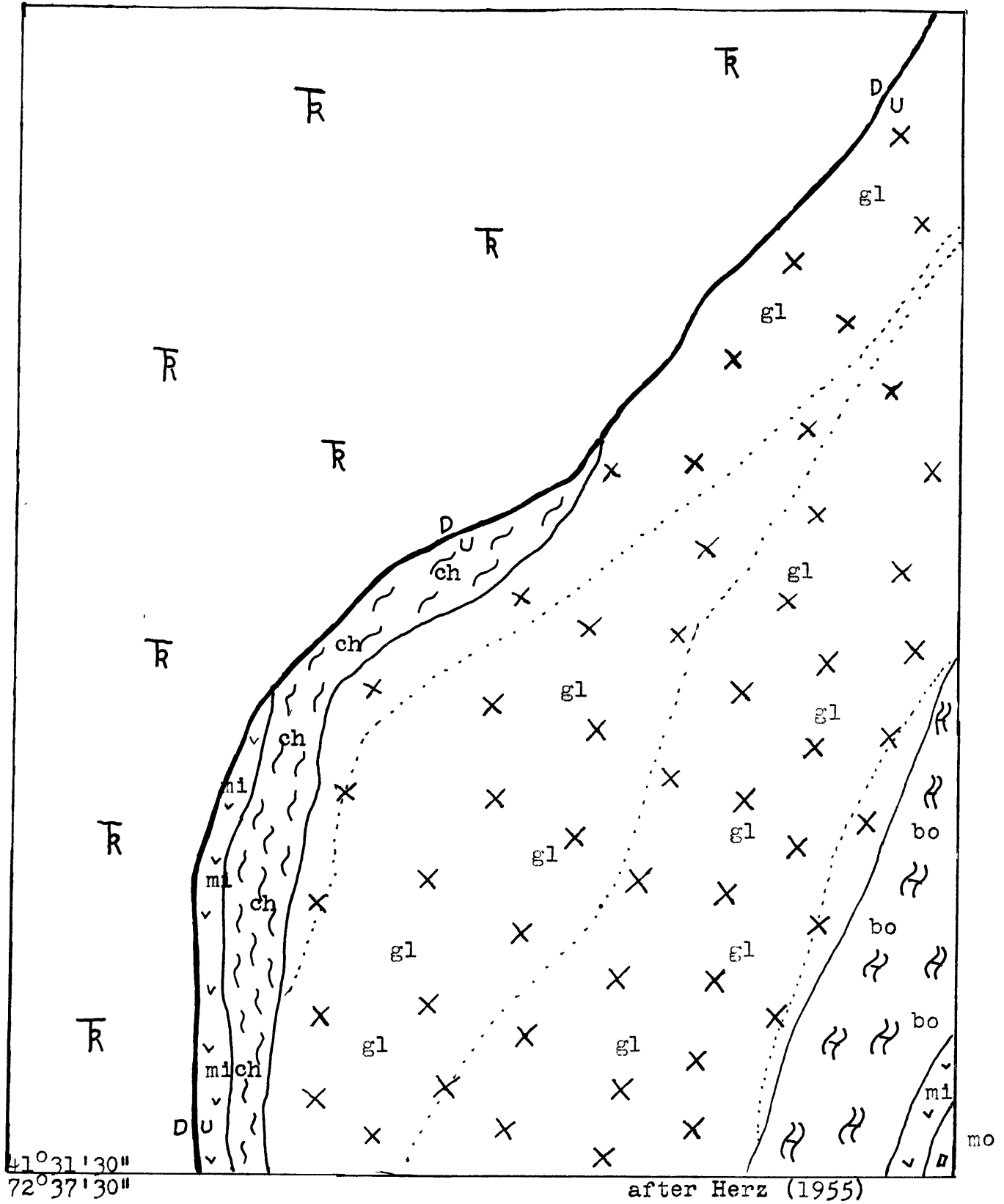
Figure 1.3

41°31'30"
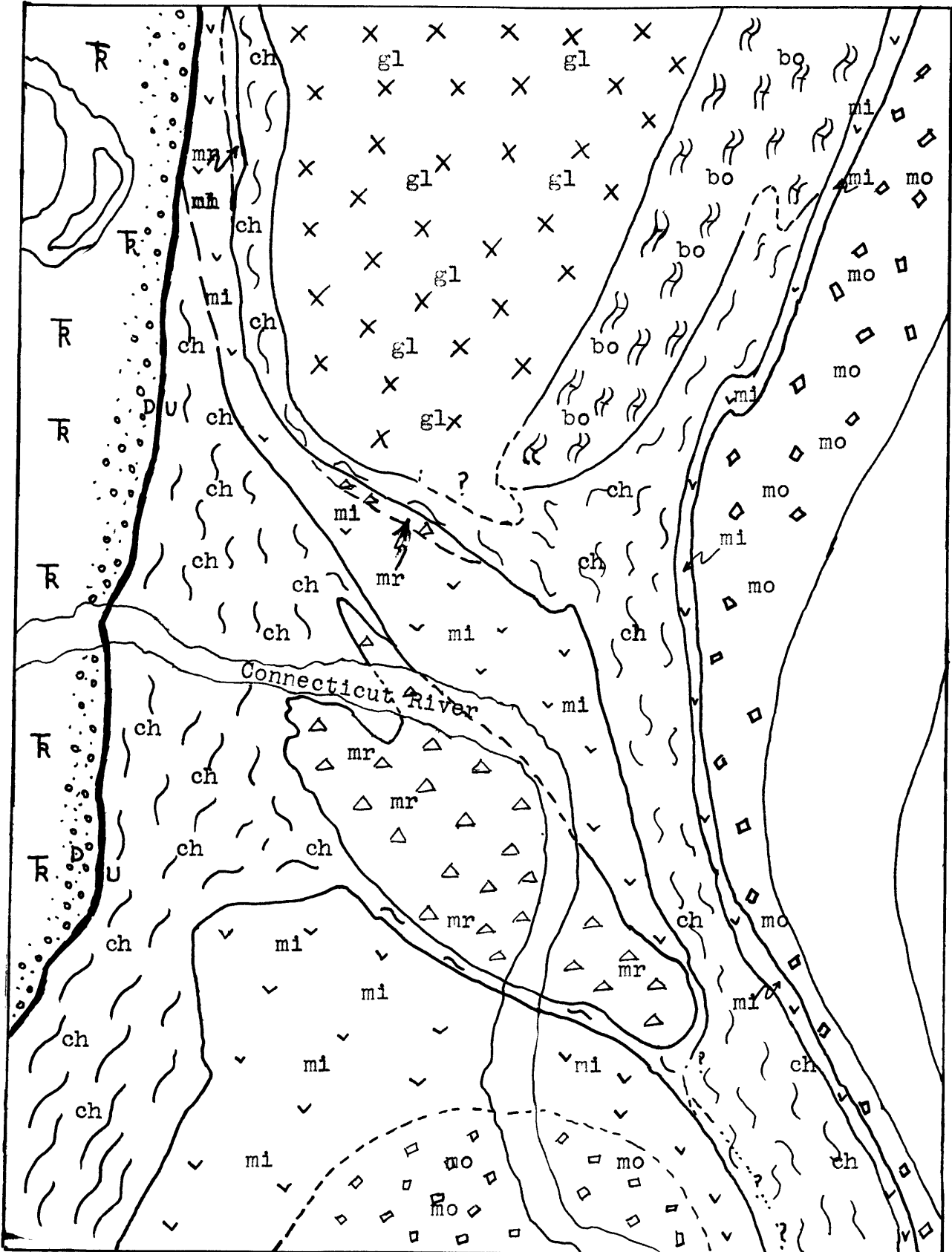
41°30'

after Rosenfeld and Eaton (1959)

0 ———— 1
scale in miles

Figure 1.4   Haddam Quadrangle
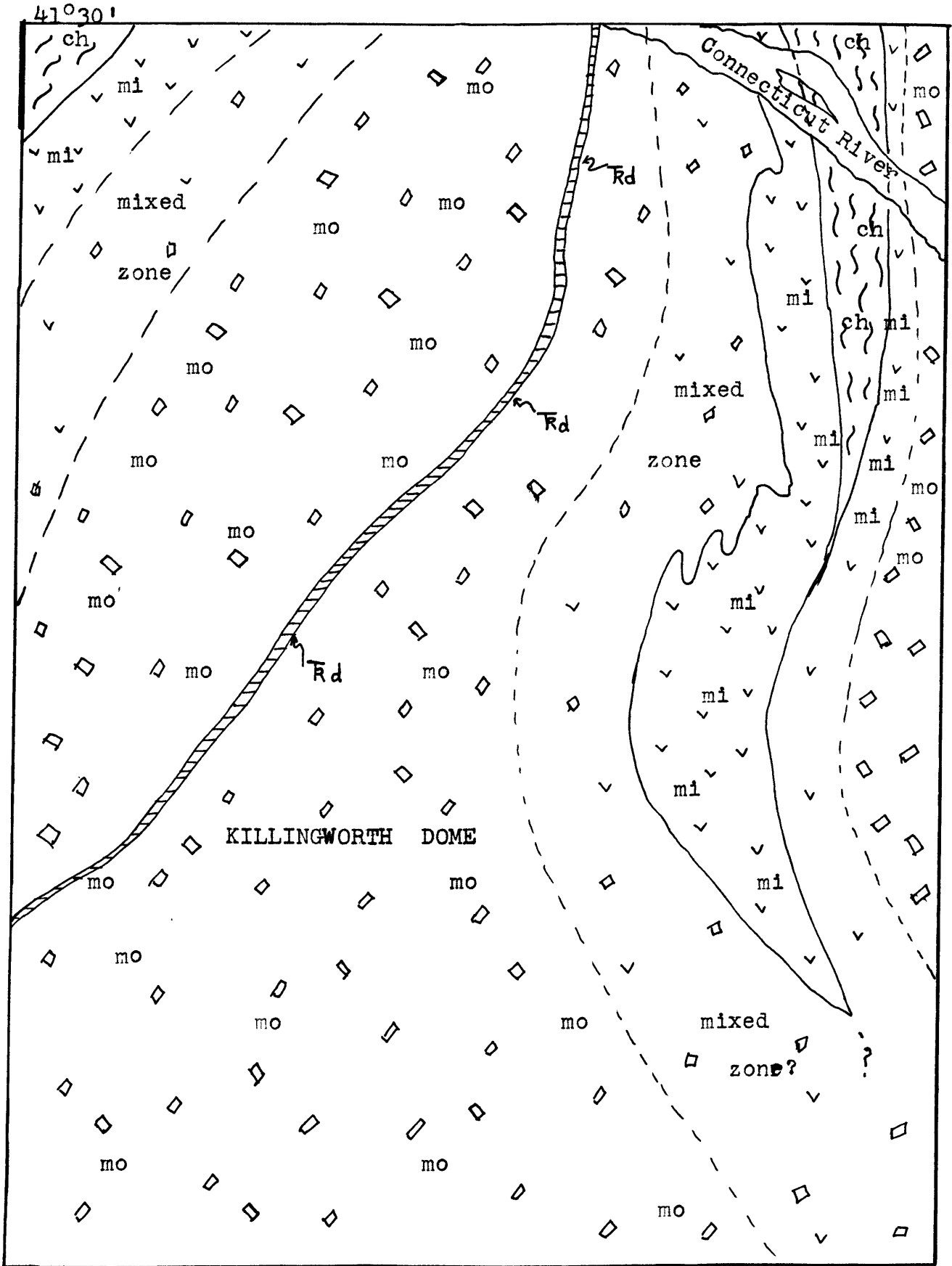
after Mikami and Digman (1957)

0 ———— 1
scale in miles

Percival (1842), and has resulted in the current separation of the Bolton Group from the Collins Hill Formation. The Bolton Group has not been studied in this work and thus will not be discussed in detail. The work of Rosenfeld and Eaton (op. cit.) has shown that the Bolton Group is definitely correlative with the Siluro - Devonian rocks of the Bronson Hill Anticline in New Hampshire. This correlation is as follows:

Connecticut Formation	New Hampshire Equivalent	Geologic Age
Camp Jenkins	Littleton	Early Devonian
Mine Brook	Fitch	Middle Silurian
Great Hill	Clough	Early Silurian

The reader is referred to Eaton and Rosenfeld (1960) and to Billings (1956) for descriptions of these rocks.

Collins Hill Formation

The Collins Hill Formation occurs as narrow, tight-folded synclines between the gneiss-cored anticlinal domes within the area. The areal distribution of the Collins Hill Formation in the Middle Haddam and Glastonbury Quadrangles is shown in Figures 1-2 and 1-3.

The Collins Hill Formation is commonly a rusty-weathering two-mica schist with subordinate garnet, pyrite, kyanite and/or sillimanite. In the basal parts apparent conglomeratic gneiss is

often present, usually immediately under an irregular sequence of garnetiferous and calc-silicate beds. Staurolite is sometimes present in the kyanitic zone. Pegmatites are extremely common in the Collins Hill, and, because of their greater resistance to weathering, often show obscure contacts with the Collins Hill Formation.

The Collins Hill Formation is correlated with the Partridge Formation of New Hampshire of possible Middle Ordovician (?) Age, and with the Brimfield Schist of Connecticut.

Glastonbury Gneiss

The Glastonbury Gneiss forms a major anticlinal dome in the Middle Haddam and Glastonbury Quadrangles and continues on an approximately N 30° E trend as a narrow band into Massachusetts (called Monson by Emerson, 1917, Cameron et al., 1954, and Foye, 1949). The Glastonbury Gneiss can be roughly divided into three main facies; an Eastern Granitic Facies, composed in main of quartz, microcline, perthite, and minor biotite (or muscovite near the contacts with schist), and oligoclase; a Central Facies of a darker, augen gneiss with K-feldspar augen in a matrix of biotite, quartz, minor oligoclase, and locally abundant hornblende and/or epidote; and a Western Schistose Facies, which is predominantly a biotite-quartz-microcline schist, with minor oligoclase. The

Central Facies constitutes the bulk of the Glastonbury Gneiss; and
is subdivided into a Western Porphyroblastic Facies and an Eastern
Flaser Gneiss Facies; the contact between which is gradational.
All of the major facies grade into each other with little abrupt
change in fabric or mineralogy, and the unique feature of all but
the border facies is the presence of biotite occurring in small,
thick patches which are sometimes smeared, but usually in isolated
knots. Quartz is abundant in all the facies, and shows sutured
boundaries in the larger grains. Mafic schlieren and aplites are
common in parts of the Glastonbury, and pegmatites are common;
especially near the aplitic parts.

The Glastonbury Gneiss has not been definitely correlated with
the New Hampshire sequence in the Bronson Hill Anticline, but it
may be similar to the Oliverian-type Domes (?); and the Glastonbury
has not been shown to occur in any of the sections further east in
Connecticut.

Maromas Granite Gneiss

The Maromas Granite Gneiss occurs as a pronounced major semi-
elliptical dome in the Middle Haddam Quadrangle, and also occurs as
two elongated intrusions between the Middletown and Collins Hill
Formations. These are shown in Figure 1-3. In

addition, the Maromas Granite Gneiss occurs as intimate injections into the Middletown Formation in much of the area and therefore postdates it. The main body of gneiss is elongated to the northwest, with a gentle to moderate (5° to 45°) dip to the northeast. The rock is generally massive, but shows a fairly good foliation also striking to the northwest.

The Maromas Granite Gneiss weathers to a dark- to light- gray rock, which is usually buff to white and rarely pink on fresh surfaces. The rock is granitic in composition, and commonly shows microcline augen. Mafic minerals are represented by biotite and/or hornblende. Minor accessories include garnet, sphene, rare allanite, and pyrite. Stugard (1958) lists some of the salient structural and mineralogical features of the principal Maromas mass, not visited by this writer, and also includes (p. 632) a tabulation of modes.

The Maromas Granite Gneiss has not been definitely linked to any other distinct formation in either New Hampshire or in Connecticut, but it is definitely post-Middletown in the area concerned.

Middletown Gneiss

The Middletown Gneiss mantles the Monson Gneiss both in the Killingworth Dome and the elongated anticlinal structure to the northeast, but is not in contact with the Monson west of the Glastonbury Gneiss Anticline. These relationships are shown in Figures 1-2, 1-3, and 1-4.

The Middletown Gneiss is well foliated, medium grained, and occasionally contains some schistose members. Hornblende and plagioclase are the most predominant minerals in the gneiss, with subordinate biotite. Hornblende-rich gneiss and hornblende-plagioclase gneiss constitute over two-thirds of the formation, with biotite gneisses and less commonly salic gneisses following. Mikami and Digman (1957) make the following broad petrographic divisions (p. 35): " 1) amphibole mafic gneisses, 2) amphibole intermediate gneiss (intermediate between salic and mafic), 3) salic gneiss and granulite, and 4) biotite gneiss and schist." Further subdivisions can be made, but the striking feature of all the Middletown Gneiss occurrences is the preponderance of amphibole and plagioclase, and in some places biotite and quartz, over K-feldspar. The plagioclase varies in composition between An_{20} - An_{70}. Cummingtonite (called tremolite-actinolite) and anthophyllite are common in some places, and garnet is locally common.

The Middletown Gneiss has been correlated with the Ammonoosuc Volcanics of New Hampshire, of possible Middle to Early Ordovician (?) Age.

Ammonoosuc Volcanics

The Ammonoosuc Volcanics are described here because they have been studied to test the Middletown-Ammonoosuc correlation.

Four distinct belts of the Ammonoosuc Volcanics occur in New Hampshire (see Billings, 1956), and only 10 to 15 per cent of the

formation is considered to be of sedimentary origin, including black slate, gray arenaceous slate, and impure quartzite. The metavolcanics are represented by chlorite and chlorite-epidote schists, with or without conglomerate; and by soda rhyolites, with some volcanic conglomerate. The volcanic nature of the formation is indisputable, and even the chlorite and chlorite-epidote schists have the chemical composition of andesites and basalts. Various grades of metamorphism are present in the four belts, up to staurolite-sillimanite rocks.

Monson Gneiss

For the purpose of this report, the gneiss which constitutes the principal mass of the Killingworth Dome will be referred to as Monson (formerly called Haddam), as this occurrence has been shown by Digman (in Rodgers, Gates, and Rosenfeld, 1959, p. 50) to be continuous with the elongated anticlinal belt of Monson Gneiss which extends to the type locality at Monson, Massachusetts. The Killingworth Dome has been thoroughly studied by Mikami and Digman (1957), who called the rock a tonalite, and it has also been called orthogneiss, leucotonalite, etc. Megascopically, the rock has a grayish salt and pepper appearance, caused by hornblende and/or biotite speckled in a plagioclase and quartz matrix. Garnets and minor opaque minerals may be present; and rarely zircon and/or sphene. The biotite is commonly chloritized, and epidote is often developed in cracks in the plagioclase. Microcline is

a rare accessory, and usually occurs near granitic dikes and sills

which cut the more basic gneiss in many places. Mafics never exceed

fifteen per cent in the gneiss of the Killingworth Dome, plagioclase

ranges from 50 to 70 per cent, and quartz 20 to 35 per cent. Mikami

and Digman (op. cit.) found that the Killingworth Dome has a central

core and a peripheral zone which takes in (and may exceed) a so-called

mixed zone adjacent to the mantling Middletown Gneiss. The fabric

changes from a granoblastic appearance in the outer zones to a hypidio-

morphic granular fabric in the central core. This change is completely

gradational, and is expressed by the outlines of the quartz and plagio-

clase crystals, as the mafic minerals are sub-oriented throughout the

sequence. The plagioclase varies in composition from An_{25} to An_{03} in

the outermost zones, and reaches An_{40} - An_{42} in the central core

portion. Hornblende decreases inwards toward the core as biotite

becomes more prevalent.

The elongated anticlinal belt of Monson Gneiss which extends

into Massachusetts is a coarse-grained plagioclase-quartz-biotite

gneiss with a pronounced foliation. Stugard (1958, p. 636) presents

modes from the area.

Pegmatites

Pegmatites cut all of the other basement rocks, but are

especially common in the Collins Hill Formation. The schistose

portions of the Middletown Gneiss and the Glastonbury Gneiss also contain abundant pegmatites. Fewer pegmatites cut the Monson Gneiss, and only one pegmatite has been shown to cut the Maromas Granite Gneiss. The pegmatites are of two distinct varieties: (1) narrow lenses and stringers conformable to the regional structure of their host rocks, and (2) large, semi-elliptical granitic masses which exhibit a roughly parallel orientation to the regional structure, but are locally discordant to and cross-cut their host rocks. This latter variety has a diversified mineralogy and is usually characterized by microcline-perthite and/or plagioclase, with subordinate quartz, muscovite, tourmaline, biotite, garnet, and many rare Li- U-, Ta-, B-, etc.- bearing phases.

Internal zoning in these larger pegmatites is common. Stugard (1958) estimates that at least sixteen per cent of the pegmatites in the area are well zoned; usually in the order, from walls inward, by a border zone, a wall zone, an intermediate zone, and a core. Some of these zones within the pegmatite cut other zones and are then designated as fracture fillings or replacement bodies. All of the large pegmatites of the area show at least a border zone, even when internal zones are lacking.

Strickland Quarry Pegmatite

Figure 1.5 shows the salient features of the main pegmatite and the so-called western pegmatite at the Strickland Quarry.

Figure 1.5 shows that the pegmatite is conformable to the regional structure, and that the schist is locally deformed to conform to the pegmatite contours. The Collins Hill Formation is the host rock for the pegmatite although the Glastonbury Gneiss occurs not far to the east. Various diamond drill holes (Cameron et al., 1954, p. 334) to depths of 360 feet show only schist and/or pegmatitic material.

Both the main pegmatite and the western pegmatite show interior zoning. The pegmatite is composed largely of plagioclase, quartz, microperthite, graphic granite, and muscovite. Tourmaline, garnet, biotite, spodumene, beryl, and apatite are minor accessories which are locally abundant. A great many unusual other minerals have been reported from the quarry, and many of these are summarized in Zodac (1937).

Five major zones exist; they are, from border inward: border zone, plagioclase-quartz-muscovite wall zone, perthite-graphic granite-quartz-plagioclase zone, plagioclase-quartz zone, and a quartz-plagioclase core. A detailed description of these zones is to be found in Cameron et al. (1954, p. 335, 336); but a brief description is as follows:
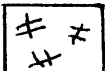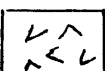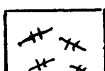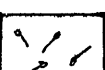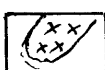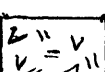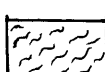
Cross section, Strickland Quarry, Looking North

Scale in feet

0 ———— 40
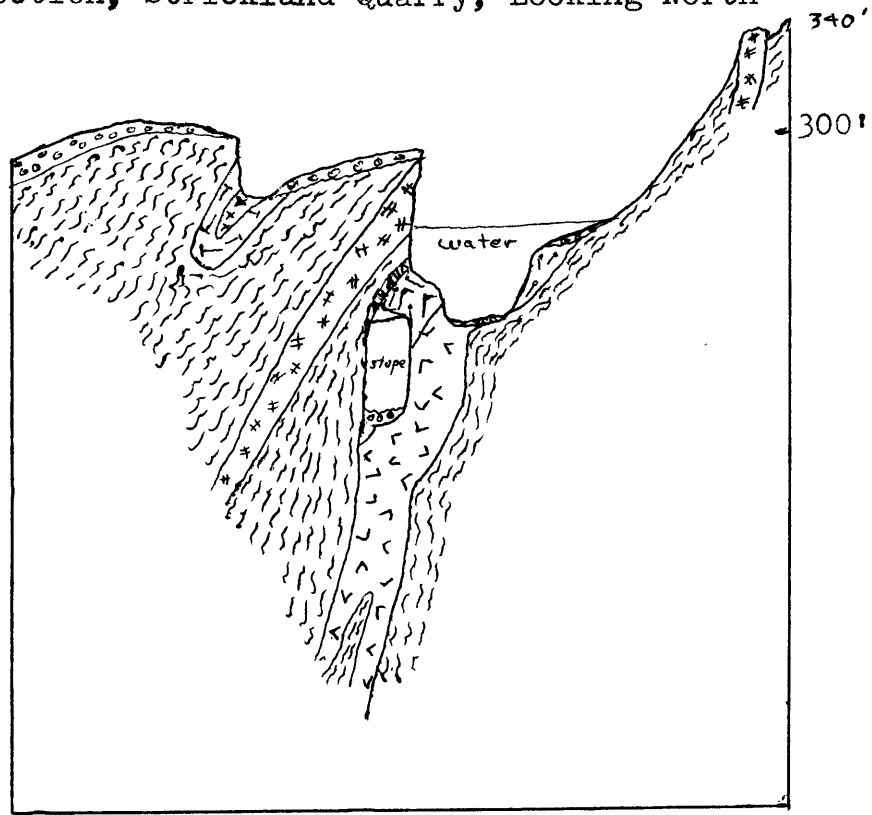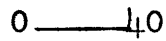
Perth-qz-plag peg.		overburden or debris	
qz-plag peg.		pegmatite, un-divided	
plag-qz peg.		cleav-qz peg.	
Perth-gr. gran-qz-plag peg.		qz peg. (core)	
plag-qz-musc peg.		Collins Hill Formation	

modified after Cameron et al (1954)

1. Border Zone: This zone is 1" to 8" thick and forms a nearly continuous layer around the entire pegmatite. It consists of a fine-grained assemblage of quartz, muscovite, and albite (An 5-9) with some tourmaline and garnet.

2. Wall Zone: This zone is 1' to 7' thick, and consists of medium- to coarse-grained plagioclase-quartz-muscovite with some black tourmaline and garnet. Massive plagioclase (An 5-9) predominates over cleavandite (An 1-4). Large books of muscovite are common in this zone.

3. Intermediate Zone: This zone is 1' to 22' thick, and is a coarse grained assemblage of perthite-graphic granite-quartz-plagioclase (An 4-8) with some tourmaline and garnet. Perthite is dominant, but is in part replaced by quartz and cleavandite.

4. Replacement Zone: This zone is up to 45' thick, and is a medium grained quartz-plagioclase (An 4-8) assemblage. This zone is probably due to replacement of the Intermediate Zone as evidenced by the presence of anhedral perthite in Zone 4 and the development of cleavandite in cracks in perthite in Zone 3, and lack of massive plagioclase replacing perthite.

5. Quartz-massive Plagioclase Core

Spinelli Prospect Pegmatite

This prospect is shown in Figure 1.7. The wall rock is

the Glastonbury Gneiss, and the pegmatite cross-cuts the

regional trend of it. Exposures are obscure, but Cameron et al.

(1954) describe the following zones:

" 1. Border Zone; 1-3 inches thick. Fine-grained quartz,
      feldspar, and muscovite.

   2. Quartz-perthite-plagioclase zone; thickness unknown.
       Consists of quartz and perthite, with subordinate
       plagioclase and accessory muscovite, garnet, tourmaline,
       and samarskite.

   3. Quartz core, at least 2 feet thick. The core is exposed
       for a length of 25 feet in the floor of the cut in the
       north eastern corner of the workings. It consists of
       coarsely crystalline quartz."

Hale Quarry Pegmatite

The Hale Quarry has been thoroughly described by Stugard (1958).

It occurs between the Collins Hill Formation and the Glastonbury

Gneiss, and is zoned as follows:

(1) Wall Zone: This zone constitutes over three-fourths of the

pegmatite on the Glastonbury side; and consists of a medium-grained

assemblage of perthite and quartz, with some albite and muscovite.

(2) Border Zone: This zone occurs on the west side adjacent to

the Collins Hill Formation and is 0 to 45 feet thick. It has

essentially the same mineralogy of the Wall Zone but also contains

tourmaline and some garnet.

Figure 1.7

Plan map of the Spinelli Prospect

Scale (feet)

0   30

N

after Shainin(1943)
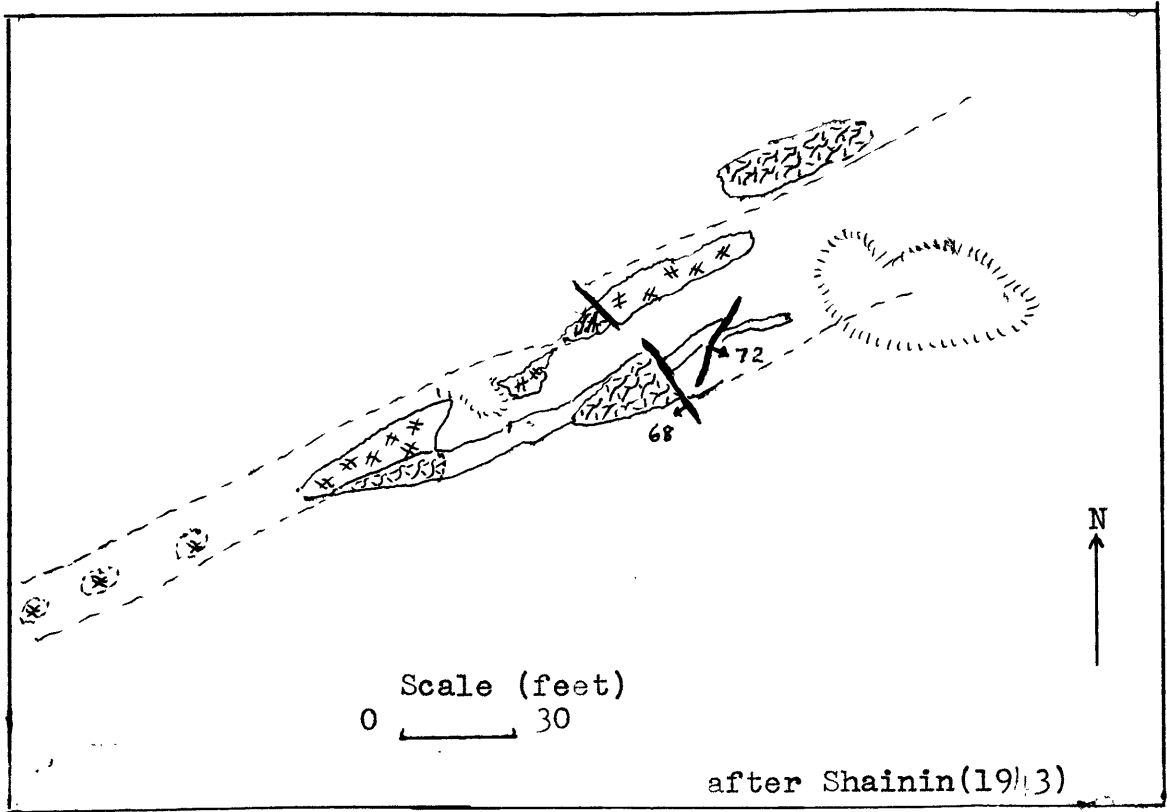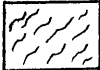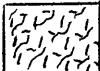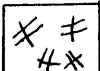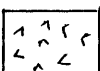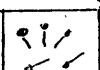
Figure 1.6

Cross-section, Hale Quarry, Looking North

Legend

350'

300'

modified after Stugard (1949)
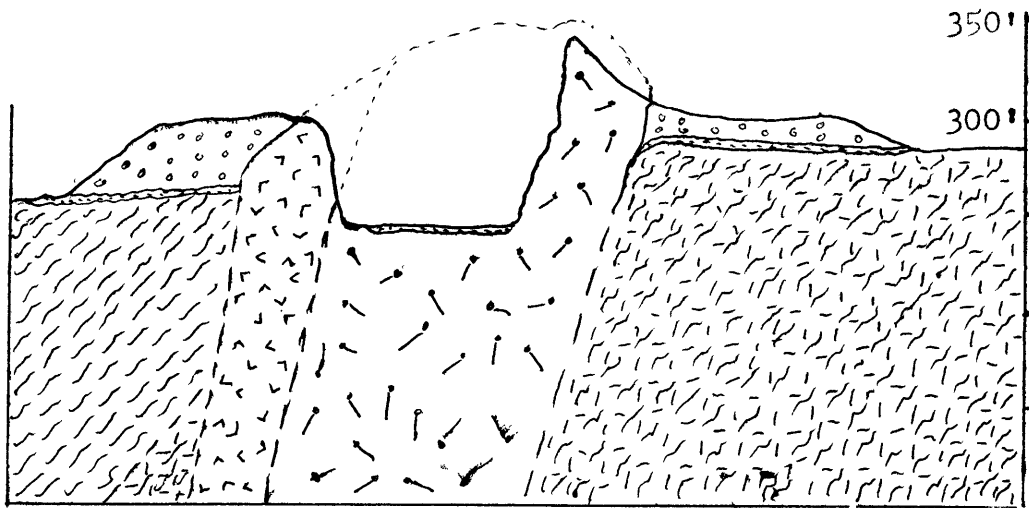
0   100

scale in feet

Collins Hill

Glastonbury

Pegmatite

Qz-ab-mica
peg.

Mcl-qz-mica
peg.

Stratigraphy of the Bronson Hill Anticline in Connecticut

Introduction

The recent work of Rosenfeld and Eaton (quoted in part in Rodgers and Rosenfeld, 1959, and part in press) has shown that a correlation exists between the Bolton Group (Camp Jenkins, Mine Brook, and Great Hill Formations) of Connecticut and the Siluro-Devonian Littleton, Fitch, and Clough Formations of the Bronson Hill Anticline in New Hampshire. Their work on this correlation confirms the original work of Percival (1842), who differentiated between the Bolton Group and the underlying Collins Hill Formation although later workers until recently have listed both as the combined Bolton Schist. However, despite the evident similarity of the Connecticut sequence of Camp Jenkins, Mine Brook, and Great Hill Formations to the New Hampshire sequence of Littleton, Fitch, and Clough Formations; the correlation of the underlying rocks is somewhat tenuous; and absolute confirmation of the proposed correlations between the Collins Hill Formation and the Partridge Formation, and between the Middletown Formation and the Ammonoosuc Volcanics has not been presented. However, the following general stratigraphic relations are noted (after Eaton and Rosenfeld, 1960) in Table 1.1.

TABLE 1.1

Connecticut Formation	New Hampshire Formation	Probable Age (Based on New Hampshire Rocks)
Camp Jenkins	Littleton	Early Devonian
Mine Brook	Fitch	Middle Silurian
Great Hill	Clough	Early Silurian
- - - - - - - - - Angular Unconformity - - - - - - - - -		
Collins Hill	Partridge	Middle to Late Ordovician (?)
- - - - - - - - - - - Unconformity - - - - - - - - - - -		
Glastonbury and Maromas	Oliverian (?)	Pre-Middle Ordovician (?)
Middletown	Ammonoosuc	Pre-Middle Ordovician (?)
Monson (including Haddam)	(?)	Pre-Middle Ordovician (?)

The above suggested column is a major revision of many
earlier proposed columns, but confirms in part the earliest work
in the area by Percival (op. cit.).

Mantled Gneiss Domes

Three major domes are present in the Middle Haddam and
Glastonbury Quadrangles; the Maromas Dome, the Glastonbury Dome,
and the Killingworth Dome. The Monson Gneiss cores the Killingworth
Dome, and the others are named for their core gneisses. These
Eastern Connecticut domes are remarkably like the Fennoscandian
Domes which have been described by Eskola (1949). Eaton and
Rosenfeld (1960, p. 172) state the following similarities:

" 1) General parallelism of the foliation of the gneisses
      with that of the mantling strata. (The foliation of the
      mantling schists is in large part bedding-plane foliation.)

   2) Relative persistence of the stratigraphic section of the
      mantling strata from dome to dome (with due allowance for
      the transgression of angular unconformities).

   3) The existence of conglomerates (?) calc-silicate rocks, and
      amphibolites in the oldest of the mantling rocks.

   4) Moderate overturning of the domes.

   5) In the Maromas and Glastonbury Domes, the intrusive
      relationship of part of the core gneisses with the older
      metavolcanic and metasedimentary rocks of the Middletown
      Formation. The latter, along with its intruding rocks,
      is unconformably overlain by the schistose strata of the
      synclines."

These authors state an objection to a purely intrusive origin,
and cite examples that part of the Glastonbury Gneiss and Monson
Gneiss (called Haddam Gneiss) were either metavolcanics or meta-
sediments; yet they do cite evidence of intrusion of both the
Maromas and Glastonbury Gneisses into the Middletown Formation. They
believe the doming to have occurred much later than the orthogneissic
genesis. Eaton and Rosenfeld (ibid., p. 172) also state:

"Structural features in the mantling strata suggest that during part of the deformation the gneisses sheared upwards past the flanking schists."

The implication requires a doming of the core gneisses by vertical emplacement, presumably resulting from the low density of the gneiss (Thompson and Rosenfeld, 1951, also describe similar phenomena in Southern Vermont). The mixed-zone of Monson Gneiss and Middletown Gneiss which forms the peripheral margin of the Killingworth Dome can thus be explained by this mechanism. However, Mikami and Digman (1957) believe this mixed-zone to be due to igneous intrusion (described earlier, p. 61).

Eskola (1949) has proposed an origin of mantled gneiss domes based on study of the Fennoscandian domes, and suggests a re-working of the contact vicinities such that apparent intrusive relations might occur, which may be accompanied by a granitization of the core gneisses. This theory is supported by the work of Eaton and Rosenfeld (1960) in part, but in general field relations are not clear.

It is interesting to compare the gneissic domes of this part of the Bronson Hill Anticline to those in the New Hampshire section, and the similarities of the domes of the two areas have been noted by Lundgren (1962):

"Readers familiar with sequence and relationships displayed around the Oliverian domes in New Hampshire (Chapman, 1942; Billings, 1956) and related domes south along the Bronson Hill Anticline (Hadley, 1949) will recognize many similarities with the Deep River domes. A typical Oliverian dome has a core of pink granite gneiss surrounded by more or less concentric envelopes of quartz diorite (plagioclase gneiss) and amphibolite (Ammonoosuc Volcanics, Ordovician), micaceous schists (Partridge formation, Ordovician), quartzite (Clough formation, Silurian), calc-silicate gneiss (Fitch formation, Silurian), and staurolitic schists (Littleton formation, Devonian). The granitic rocks in the cores typically do not cut any of the units above the Ammonoosuc formation...."

This comparison with the Deep River Area is possible because of the correlation of the Plagioclase Gneisses with the Monson and Middletown Gneisses and the correlation of the Brimfield Schist with the Collins Hill Formation. The Killingworth Dome has no true granitic core, but the fabric changes inwards from granoblastic to hypidio-morphic granular.

Billings (1956) has suggested that the Oliverian domes are intrusive into both the Ammonoosuc (Ordovician ?) and the Clough (Silurian), as dikes and sills of some domes intrude the former; (Billings, 1937, 1941; Hadley, 1942); and the latter is feld-spathized, presumably from solutions during Oliverian intrusion (Billings, 1937). Billings (1956) also believes that the Oliverian domes are contemporaneous and related in origin based on mineralogic and textural similarities, equivalence of structural position, and other evidences (p. 52). Also, all of the domes have undergone at

least one metamorphism. Billings (ibid. pp. 123-124) summarizes

his arguments as follows:

"The origin of these domes is problematical (Billings, 1945,
pp. 63-65; Eskola, 1949). Many suggestions have been made. One is
that the Oliverian series consists of metamorphosed volcanic rocks
similar or identical with the Ammonoosuc Volcanics. This seems un-
likely because: (1) The Oliverian series and the Ammonoosuc
Volcanics are distinctive units that can be separately mapped in the
field; (2) the Oliverian series, although much of it now has a
granoblastic texture, was at one stage considerably coarser in grain
than the Ammonoosuc Volcanics; (3) although the Ammonoosuc Volcanics
are massive and unbedded in places, bedding can be recognized when
sufficiently large areas are studied; (4) the Oliverian series oc-
curs in much larger units; and (5) intrusive contacts of the
Oliverian series indicate a molten rock."

He then suggests that all known facts related to the Oliverian series

can be explained by this intrusive theory, and suggests all of the

domes were tapped from a single, unique magma chamber. This will be

discussed later.

Eskola (1949) has proposed an involved genetic theory favoring

the mantling rocks to be younger, which can be generalized by the

following steps: (1) Intrusion of a plutonic mass and subsequent

eroding, representative of one orogenic period; (2) a period of

sedimentation of the mantling rocks; (3) remobilization of the

pluton during a subsequent orogenic cycle accompanied by new granitic

intrusion and gneissic deformation of the main pluton; causing its

migmatization and granitization. Eskola (ibid.) emphasizes the apparent need of two periods of deformation for this complex procedure, and points out that this is the case for numerous areas in the world; and while he does believe that contact effects can be altered by the later deformation, he also believes the principal dome gneiss to be of plutonic origin.

Mikami and Digman (1957) favor an intrusive history of the Monson Gneiss in the Killingworth Dome into the overlying Middletown Formation, and cite evidence of mineralogical and textural change towards the center of the dome. The so-called mixed zone they attribute to incomplete assimilation; and they infer that the granitic dikes and sills cutting the tonalitic Monson may be equivalent to the Clinton Granite (see Lundgren, 1962 for description), and that it might represent trapped differentiation products of the tonalitic mass. They thus propose that the doming was caused by the intrusion; but they do (pp. 55-56) mention the possibility that if the Monson Gneiss were originally dacitic volcanics, it could grade upwards into the metasedimentary and metavolcanic Middletown Formation; and that the doming occurred in a subsequent metamorphism. This theory does not, however, explain the aforementioned fabric change in the Monson nor the granitic dikes; and hence they favor the intrusive theory. However, Lundgren (1962, p. 17) has also pointed out that:

".... The complicated internal structure indicated by the configuration of marker beds in the gneisses of each dome is also reflected in the distribution of boudinage and small isoclinal folds in amphibolite and quartzite beds interleaved with granite gneiss and plagioclase gneiss. The extensive development of boudinage indicates that all the rocks were plastically deformed together, presumably during doming."

The need for regional deformation after emplacement results from the apparent distortion of contact relationships. This would explain both the pseudo-intrusive migmatized contacts described by Eskola (1949) and the mixed-zone described by Mikami and Digman (1957).

Discussion

The Bolton Group has been correlated along regional strike with the Siluro-Devonian sequence in New Hampshire; the latter being a well defined group of three formations. It is permissible, therefore, to assign an Early Devonian through Early Silurian Geologic Age to the Bolton Group; but this correlation of these two groups does not necessarily imply correlation of their respective underlying formations. The Collins Hill Formation of Connecticut has been found by Rosenfeld and Eaton (in Rodgers and Rosenfeld, 1959) to lie unconformably in narrow, tight-folded synclines between gneissic anticlines; and an angular unconformity exists between the Collins Hill Formation and the overlying Bolton Group. As an angular unconformity exists between the Clough and the Partridge Formations in New Hampshire, the Collins Hill Formation is therefore assumed to be the Connecticut equivalent of the Partridge. This allows a geologic age to be tentatively placed on the Collins Hill Formation because the Partridge Formation has also been correlated across the Connecticut Valley Synclinorium with the Cram Hill Formation in Vermont, which in turn has been correlated along strike with the Magog Slate north of Lake Memphramagog, in which graptolites of possible Middle Ordovician Age occur.

The original fossils are not available for re-examination, however (see Billings, 1956). Thus this Middle Ordovician (?) Age is probably only approximate at best, but sufficient to distinguish the Collins Hill from the surrounding formations.

It has been proposed by Rosenfeld and Eaton (op. cit.) that the Collins Hill Formation was deposited on older gneissic basement rocks, which therefore necessitates the placing of both the Maromas Granite Gneiss and the Glastonbury Gneiss as Pre-Collins Hill. This is a revision of previous thought, as Foye (1949) and other earlier workers have proposed that both the Maromas and the Glastonbury were intrusive into the Collins Hill (called Bolton Schist). Eaton (written communication) has suggested that the Maromas may be intrusive into the Collins Hill, hence a discussion of the Maromas Granite Gneiss-Collins Hill Formation contact is in order. The type Maromas Granite Gneiss shows definite intrusive contacts with the Middletown Gneiss, but the contact with the Collins Hill Formation is obscure. Further to the north (see Figure 1.3), however, the Maromas Granite Gneiss also occurs as two semi-elliptical masses wedged between the Middletown-Collins Hill contact. Schlieren of Collins Hill schist exist within the Maromas near the contact, and Maromas - related aplitic apophyses commonly cut the Collins Hill. In addition, the biotite grains in the

Collins Hill schists near the Maromas contact show, microscopically, a lack of regional influence on their orientation; and this random orientation disappears and a well defined foliation is observed away from the contact.

The Glastonbury Gneiss also exhibits schlieren of presumed Collins Hill derived schist in its border facies; but, unlike the Maromas Granite Gneiss, shows a well developed foliation conformable to regional structure; and no obvious intrusive features into the Collins Hill. The Clough Formation, on the other hand, exhibits a locally conglomeratic zone immediately over the Glastonbury along their contact. The Glastonbury also shows intrusive contact features against the Middletown Formation, but the relation of the Maromas to the Glastonbury is unknown due to lack of mutual contact between them.

The relationship of the Monson Gneiss to the Middletown Gneiss is also obscure, and a zone of apparently mixed Monson and Middletown exists between them. The Middletown does not decrease regularly in this zone, but is rather sporadic as it wedges out abruptly; and this zone may represent either discontinuous inter-layering or possibly incomplete assimilation of the Middletown by the Monson. The latter hypothesis is somewhat difficult to accept, however, because of the considerable width of this mixed zone; and the lack of sialic fragments of the Middletown Formation within in.

Granitic dikes cut the Monson Gneiss in many places, but their
relationship to the Monson is not clear. Mikami and Digman (1957) have
discussed the Monson (called Haddam) Gneiss in the Killingworth Dome
in great detail, and have favored an igneous origin on the basis of the
arguments that, despite the mosaic and granoblastic texture of the
gneiss, which is generally a product of static metamorphism, it is pos-
sible that early crystallizing mafic phases achieved their orientation
by a fluxion movement during the emplacement of the magma. The grano-
blastic fabric of the quartz and plagioclase could have resulted from
differential flow continuing after the rock was nearly solid; and
thus explain the gradation to the hypidiomorphic core. They do point
out'

(p. 29, 30) that "If the crystalloblastic facies of the Haddam
tonalite were considered alone, there would be no inherent
characteristic to distinguish it from a granulitic gneiss re-
crystallized, say, from dacitic volcanics of other rocks of
appropriate composition. But the distribution of this facies
peripheral to and grading into a central eugranitic facies calls
for an explanation."

In addition, Billings(1937) and Chapman, Billings, and
Chapman (1944) have noted in New Hampshire that for some igneous
cored domes a hypidiomorphic granular to granoblastic outward
sequence exists.

As another offered evidence for intrusion of the Monson Gneiss
into the Middletown Formation, Mikami and Digman (1957) cite the oc-
currence of a tonalite dike near Guilford, correlated by composition

with the Haddam, clearly intrusive into the Middletown. Also, slabs of the Middletown Formation within the Monson Gneiss near the contact are offered as other evidence of intrusion. However, they do cite the possibility that if the Haddam were originally composed of dacitic volcanics, then these could grade upwards into the Middletown which is believed to have originated from both sediments and basic volcanics. In this case, the doming must have been a regional event. This theory is inconsistent with the eugranitic fabric of the central core, however. The amount of quartz and other evidences (see Stugard, 1958) suggest a metamorphic origin from sediments and tuffs; or by siliceous contamination of a metamorphosed intrusive. Stugard (ibid.) also proposed that the Monson Gneiss is younger than the Collins Hill Formation (called Bolton schist). Rosenfeld and Eaton (1958) do not believe that the doming was igneous, and hence favor derivation from metasediments and metavolcanics. Due to the prevalence of plagioclase, quartz, hornblende and/or biotite in both the Middletown and Monson, Lundgren (1962) has grouped them together as Plagioclase Gneisses; which infers a gradational (or conformable) contact to exist between them.

The relationship of the Collins Hill Formation to the Middletown Formation is obscure in the immediate contact zone,

although localized interfingering at the contact has led to theories of a conformable sequence of Middletown upwards into Collins Hill. Rosenfeld and Eaton (in Rodgers and Rosenfeld, 1959) have, however, shown that an unconformity exists between the Middletown Formation and the Collins Hill Formation, and that the Collins Hill Formation occupies a narrow syncline flanked by older, anticlinal Middletown Gneiss in parts. In addition, basal members of the Collins Hill Formation show a conglomerate in some places along the contact with the Middletown Formation.

The large, granitic pegmatites in the area were emplaced during the last major metamorphism of the area, as evidenced by their lack of regionally-influenced structures in their interior zones. They have been injected into all the older basement formations, but are most common in the Collins Hill Formation. Stugard (1958) estimates that over 300 of 400 pegmatites mapped occur in the Collins Hill (called Bolton). Pegmatites are also common in the Middletown and Glastonbury, and less common in the Monson, but only one pegmatite has been definitely shown to occur in the Maromas. This distribution of pegmatites within the various formations cannot be used as a stratigraphic indicator as the factors involved in the genesis of these pegmatites are unknown. For example, that the Collins Hill Formation contains most of the pegmatites is not surprising as a

schistose rock is more likely to be subjected to intrusion than the more resistant granitic and basic gneisses.

Summary and Conclusions

Contacts between many of the basement formations in the Connecticut section of the Bronson Hill Anticline are obscure, and clear effects indicating intrusion or conformability have been erased by the repeated metamorphisms. Thus apparent intrusive phenomena, such as schlieren of a proposed host rock within the intrusion, can also be explained by migmatization and by other metamorphic processes. Similarly, these metamorphic events can erase evidence of an unconformable or conformable sequence, and alter original intrusive evidences so that they appear otherwise. Prior to the work of Rosenfeld and Eaton (op. cit.), the above mentioned factors led to numerous stratigraphic sequences. These proposed sections are reviewed in Rodgers and Rosenfeld (1959).
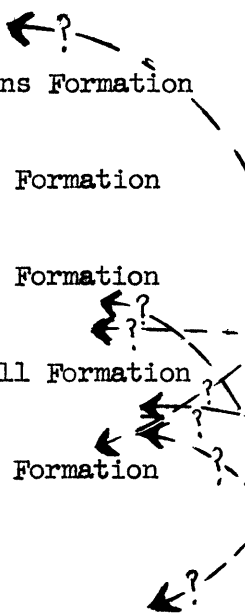
Due to the correlation of the New Hampshire section of the Bronson Hill Anticline with the Connecticut section, the Stratigraphic Column given in Table 1.1 is probably valid for all but the Maromas Granite Gneiss, the Glastonbury Gneiss, and the Monson Gneiss. The Maromas and the Glastonbury are post-Middletown, and the

Glastonbury is pre-Great Hill (?) . The Maromas may be post-Collins

Hill (Eaton, written communication), but the relation of the

Glastonbury Gneiss to the Collins Hill Formation can only be specu-

lated due to obliteration of contact effects between them by

metamorphisms.

Considering all these possibilities, Table 1.2 shows a more

realistic stratigraphic column for the area than Table 1.1, but

the obvious conclusion to be reached from examination of either

column is a need for more exhaustive field and petrographic study

and/or use of a more powerful method of investigation.

TABLE 1.2

Stratigraphic Unit	Possible Geologic Age

Pegmatites

Camp Jenkins Formation

Mine Brook Formation   Siluro-Devonian

Great Hill Formation

                        Maromas Gneiss

Collins Hill Formation   Late Ordovician (?)

                Glastonbury Gneiss

Middletown Formation   Ordovician (?)

               Monson Gneiss

CHAPTER TWO - Theory of Rb-Sr Geochronology

Introduction

Rb^{87} decays naturally by beta-minus emission to Sr^{87}, but the decay constant for this reaction is not known precisely. Aldrich et al. (1958) have proposed $\lambda = 1.39$ x 10^{-11} yr^{-1} based on comparison of Rb-Sr age in materials for which the age is known by other absolute techniques. Flynn and Glendenin (1959) and Glendenin (1961) have found a value of $\lambda = 1.47$ x 10^{-11} yr^{-1} by direct counting. However, there is still some uncertainty in the low energy end of the beta spectrum, so that, unless stated otherwise, $\lambda = 1.39$ x $10^{-11} yr^{-1}$ will be used until a firm value is established.

Although all elements are radiogenic, the only Sr isotope which shows any variation is Sr^{87} due to the Rb^{87} decay with a measurable half-life; and Sr^{84}, Sr^{86}, and Sr^{88} are constant in abundance within limits of current experimental techniques. The Rb^{87}-Sr^{87} method of age determination is applicable to many geologic problems where other absolute age techniques have difficulty. For example, the K^{40}-Ca^{40} method is often limited in use because of the great abundance of common Ca, the K^{40}-Ar^{40} method is limited because of Ar^{40} diffusion during diagenesis and/or metamorphic events, and the $(U^{238}$-$Pb^{206})$ $(U^{235}$-$Pb^{207})(Th^{232}$-$Pb^{208})$ methods are limited because (a) U, Pb, Th are not common rock-forming constituents, and (b) U and Pb often show

similar geochemical trends in different rock types (e.g. Pb/U ratio approximately constant). Rb and Sr, however, are strongly differentiated from each other during many natural processes, as Rb is enriched in alkali members of a differentiated series whereas Sr will be enriched in alkaline members. This geochemical dissimilarity allows investigation of a great many geologic problems providing an accurate model is applied. These models will be discussed below.

Commonly Used Formulae for Rb-Sr Age Dating

The basic equation in this case is:

$$^{*}Sr^{87} = Rb^{87}(e^{\lambda t} - 1) \tag{2.01}$$

where $^{*}Sr^{87}$ is the number of daughter atoms at time, t, and Rb^{87} the number of parent atoms at time, t, and λ is the decay constant. In any system containing non-radiogenic Sr, we have:

$$Sr^{87} = Sr_{o}^{87} + Rb^{87} (e^{\lambda t} - 1) \tag{2.02}$$

which is entirely rigorous. For convenience in measurement, dividing each term by the abundance of stable Sr^{86} yields:

$$(Sr^{87}/Sr^{86}) = (Sr^{87}/Sr^{86})_{o} + (Rb^{87}/Sr^{86})(e^{\lambda t}-1) \tag{2.03}$$

but $e^{\lambda t} -1 \cong t$ when $\lambda t \ll 1$, so Equation (2.03) becomes:

$$(Sr^{87}/Sr^{86}) = (Sr^{87}/Sr^{86})_o + (Rb^{87}/Sr^{86})\lambda t \qquad (2.04)$$

Application of Equation (2.04) results in a maximum error in age of 2.1 per cent for $t = 3.0$ b.y. and 3.4 per cent for $t = 4.5$ b.y. due to the logarithmic approximation involved. Compston and Jeffery (1961) propose use of a function $\theta = \lambda t$ to eliminate this departure from linearity. To show this, let us re-write Equation (2.04) as:

$$\theta = \frac{(Sr^{87}/Sr^{86}) - (Sr^{87}/Sr^{86})_o}{(Rb^{87}/Sr^{86})} \qquad (2.05)$$

and the function θ is very interesting, because from Equation (2.01) it is obvious that $\theta = {}^{*}Sr^{87}/Rb^{87}$ also, which gives a measure of Rb enrichment or depletion relative to Sr. Nicolaysen (1961) has proposed usage of (Sr^{87}/Sr^{86}) as ordinate plotted against (Rb^{87}/Sr^{86}) as abcissa, which defines a straight line known as the isochron, and all samples of equal age and initial (Sr^{87}/Sr^{86}) ratio will fall on this isochron. The age represented by the isochron is obtained by dividing the tangent of the angle between the isochron and a line parallel to the abcissa by λ. The method is quick and accurate for this investigation, and is especially convenient for accurate determination of the initial (Sr^{87}/Sr^{86}) ratio, which is of extreme importance in most cases. The (Rb^{87}/Sr^{86}) ratio is an atomic ratio and not measured directly, but may be calculated from the measured weight

ratio by the relation:

$$(Rb^{87}/Sr^{86})_{at.} = k(Rb/Sr)_{wt.} \qquad (2.06)$$

where k is given by

$$k = \frac{(At.\ Wt.\ Sr)\ (Rb^{87}/Rb)_{at.}}{(At.\ Wt.\ Rb)\ (Sr^{86}/Sr)_{at.}} \qquad (2.07)$$

but only the terms involving Rb are constant for all cases, as the variation in Sr^{87} due to $*Sr^{87}$ results in different atomic weights and $(Sr^{86}/Sr)_{at.}$ fractions for the Sr in every sample. Figure 2.01 shows the variation of k as $*Sr^{87}$ increases in a system. Equation (2.07) should then be more properly written as:

$$k = (0.003255)\ (At.\ Wt.\ Sr)/(Sr^{86}/Sr)_{at.} \qquad (2.08)$$

and this Equation (2.04) may then be written for a solution of t as:

$$t = \frac{(Sr^{87}/Sr^{86}) - (Sr^{87}/Sr^{86})}{(Rb/Sr)_{wt.} \quad k} \qquad (2.09)$$

Importance of the Initial (Sr^{87}/Sr^{86}) Ratio

General

A value of $Sr(87/86)$ initial = 0.71 is commonly used in either Equations (2.04) or (2.09) when the graphical method is not employed. For samples with very high $Sr(87/86)$ ratios this value is approximately valid, but may lead to serious errors for samples in which

Figure 2.01

$Rb^{87}/Sr^{86} = (Rb/Sr)_{wt.} k$

where $k = 0.003255$(at.wt. Sr/at. frac. Sr^{86})

and $k = f(Sr^{87}/Sr^{86})$
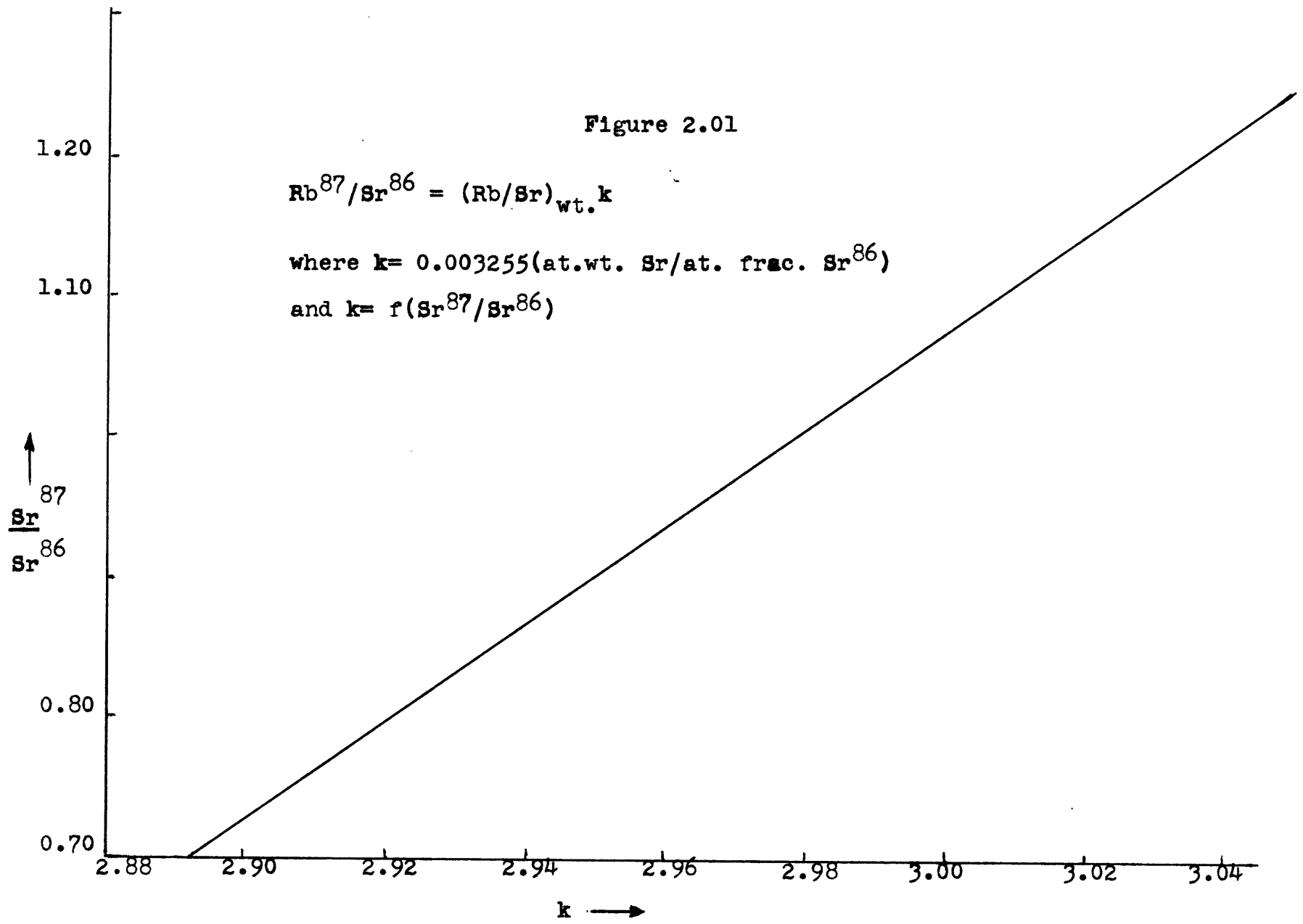
the $Sr(87/86)$ ratio is relatively close to 0.71. For example, let us

consider three samples from the same original reservoir of an equal

$Sr(87/86)$ ratio = R_i but with different $(Rb/Sr)_{wt.}$ ratios. Now assume

these samples to be removed from this reservoir and allowed to remain

as three isolated systems from t_o, time of removal from the reservoir

(e.g. = time of homogenization, time of emplacement, time of deposi-

tion, etc.). After t m.y., the span from t_o to now, the three samples

will define an isochron (using the Nicolaysen, op. cit., coordinates)

as shown in Figure 2.02. Let us now consider the three cases (1)

R_i = 0.71, (2) $R_i > 0.71$, and (3) $R_i < 0.71$. Case (1) shows that

$t_A = t_B = t_C$, but Case (2) indicates the apparent ages $t_A > t_B > t_C$,

and Case (3) the apparent ages $t_A < t_B < t_C$. These relations are shown

in Figures 2.02, 20.3, and 2.04. The point of emphasis in the above

discussion is the importance of the accurate determination of the ini-

tial $Sr(87/86)$ ratio by multiple analyses on the same system rather

than by assuming the value 0.71. This is particularly true in samples

of low $Sr(87/86)$ ratios and low $(Rb/Sr)_{wt.}$ ratios but of a relatively

old age (e.g. Cretaceous or older for most cases).

Figure 2.02
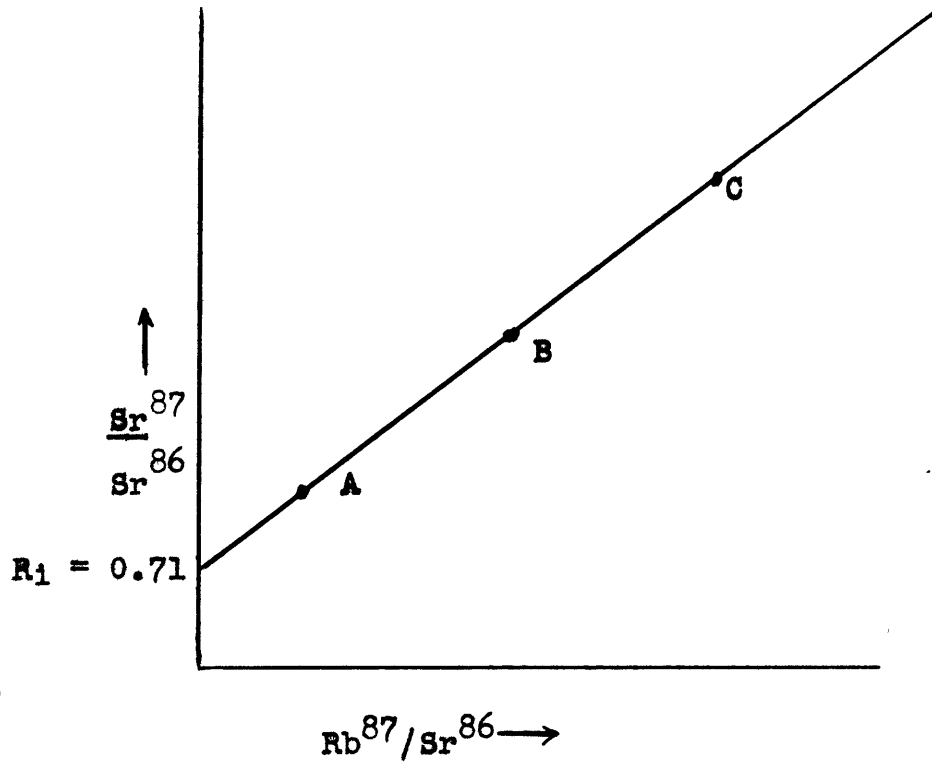
Figure 2.03
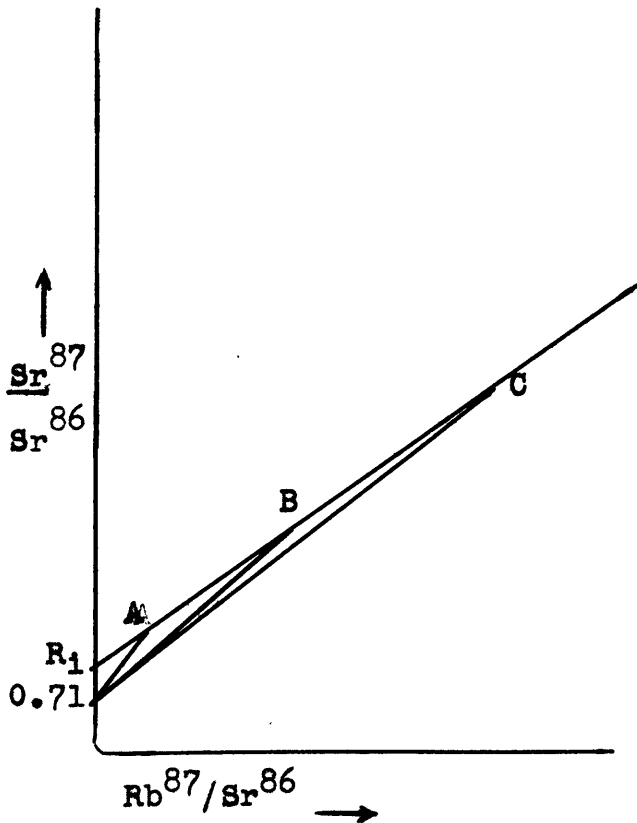
Figure 2.04
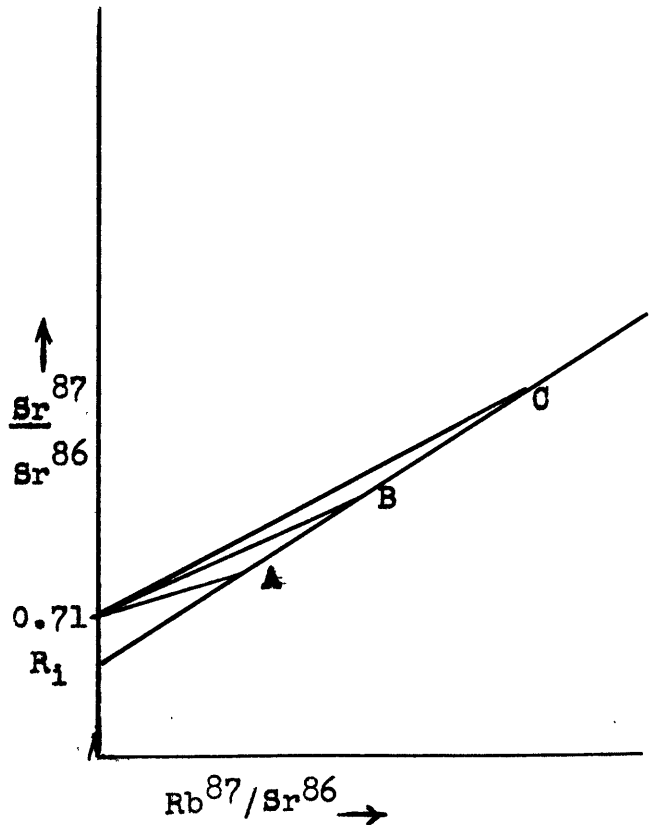
Initial Sr(87/86) Ratios in Various Reservoirs

The terminology introduced by Hurley et al. (1962) will be used

in this section. This includes the following definitions:

"Basement- The continental crystalline rocks presently accesible
to sampling or to secure inference as to composition, i.e., the
top 5-10 kms. of the continents as a minimum, excluding the sedi-
mentary veneers.

Sial- Material with the average composition of the basement, i.e., with
greater proportions of alkalis, silica, and alumina than basalt or the
mantle.

Subsialic Source Region- The source, at some time or other, of sial by
differentiation with enrichment of the Rb content and of the content
of other alkalies, silica, alumina, etc. Its composition is not di-
rectly observable. Its Sr(87/86) ratio (R_m) can be estimated for
past time by measuring the Sr (87/86) ratio in igenous rocks of deep
seated origin of various ages. So far these estimates have indicated
that there is a low degree of variability relative to the Sr(87/86)
variations in the sialic crust (Faure and Hurley, 1962). This source
region is presumably below the M discontinuity, but it could be
either above or below as long as its composition is no less mafic than
basalt.

Primary Age- Time since the material developed a greater Rb/Sr ratio,
and so the beginning of a greater Sr(87/86) ratio, than that in the
source region, by differentiation, metasomatism, or other processes,
i.e., first became part of the sialic crust. Gradual increments of
Rb by repeated reworking are treated as a weighted average over the
time span involved.

Geologic Age- Age of emplacement of material in its present site,
structural form, or degree of metamorphism. For igneous rocks it is
time of intrusion or extrusion; for sediments, time of deposition;
for metamorphic rocks, time of metamorphism or metasomatism. It is
determined by geological relationships or age measurements by the
best of the radioactivity measurements on single minerals."

(I) Rb and Sr in the Subsialic Source Region

Gast (1960) and Faure (1961) have independently arrived at an

initial Sr(87/86) ratio for the subsialic source material equal to

0.708, based on the analyses of continental and oceanic basalts; presumed to have been derived from near the M discontinuity. The probable limits of this 0.708 value are 0.705 to 0.710 (Faure, 1961). Hurley et al. (1960) also report initial $Sr(87/86)$ ratios within these limits for other igneous rocks of presumed deep-seated origins. The absolute value of 0.708 is not meant to be interpreted as an infallible number for the subsialic source region, but rather as being typical of values from this region.

The $(Rb/Sr)_{wt.}$ ratio of the subsialic source region is estimated as approximately less than 0.1 from the recent data presented in Faure (1961) and in Hurley et al. (1962). While more analyses are needed to make a more accurate estimate of this Rb/Sr ratio, the present data are sufficient to show that the ratio is very low and thus the $Sr(87/86)$ ratio of this region is not increasing at any appreciable rate.

(II) Rb and Sr in the Sialic Crust

Gast (1960) has estimated the average Rb/Sr ratio of the sialic crust to be 0.33, and Faure (1961) has estimated the same ratio to be 0.25. Both of these estimates are well above the maximum 0.1 ratio taken to be indicative of the near-mantle region.

Faure and Hurley (1963) estimate that the Rb/Sr ratio may be 3- or even 5-fold greater in the crust than in the mantle. The

source of this enrichment must ultimately lie in the mantle, and suggests cumulation over long periods of time with subsequent reworking of material derived from the mantle.

Rocks which have been derived from the sialic crust (e.g. acid differentiates, sediments, etc.) would normally be expected to have a higher initial $Sr(87/86)$ ratio than the near-mantle derived because of the excess of Rb in the system. However, evidence has been presented for rocks presumably derived from the sialic crust (e.g. granites, granodiorites, etc.) which show initial $Sr(87/86)$ ratios close to the basalt range, 0.708 ± 0.002. Sedimentary rocks present more of a problem, but it is probable that the initial $Sr(87/86)$ ratio at the time of deposition can be closely approximated by the ratio in sea water due to the incorporation of sea water Sr into the non-clastic material of the aggregate sediment. This requires that the clastic material not have too great a $Sr(87/86)$ ratio and thus infers lack of a great primary age at the time of sedimentation. K-bearing phases are generally more resistant to weathering than Ca-bearing phases, and a higher $Sr(87/86)$ ratio than that in sea water may result. However, it is known that K is commonly released during the weathering cycle, and this may well be the case for Rb and some $*Sr^{87}$ due to their occupancy in K-sites in the primary phase. In addition, the contribution of Sr

in K-bearing phases to the total system is small. By consideration
of the above arguments, Hurley et al. (op. cit.) have suggested a
value for sea water of 0.712, and have also estimated the initial
Sr(87/86) ratio on rocks derived from the sialic basement includes
both re-worked crustal material and material derived from the sub-
sialic source region. Due to uncertainties in the theoretical
treatment, Hurley et al. (op. cit.) state that:

"The reworked sial must be very low in abundance if it is of great
age at the time of incorporation, and conversely, if it is young at
the time of incorporation it can be a major proportion of the newly
formed basement."

The authors suggest that the second of these statements is more
probable, and that therefore much of the newly incorporated sialic
material cannot have gone through an extensive length of time
(e.g. greater than 400-500 m.y. maximum) between original formation
and time of sedimentation.

The Whole-Rock Rb-Sr Method

Two fundamental assumptions are needed for use of the whole-
rock method; they are (1) the megasystem considered (e.g. the en-
tire body of rock or the formation) has remained closed with respect

to gain or loss of both Rb and Sr since time of formation, and (2)
the megasystem was homogenous with respect to Sr(87/86) at time of
formation. Any whole-rock sample within the megasystem which is
sufficiently large so that it may be considered closed to gain or
loss of Rb and Sr may be referred to as a local (closed) system. The
size required for a whole-rock sample to represent a truly closed
system varies from megasystem to megasystem, and there is no safe
empirical rule to apply in field sampling of such megasystems.
However, based on the work of Phinney (1959) and others, a sample
with smallest mean diameter equal or greater than ten times the
mean diameter of the largest mineral grain within the sample is
probably a safe working limit for most fine- to medium-grained
samples. The reason for selecting such an apparently large sample
is due to the possibility of intergranular diffusion even in cases
where no metamorphism has occurred. Thus a Rb-rich grain could
lose $*Sr^{87}$ along a grain boundary and then be separated from the
adjoining grain such that neither represents a closed system;
but if the sample selected is sufficiently large there is an equal
probability of Sr gain and loss along the entire boundary of the
local system. Several such local systems (e.g. Figure 2.02) will
define the whole-rock isochron and in turn allow the initial

Sr(87/86) ratio to be determined by extrapolation.

Theoretical Models

(I) Unmetamorphosed Closed Megasystem and Local Systems

Natural examples of this type are intrusives and volcanics. A
suite of whole-rock samples of different Rb/Sr ratios will define
an isochron as shown in Figure 2.05a, and this isochron will also
be unique for any mineral separate from any whole-rock. Figure
2.05b shows the growth curves (development curves) for the samples
which define the isochron in Figure 2.05a. In Figure 2.05b it is
shown that all curves intersect R_i at t_o. This greatly simplified
model dates the time at which the megasystem was homogenous, that
is, the time at which the Sr(87/86) ratio = R_i in any local system.
This is very easy to envisage in a melt, for example. The value
of the initial Sr(87/86) ratio gives some idea of the material
before it was homogenous.

(II) Singly-Metamorphosed Closed Megasystem

(A) Complete Re-distribution of $^*Sr^{87}$ in a Local System

The whole-rock isochron for such a case is shown in Figure
2.06a and is similar to Figure 2.05a, but the growth curves shown in

Figure 2.05a
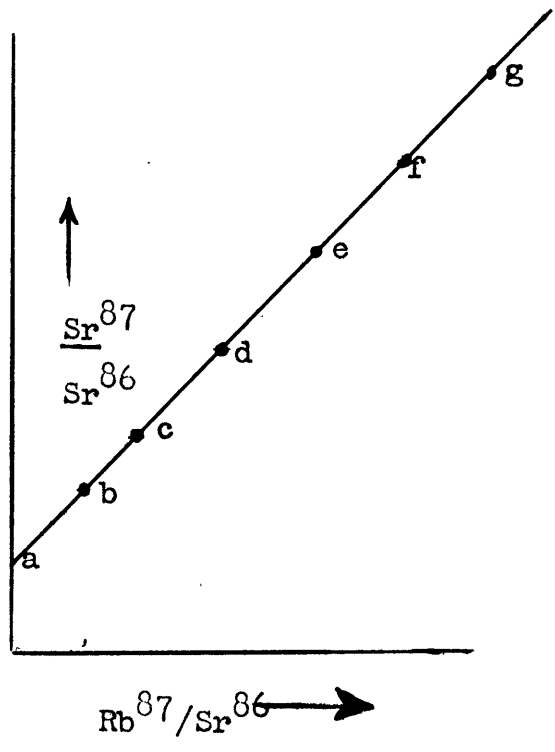
Figure 2.05b
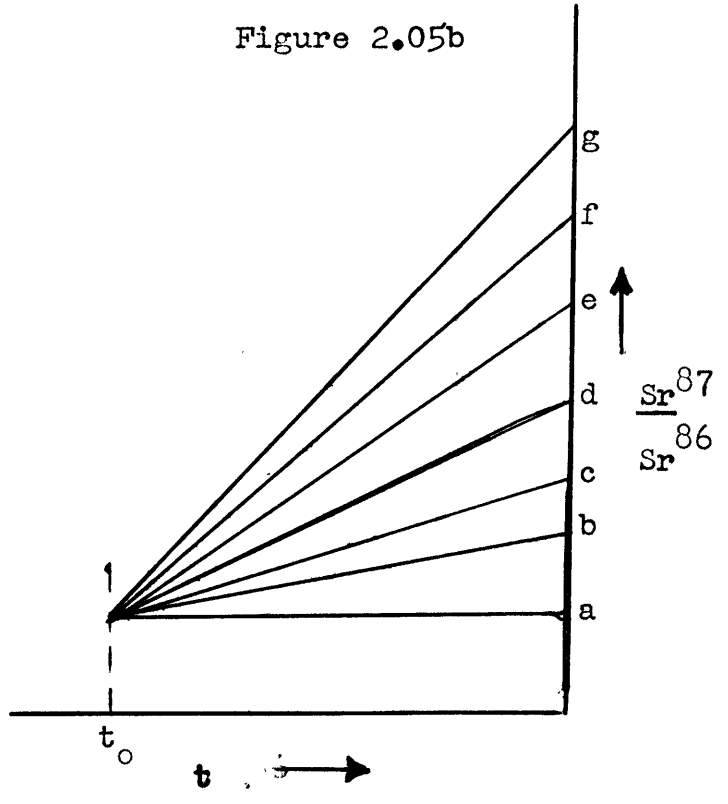
Figure 2.06a
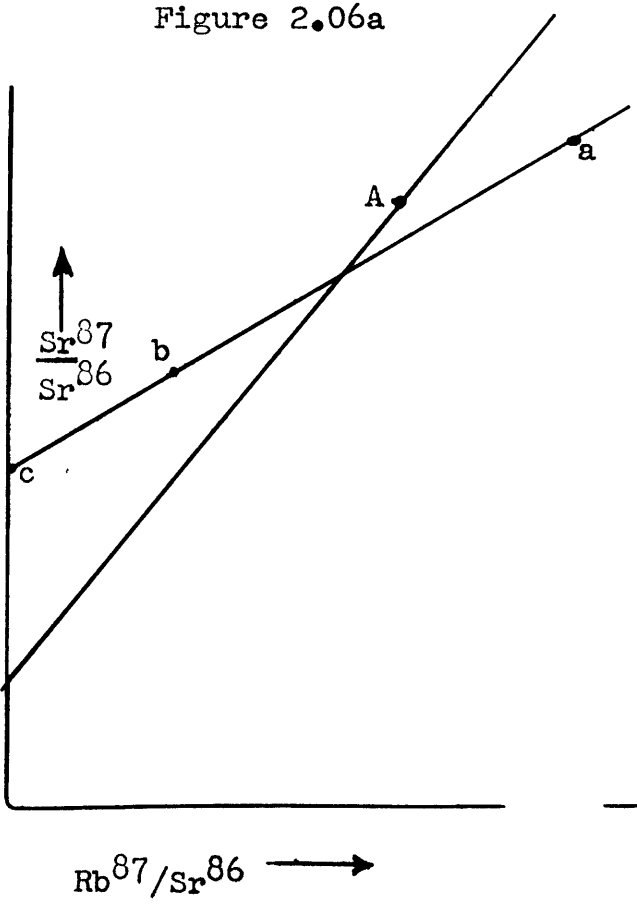
Figure 2.06b
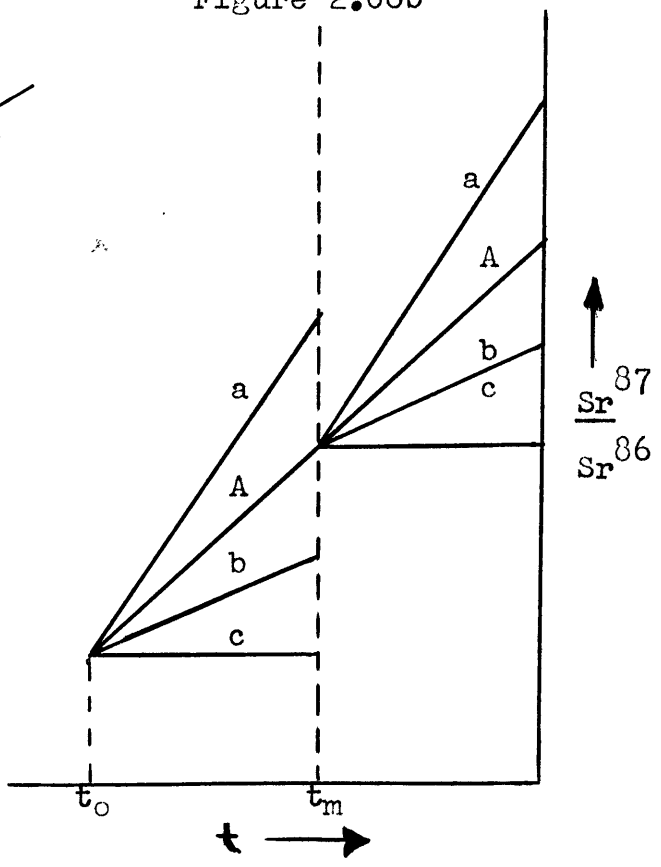
Figure 2.06b for one whole-rock and three of its constituent minerals is different from Figure 2.05b. This is due to the complete homogenization of the $Sr(87/86)$ ratio in the closed local system at the time of metamorphism, among the various minerals within the local system. The initial $Sr(87/86)$ ratio defined by the mineral isochron, R_{im}, is significantly higher than R_i. Figure 2.06b shows that the whole-rock is unaffected by the metamorphism. It is again evident that, for the minerals a and b in whole-rock A, that use of any other initial $Sr(87/86)$ ratio than R_{im} will result in two very different ages. For example, if R_i is used, then $t_b \gg t_A > t_a$; and failure to consider redistribution of $^*Sr^{87}$ and the usage of "normal" $Sr(87/86) = 0.71$ leads to anomalous results.

(B) Incomplete Re-distribution of $^*Sr^{87}$ in a Local System

In this case, the whole-rock isochron is again unaffected and similar to Figures 2.05a and 2.06a, but the minerals from any local system will probably not define an isochron. Figure 2.07a shows the apparent mineral isochrons which could be constructed from any two mineral points which would yield false ages. This emphasizes the fact that mineral isochrons defined by only two

Figure 2.07a

Figure 2.07b
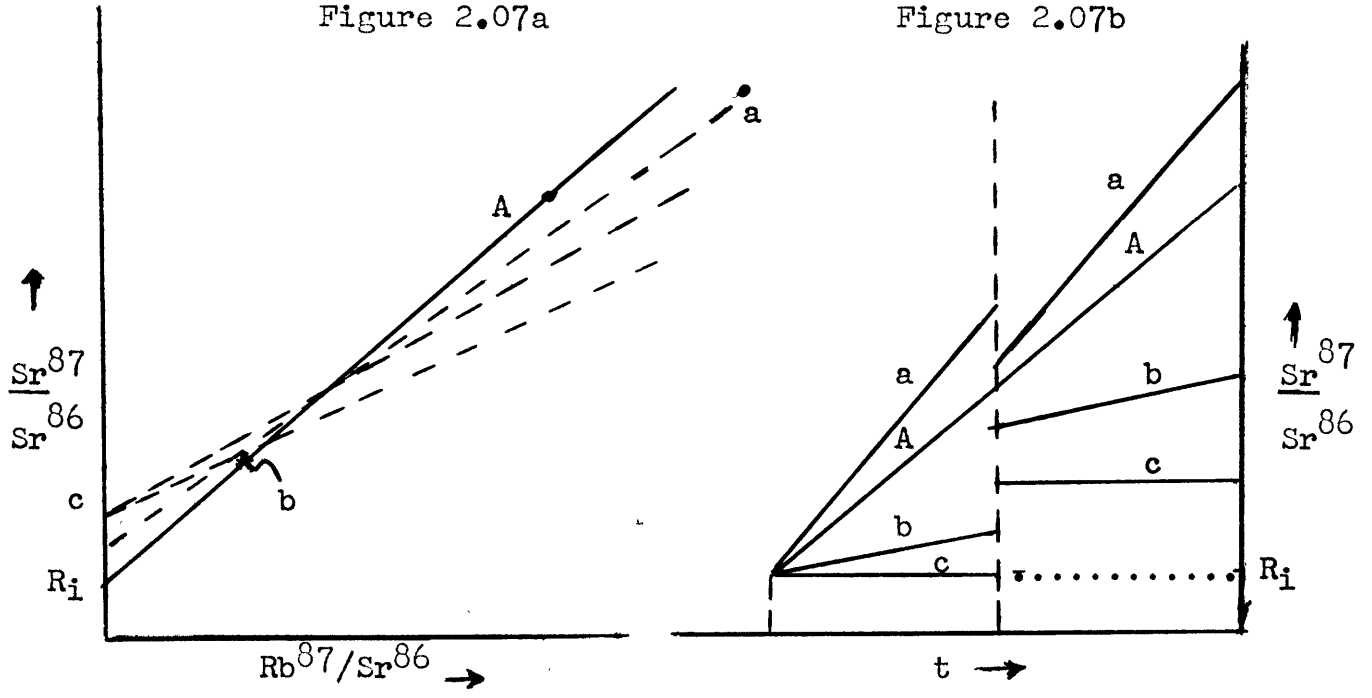
Figure 2.08
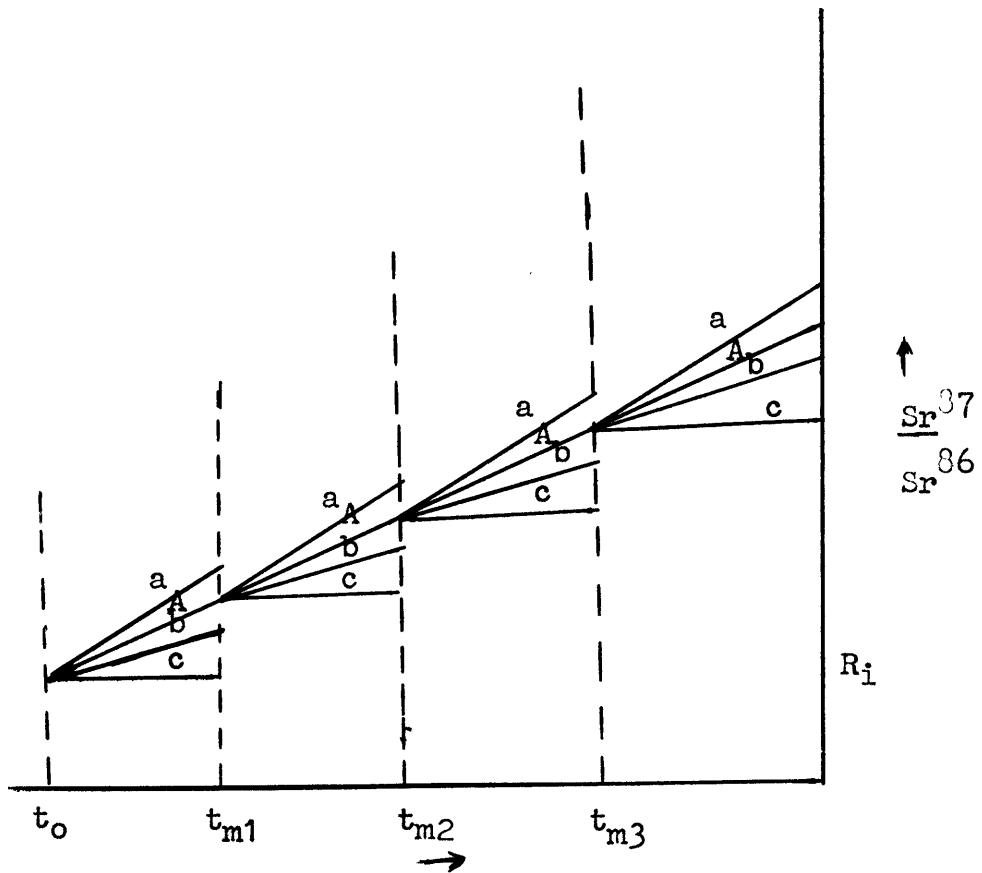
points, unless substantiated by K-Ar or other absolute means, may
give a false age of metamorphism; and at least three points may be
necessary to define an isochron for any one local system. If
several such local systems are analyzed, then a test for accuracy for
any one mineral isochron can be made by checking the parallelism with
the other mineral isochrons.

III Polymetamorphosed Closed Megasystems

In this case the whole-rock method still allows determination
of the original time of emplacement as the subsequent metamorphisms
have caused redistribution of $^{*}Sr^{87}$ within the local systems only,
and the degree of completion of redistribution of $^{*}Sr^{87}$ within any
local system does not affect the closure of the local system. Let
us assume a reservoir of R_i at t_o which has undergone three sub-
sequent metamorphisms. Figure 2.08 shows the growth development
curves for the example three minerals, assuming that Case (II-A)
holds for each metamorphic event, although only the conditions for
(II-A) need hold at t_{m3}. in order than the age of the last meta-
morphism be obtained.

(IV) Continuously Cooling Megasystem

Consider now an intrusion into an older host rock. Case (I) is an ideal model for closure of the megasystem after time of emplacement; but does not consider the possibility that the cooling rate can affect the distribution of $^*Sr^{87}$ in any local system. The possibility exists that the intrusive megasystem may remain at a high temperature after initial emplacement such that crystallizing minerals will lose $^*Sr^{87}$ upon generation until the intrusive megasystem rises and cools. This may be thought of as a continuous process of diffusion of $^*Sr^{87}$ during the cooling interval such that apparent anomalous mineral ages result. The true initial $Sr(87/86)$ ratio is again given by the whole-rock isochron because of the closure of each local system. However, observation of natural systems shows that the minerals of the intrusive commonly yield the same age as the minerals from the host rock despite lack of any metamorphic event. This implies that the intrusive and the surrounding rock remained at a significantly high temperature for some time after initial emplacement. Consider now the probable equation for diffusion of $^*Sr^{87}$ in a spherical medium:

$$D/a^2 = D_o/a^2 \, \exp(-E/RT)$$

where a is the radius of the region in which diffusion occurs, and E is the activation energy. E may vary between 30 to 70 kcal/mole according to recent experimental work, but there is a break between loss and retention of daughter $^*Sr^{87}$ in the range of D/a^2 from 10^{-17} to 10^{-19} which implies a small range of T (e.g. less than 50° C), and Rb-rich minerals would lose $^*Sr^{87}$ down to a certain T (controlled by E) during the cooling process and then retain $^*Sr^{87}$. Figure 2.09 shows that by plotting t against Θ ($= ^*Sr^{87}/Rb^{87}$) the apparent discrepancy is normalized. Further application of this approach implies that the growth curves shown in Figures 2.06b, 2.07b, and 2.08 probably also represent continuous changes near any t_m.

Figure 2.10

$$\frac{Sr^{87}}{Sr^{86}} \uparrow$$

$$Rb^{87}/Sr^{86} \longrightarrow$$

Figure 2.09

Whole-rock

mineral A

mineral C

mineral B

$$*\frac{Sr^{87}}{Rb^{87}} \uparrow$$

$$t \longrightarrow$$
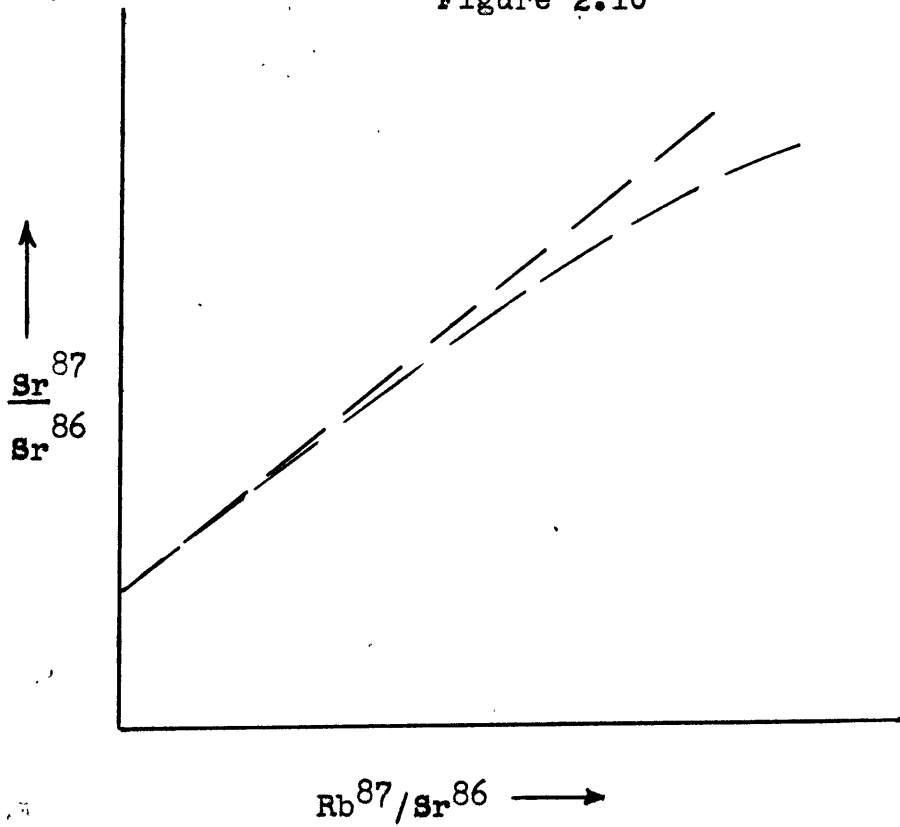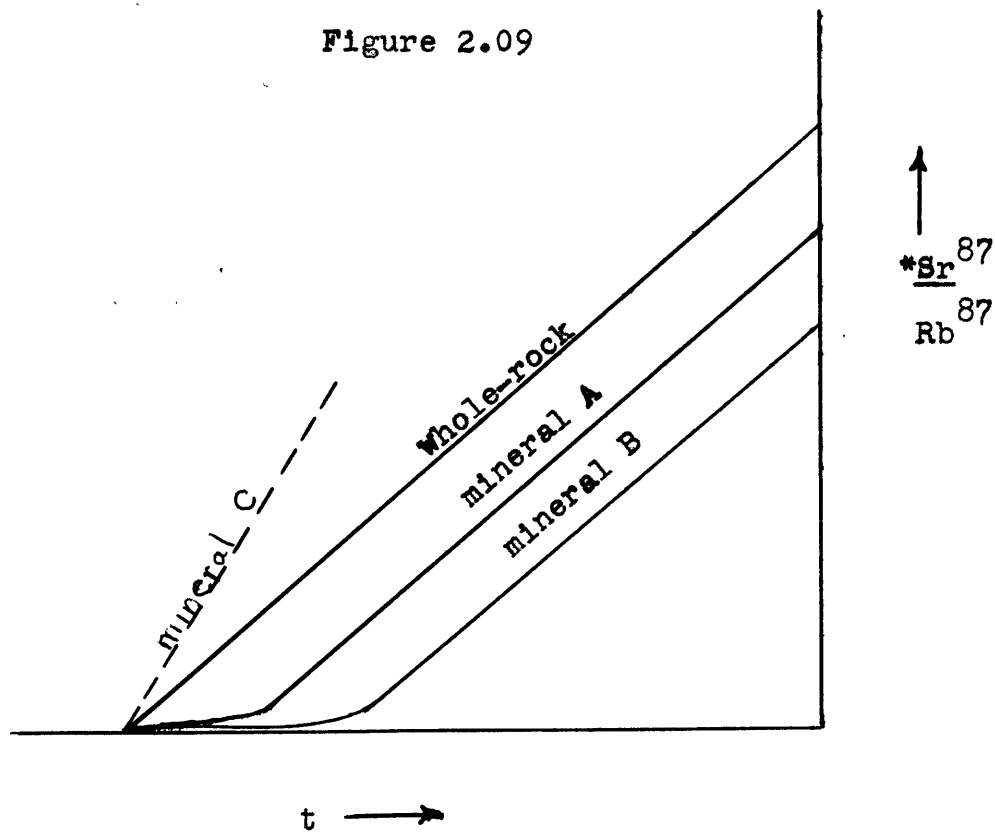
V Alkali-metasomatism in an Open Megasystem

The basic laws of geochemistry indicate that any alkali
metasomatism will have the effect of enriching the megasystem in
Rb, and that this enrichment will probably take place in or near
Rb-rich sites relative to Rb-poor (e.g. Ca-rich) sites. In any
natural system, this will have the effect of causing an isochron to
be no longer a straight line, but rather will be concave downward as
$(Rb/Sr)_{wt.}$ increases due to the added Rb. This is shown in Figure
2.10. A proportionate amount of Rb added to Rb/Sr-varying systems
such that the resultant isochron would be displaced to the right but
still linear is unlikely. That alkali metasomatism could cause an
increase in Rb in Rb-poor samples is not consistent with geochemical
partitioning of the alkali and alkaline-earth elements.

VI Sedimentary Megasystems

The primary problem of sedimentary (and metasedimentary)
systems is the probable lack of homogenization of Sr isotopes at
the time of deposition; because detrital material will have various
$Sr(87/86)$ ratios whereas precipitated material will have the
$Sr(87/86)$ ratio of the sea water of the environment. The $Sr(87/86)$
ratio of the detrital grains will probably be higher than that of
sea water as K- (and Rb-) bearing phases are more resistant to

weathering than Ca-bearing phases. Whitney (1962) states (p.42)

"The presence of these two kinds of Sr, in varying proportions, will

cause a difference of the initial Sr(87/86) ratio in samples of the

same age. This makes impossible a direct calculation of an age from

the isochron diagram. The situation is further complicated by the

fact that varying amounts of Rb will be added to the detrital material

by adsorption or fixation." If all the Rb and Sr in a sediment are

authigenic, then a true isochron age will result, but otherwise the

"age" will be too old because of the inherited high Sr(87/86) ratio

of the detrital material. Whitney (1962) and Compston and Pidgeon

(1962) discuss this problem in detail. The K-Ar studies on various

size fractions in shales by Hurley et al. (1962) and Evernden et al.

(1961) indicate that the smallest size fractions are largely authi-

genic, and thus are also probably authigenic with respect to Rb

and Sr.

(VII) Models for the Origin of Pegmatites

(A) Magmatic Injection from an Unexposed Source Material

This model is simple if there is no subsequent metamorphism

after the time of emplacement. The pegmatite minerals will define

an isochron that may parallel that of the host rock mineral isochron,

but will not be parallel to the host rock whole-rock isochron.

The initial $Sr(87/86)$ ratio defined by the pegmatite mineral isochron may or may not be higher than that of the host rock dependent on the source of the latter. If the pegmatitic material is derived from deep in the crust (near the subsialic source region) the initial $Sr(87/86)$ ratio will be low (near 0.710), but if derived from material which has undergone a significant pre-history in the sialic crust before injection the initial $Sr(87/86)$ ratio will be greater than 0.710, and probably greater than that of even a sedimentary host. Relations for a hypothetical case are shown in Figure 2.11.

, (B) In Situ Diffusional Theory

This theory requires that all of the pegmatitic material has diffused from the surrounding wall rocks, with material continually diffusing into the pegmatite as regional forces allow cavities to occur. Host rock facies nearest the pegmatite should show the greatest effect of this diffusion unless the megasystem is open, that is, if an equilibrium distribution of Sr^{87} is achieved. In this case, host rock whole-rock and mineral samples, pegmatite minerals will define a unique isochron with a high initial $Sr(87/86)$ ratio.

(C) Injection of Re-mobilized Material

This model applies to pegmatites which have been injected
from a homogeneous source material, but does not specify how the
source material developed. Thus both partial fusion of pre-
existing rocks, or accumulation of material by secretion may account
for the source. It also does not specify the mechanism of injection,
but does require that there be no relationship with the enclosing
rocks in the immediate vicinity. The necessarily high initial
$Sr(87/86)$ ratio (e.g. because of a significant pre-history in the
sialic crust) distinguishes this case from the model of Case (VII-A).
The possibility exists that such a pegmatite may originate by partial
fusion of rock similar to its present host rock, but this would only
affect the R_i of the pegmatite and not that of the country rock.

Figure   2.11
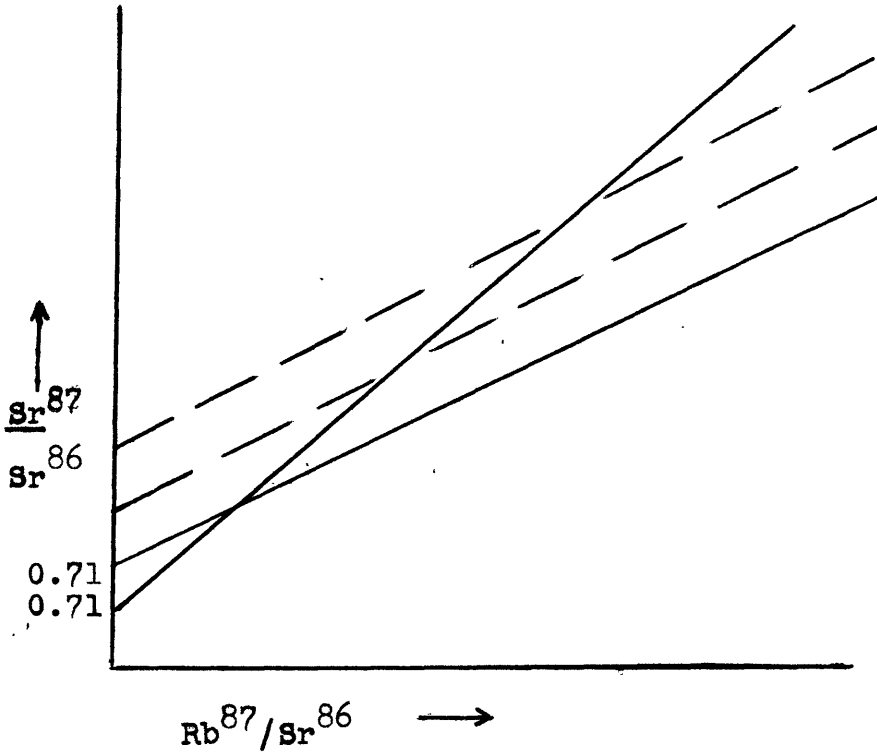
Figure 2.13
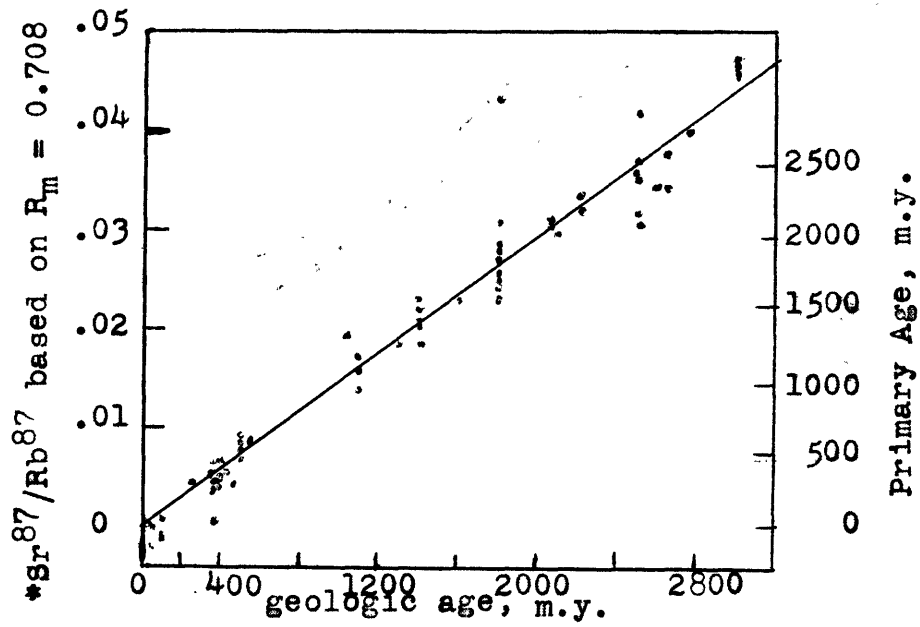
Radiogenic Sr^{87}/Rb^{87} in Whole
Rocks vs. Geologic Age

after Hurley et al (1962)

(VIII) Continually Homogenizing Source

Consider now a magma chamber or some other type of reservoir in which material is removed periodically, and that the source material re-homogenizes after after any such removal of material. Such a case may be represented, say, from successive lava flows of different composition from the same vent; or by successive intrusions from the same parent magma chamber. Figure 2.12 shows the predicted features for such a case, and it is noted that the initial $Sr(87/86)$ ratio of each periodic removal of material from the parent source increases because of the continual re-homogenization.

Figure 2.12

$t_A > t_B > t_C$

$R_C > R_B > R_A$
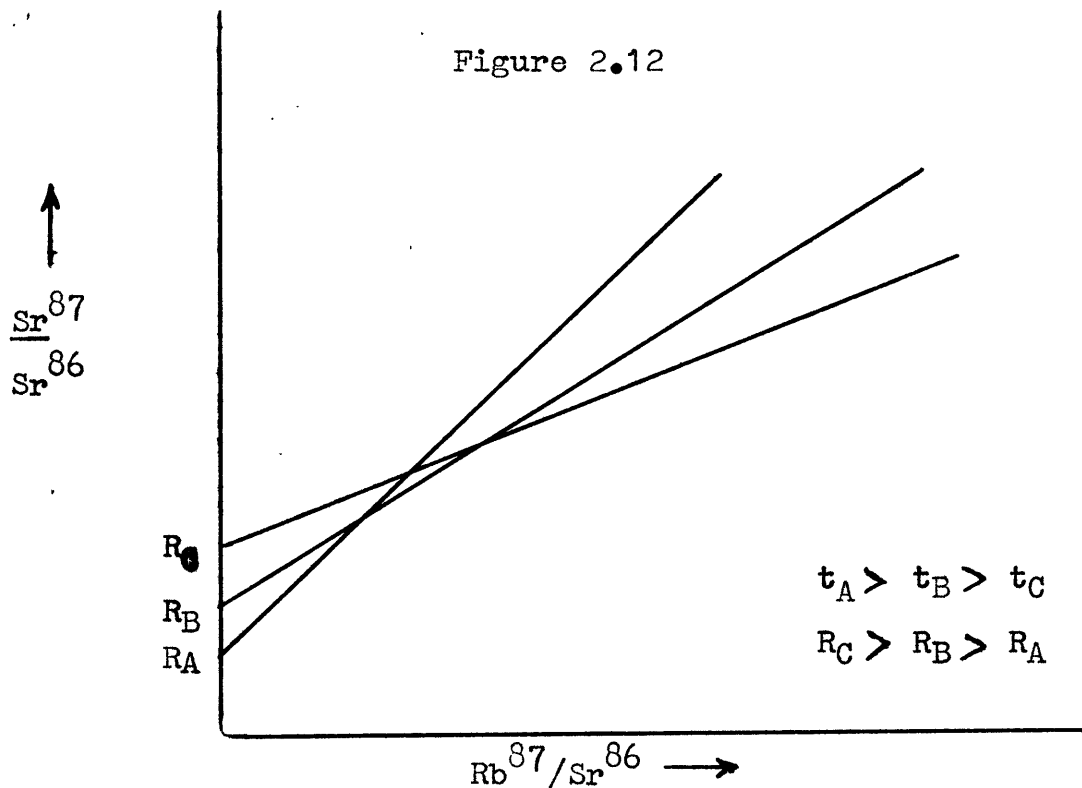
Relation of the Sialic Crust to the Subsialic Source Region

If most of the sial had been derived from the subsial during one great episode of differentiation at a very old age of greater than 3000 m.y. ago, then subsequent processes would show no close association of primary age and geologic age. For example, a reworked section would yield a very high initial $Sr(87/86)$ ratio (e.g. 0.720 to 0.730 or greater if reworked Precambrian material). These possible high values are inconsistent with measurements on some of the more recently formed sialic components, which commonly show initial $Sr(87/86)$ ratios near 0.708. In addition, Hurley et al. (1962) show that a close relationship between primary age and geologic age exists. Figure 2.12 is a reproduction of their (ibid.) Figure 1, in which $^*Sr^{87}/Rb^{87}$ is plotted versus geologic age. $^*Sr^{87}/Rb^{87}$ is used as the ordinate because "this ratio gives a measure of the aggregate history of Rb enrichment relative to Sr, as it has increased over and above the Rb/Sr ratio in the subsialic source region." By thus using Rb enrichment relative to Sr as a tracer, it suggests continual evolution of sialic basement material from the subsialic source region throughout geologic time such that Primary Age is only slightly greater than Geologic Age. A theory requiring one ancient evolution of sialic material and subsequent reworkings to give the variance in geologic

ages observed today should not give the straight line of Figure 2.12, but rather vertical scatter of points about an approximately horizontal line with an extremely high $*Sr^{87}/Rb^{87}$ ratio. As this type of relationship has not definitely been shown, a continual evolution of sial from subsial is logical, because the slope of Figure 2.12 is close to the ideal slope (e.g. within six per cent of $\lambda = 1.47 \times 10^{-11}$ yr^{-1}, used in the construction). The slight deviations from this slope do not alter the main conclusion and are probably due to uncertainties in the distribution of metasediments in the basement. Lanphere et al. (1962) have presented an example in which $*Sr^{87}/Rb^{87}$ is anomalously high relative to a Cretaceous Metamorphic Age; but as the premetamorphic age is Precambrian, this evidence is not in conflict with the foregoing statements, and is interpreted as a redistribution of $*Sr^{87}$ within an open megasystem.

CHAPTER THREE: Experimental Procedures and Errors

Field Sampling

Field sampling is probably one of the most important steps in a successful Rb-Sr analysis, and great care has been taken to insure that representative samples were obtained. For pegmatitic material, fresh in place mineral samples were obtained by grab sampling of carefully selected dump material. Whole-rock samples from the other basement rocks were taken on trends normal to the regional foliation, and of sufficient size to insure that a local system could be assumed (see discussion, page 96, this report). A sample of smallest diameter at least ten times greater than that of the largest mineral diameter was judged to be sufficient. Only fresh material showing no evident sign of weathering was collected, and thin sections were prepared for most of the samples to insure that no introduced alteration products were present.

Sample Preparation

Samples were first run through a coarse jaw crusher, care being taken to collect all material passing through the crusher. This coarse material was then crushed and mixed for ten minutes in a pre-contaminated Pica Blender Mill (Pitchford Scientific Instruments Corporation) which reduced all of the minerals, including micas, to a minus 200 mesh size. When more than one cylinder was required for this grinding, the products were combined and rolled and thoroughly mixed.

The resultant powder was stored in a clean bottle. The cylinders were cleaned by a thorough scrubbing followed by a distilled water rinse and were dried by an acetone rinse.

Rb/Sr Ratio Determination by X-Ray Spectography

$(Rb/Sr)_{wt.}$ ratios have been determined by X-Ray Spectrographic techniques for some samples; and although this analytical method is subject to several sources of error, agreement with samples of previous isotope dilution $(Rb/Sr)_{wt.}$ ratios indicates the accuracy to be ± 5 per cent. One of the main problems in application of this technique is the elimination of the matrix effect, and Hower et al. (1961) list several contributing factors: "(1) Absorption of the incoming (polychromatic) beam, (2) absorption of the outgoing (monochromatic) characteristic radiation of the analysis element, and (3) enhancement of the characteristic radiation of other elements by the characteristic radiation of other elements in the sample or in each other." The last of these criteria may be neglected if there is no concentrated amount of an element with a higher atomic number than that of the analysis elements present (e.g. Rb and Sr); but this is true only if a truly homogenuous matrix is analyzed. Shalgosky (1960) recommends grinding of a sample to minus 200 mesh to eliminate such matrix effects, but this may be an oversimplification because of the possibility of random distribution of particles with abnormal concentrations of either Rb or Sr

or any element which may enhance either. The problem of homogeneity
is best handled by conversion of the analysis powder to another form,
and for Rb and Sr work this is best accomplished by conversion of the
rock powder to a fluoride matrix by slow digestion of the sample in HF.
This insures (a) a greater homogeneity of the sample, and (b) increase
of the intensity of the Rb and Sr due to the elimination of the SiO_2
diluent, which is evaporated as SiF_4.

The intensity ratio of any two elements, a and b, is then
given by:

$$I_r = \frac{f'}{f''} K'$$

where

f = no. atoms of analysis element/total no. atoms

K' = constant which includes fluorescent yield factors
for specific wavelengths of f' and f''.

The $(f'/f'')_{wt.}$ ratio depends on K' matrix variables, and a weight
conversion factor, such that:

$$(Rb/Sr)_{wt.} \doteq (Rb/Sr)_{Int.} K$$

There is no warranted experimental proof that $K \neq f$ (chemical
composition), yet application of a K-value determined by periodic
analysis of a standard during any set of analyses is probably valid

providing the matrices of standard and sample are equivalent. The

G-1 Standard (Westerley Granite) was used as standard during this

investigation, but only after it had been converted to a fluoride

matrix.

The machine used was a Norelco vacuum unit with a Mo target tube

run at 50 Kv and 40 mA, with a topaz analyzing crystal and a 0.004

inch entrance collimator. Fixed-count determinations were accomplished

for Rb and Sr and three background positions for each sample. The

background was measured at $41.00°2\theta$, $38.78°2\theta$, and $36.58°2\theta$; and Sr

was measured at $37.66°2\theta$ and Rb at $39.91°2\theta$. The time (in seconds)

was recorded at each setting, and counts/second was determined for

all positions. A background correction curve was plotted for

counts/second versus $°2\theta$, and the background value at 39.91 (Rb) and

at 37.66 (Sr) were subtracted from the recorded values at these

angles. The background working curves were remarkably uniform with

few exceptions, and these exceptions were re-run.

Prior to refined X-Ray Spectographic or Isotope Dilution

Procedures, samples were run on the Norelco spectograph to give an

estimation of the Rb/Sr ratio. This was accomplished by continuous

rapid scanning in the $°2\theta$ range of 41 to 36. These rapid scans are,

in general, subject to large error, and are also determined on mineral or rock powders, and thus cannot be trusted for fine analytical work.

Table 3.1 shows a comparison of $(Rb/Sr)_{wt.}$ ratios which have been determined by both isotope dilution and by fixed-count X-Ray spectography:

TABLE 3.1

COMPARISON OF $(Rb/Sr)_{wt}$ RATIOS BY ISOTOPE DILUTION AND BY X-RAY SPECTOGRAPHY

(FIXED COUNT)

Sample	$(Rb/Sr)_{I.D.}$	$(Rb/Sr)_{X-Ray}$
R4720a	44.6	43.4
R4791b	1.62	1.55
R5053a	0.82	0.78
R5053c	1.61	1.64
R5056c	0.37	0.34
R5058a	17.4	16.9

Chemistry

Procedure for Isotope Ratios

Pre-ground and mixed samples for isotopic ratio measurements were treated as follows: (1) The stored sample was spread on clean paper and a sample for dissolution taken by either cone and quartering or by random grab sampling, and the former process was always employed for samples with a high (e.g. >5) Rb/Sr ratio. The sample was then transferred to a Pt dish which had been cleaned by boiling 6N HCl (discard) in it followed immediately by washing the dish thoroughly with hot tap water and cleanser, and by successive thorough rinsing with Vycor Distilled 2N HCl, and demineralized H_2O. (2) To the contents of the Pt dish, approximately 10 ml 70 per cent pure reagent $HClO_4$ and then 25 ml pure reagent HF were added under a Perchloric Acid Resistant Chemical Hood. (3) The Pt dish plus contents was then transferred to a hot plate in the hood with the automatic control set to effect rapid evaporation without boiling. This evaporation was completed to near dryness until no obvious perchloric acid fumes were observed over the Pt dish when there was no evident residue. When residue persisted after this step, it was repeated. The assurance of complete volatilization of the HF is monitored by this step. (4) After a short cooling period off the hot plate, an excess of 150 ml demineralized

H_2O was added to the contents of the dish and this was evaporated slowly until a mush of liquid and alkali perchlorate crystals persisted. If the preceding step resulted in a dry residue, it became necessary to add some (a few ml) Vycor Distilled 2N HCl to the dish to insure solution. (5) The contents of the Pt dish were allowed to cool either in the Pt dish or in a clean 100 ml pyrex beaker for at least twelve hours. (6) After cooling, the contents of (5) were then filtered into a clean 100 ml beaker (Filter Paper: Schleicher and Schuell, no. 576, 100 circles/cm). (7) To the filtrate, a few ml of radioactive Sr^{85} Tracer was added until the monitoring scintillation counter registered at least 2-1/2 to 3 times background. The tracer could have been added earlier to insure a complete filtration (pre-Step (5)), but (a) work of Powell (1962) and others has shown the Sr to occur in the filtrate, and (b) the possibility of boiling of Sr^{85}-bearing solutions could conceivably contaminate another's work. (8) The filtrate plus tracer was then diluted to approximately 20 ml with Vycor Distilled 2N HCl and put through a cation exchange column. The sample was placed on the column either by careful pipetting onto the resin surface or by slowly pouring the sample over a glass wool plug above the resin level. It is imperative that the top of the resin (Dowex 50W-X8, cross linked, 200-mesh) is not disturbed during this transfer of sample to column.

(9) The sample in solution was then allowed to infiltrate the resin top and then 25 ml of eluant Vycor Distilled 2N HCl was carefully added, and the walls of the column were carefully washed. This step was repeated after the eluant plus remaining sample had entered the resin.

(10) After the sample was definitely below the resin top by 2 or 3 centimeters, Vycor Distilled 2N HCl was added until the sample had passed through the column. Approximately 500 ml were required to complete this passage for a typical column, but ∿ 450 ml was required for new, short columns, and over 600 for old, packed columns. In all cases, the position of the sample on the column was determined by monitoring with a scintillation counter. (11) When the sample had reached within one inch of the bottom of the column, collection of eluant and/or sample plus eluant was started. To insure clean separation of Sr from Ca and Ba, several beakers were used, with approximately 20 to 50 ml per beaker. However, when the monitoring scintillation counter was able to more rigidly control this recovery, fewer beakers were collected. To insure against any possible isotopic fractionation of the column, beakers were collected immediately before and after the Sr had passed through the column. This effect is probably negligible because previous work has shown that addition of these beakers to any subsequent sample does not alter the other results.

(12) The beakers were then evaporated to dryness and the Sr was concentrated into one beaker. (13) After concentration, the beaker plus sample was diluted with Vycor Distilled 2N HCl and again evaporated to dryness. The sample was either then stored or prepared for the mass spectrometer. (14) For the latter purpose, the sample was dissolved with demineralized H_2O, and then a few small crystals of ammonium oxalate were added. This induced precipitation of Sr (and Ca) oxalate. If the precipitate was extremely small, (e.g. less than 2 or 3 grains) it was evaporated to dryness after addition of 1 or 2 ml of Vycor Distilled HNO_3, and prepared for mass spectrometrical analysis. If the precipitate was larger, then it was washed several times with demineralized H_2O, and the supernatant liquid above the precipitate was removed with a clean glass capillary tube attached to the base of a hypodermic syringe. (15) Either the oxalate precipitate or the nitrate concentrate was then carefully placed in the center of the filament of the mass spectrometer source. Evaporation was aided by passing a small current through the filament. (16) After the sample had been precipitated on the filament, the current was raised momentarily to red heat and then lowered. This step drives off much undesirable excess gas and insures that the sample is firmly placed on the

filament.

Discussion of the Oxalate and the Nitrate Methods

The oxalate method allows for sufficient washing to remove Rb which may be present, but the precipitate does not adhere as well to the filament surface as the direct nitrate precipitate. However, the nitrate method offers greater possibility for contamination by Rb, and, unless great care is taken during the precipitation, the sample commonly will run to the posts and thus contaminate them. The emission of Sr from both methods is equivalent and neither method offers any unique advantage over the other. The oxalate method was employed during this investigation to reduce chances of contamination and because the filament is much easier to clean after an oxalate-mounted run than a nitrate-mounted run. Isotope dilution analyses for Rb were always undertaken by the nitrate method because the filament was always discarded after each run and problems of cleaning were not necessary.

Procedure for Isotope Dilution Analyses

In isotope dilution analysis greater care is needed in sample preparation and weighings because the solutions must be spiked

quantitatively.

(1) After the carefully weighed sample is in the Pt dish, Rb^{87} and/or Sr^{86} spike solutions were added to the dish. The amount of spike added and the concentration of the spike needed were estimated from quick-scan X-Ray Spectographic analysis of the samples. All spikes were delivered from carefully calibrated pipettes. (2) After spiking, the chemical procedure was similar to that used for isotope ratio analysis until (Step 4, page 118) the perchlorate mush was obtained. Most of the Rb is contained in the alkali perchlorate crystals, but the Sr remains in solution. Separation of the Sr was made at this time by decanting off the supernatant liquid containing the Sr from the mush, and by washing the remaining mush with either demineralized water or ethyl acetate and repeating the decantation. To confirm separation of Sr during this step, radioactive Sr^{85} tracer was occasionally added during the previous dissolution and was monitored by the scintillation counter. Ethyl acetate and $HClO_4$ form an explosive combination at any high temperature, and the ethyl acetate must be slowly evaporated over a low temperature hot plate or on the steam bath before proceeding further. Demineralized water presents no such problems, but sodium perchlorate is soluble in H_2O and, for

Na-rich, Rb-poor samples, may result in the Rb being transported with the Sr during the decantation. However, due to the possibility of explosions and possible laboratory contamination, the demineralized water method is to be preferred when possible. (3) The Rb-rich portion was then taken to dryness, fumed, and taken to dryness again after adding a few ml of Vycor Distilled HNO_3. It was then concentrated into a 10 ml or 50 ml beaker and stored until ready to be placed on the filament. (4) The Sr-rich portion was taken to dryness and fumed until no white perchloric acid fumes were noticeable, and was then put into solution with demineralized water. A few ml of Vycor Distilled 2N HCl had to be added to complete solution in some cases. (5) The solution was then allowed to cool, filtered, and radioactive tracer was added to it. The solution was then placed on the exchange column and procedure similar to that for isotope ratio analysis then followed.

Exchange Column Cleaning

The exchange columns were cleaned either by washing with 200 ml of Vycor Distilled 6N HCl followed by 200 ml of Vycor Distilled 2N HCl, or by washing with approximately 1000 ml of Vycor Distilled 2N HCl. Both methods are satisfactory, but the latter procedure has the advantage

in that the life of the column is extended as 6N HCl causes the glass wool plug in the bottom of the column to disintegrate.

Every step in the chemical procedures listed above must be conscientiously and dilligently applied to prevent contamination of the sample under preparation for analysis.

Mass Spectometry

All isotope ratio analyses made during this thesis were run on the mass spectrometer referred to as Snagtooth to eliminate any possible inter-machine deviations, although such effects are probably negligible (see Eighth and Ninth Annual Progress Reports for 1960, 1961, NYO - 3941, 2). Isotope dilution analyses were run on three mass spectrometers (Snagtooth, Iris, Lulu) as the isotope dilution runs do not require the same precision of mass ratio measurement.

Snagtooth is a 6", 60° sector, solid source, single collector mass spectrometer constructed at the Massachusetts Institute of Technology. A model 400 EDA power supply (John Fluke Manufacturing Company, Inc., Seattle) was used to supply ion accelerating voltages of approximately 2100 volts. An AC voltage regulator (Model 500S, Sorenson and Company, Inc., South Norwalk, Connecticut) was used to stabilize the filament current. The ion beam is scanned by a motor-driven automatic magnet sweep and amplified by a vibrating reed electrometer (Model 30, Applied Physics Corporation, Pasadena, California). Tantalum ribbon (Fansteel Metallurgical Corporation, North Chicago, Illinois) of 0.001" x 0.003" dimensions was used as filament material, spot welded to posts in the source.

Pressures of less than 5×10^{-6} mm Hg were obtained during
operation by a Hg diffusion pump of 80 liters/sec. capacity (H. S.
Martin Company, Evanston, Illinois) using a liquid Nitrogen cold
trap, backed by a mechanical fore-pump (Duo-seal Pumps, Welch
Scientific Company, Chicago). A 25 mv full scale, 2 second sweep,
Brown Electronic Strip Chart Recorder (Brown Instrument Company,
Philadelphia) was used to record the amplified ion currents.

Teflon gaskets were used for the vacuum seal in the source, and
an aluminum gasket in the collector. The teflon gasket in the source
is preferable because it (1) gives a good seal, (2) eliminates the
stress on the mass spectrometer tube resulting from strenuous over-
tightening of bolts, (3) can be used for many runs whereas a new Al
gasket must be used for each run, (4) can be loosened or tightened
as necessary to improve the seal, and (5) are easy to machine.

After a vacuum of less than 10^{-4} mm Hg was obtained, usually
after 15 to 20 minutes as measured by an ion gauge (Type DPA 38,
Consolidated Electrodynamics Company, Pasadena) , the ion gauge was
degassed for approximately five minutes. Current was then passed
through the filament and increased until a conditioning temperature
had been obtained, care being taken to keep the pressure less than

2×10^{-5} mm Hg at all times during the raising of the filament current.
For Sr analyses, the settings were approximately 45v, 2.0 to 2.3 amps,
and for Rb, 15-20 v, 1 amp. These settings give temperatures well be-
low those necessary for the emission of Sr and Rb, respectively. For
isotope ratio analyses, the sample was conditioned for at least two to
five hours, and occasionally longer, until the pressure was less than
3×10^{-6} mm Hg. Pressure was monitored to insure against arcing or
erratic emission. By the time adequate Sr peaks were obtained there
generally was no mass 85 peak observable on the 10 mv scale indicating
Rb, but if so, the sample was conditioned further at a higher temperature
that kept the Sr peaks level or growing slowly while the Rb peaks died.
Even when Rb did not present a problem and a working pressure was ob-
tained quickly, conditioning was still found to be necessary because
it helps stabilize the processes involved in thermionic emission and
thus helps develop a better and longer performance during the run.
After conditioning, the filament current was raised until Sr emission
gave peak heights greater than 2-3 inches for measurement and the run
seemed stable. During this thesis, most runs were made on the 30 mv
scale for Sr (87,86) and on the 300 mv scale for Sr (88). The 10 mv
and 100 mv scales were not used, unless sample depletion made it

necessary, due to background noise. However, Powell (1962, p. 132) reports no difference in answer on the Standard $SrCO_3$ using both scale pairs during the same run. Some runs were made on the 100-1000 mv and 300-3000 mv scale pairs, but only when the temperature was in the normal emitting range (and the intensity of the ion beam in these cases was probably due to abundance of sample). Working at higher temperatures was avoided when possible because the sample may vaporize so rapidly that there is no time for a measurement to be made, and the possibility of emitting Sr and/or Rb from cooler parts of the filament is increased. During the run, approximately 72 to 90 scans of the mass 86 through mass 88 range were continuously recorded. This lengthy duration of emission insures a proper set of statistics for a precise measurement of an isotope ratio, as drifting or variation in the ion source and other factors may cause fluctuation in the ion beam. Occasionally fewer than this amount of statistics were obtained because of sample and/or filament failure, and these runs were repeated in most cases.

Sr isotope dilution analyses require less conditioning time and were run at pressures of less than 10^{-5} mm Hg. because only mass 86 and mass 88 are recorded, and thus problems of resolution are greatly reduced and Rb (which may contribute to mass 87) is not a problem. 42

or more continuous scans were recorded for both Sr and Rb isotope dilution analyses.

Rb isotope dilution analyses were made at a lower temperature due to the lower temperature of emission of Rb from the filament. Operating pressures of less than 10^{-5} mm Hg were satisfactory for most runs, but conditioning periods varied from less than thirty minutes to several hours. In the latter cases, the longer conditioning period was necessary because of erratic emission probably due to excess diluents in the sample and sample position on the filament.

Different basic source parts (e.g. box, half plates, plates) were used for isotope dilution analyses and isotope ratio analyses during most of the investigation. It was formerly thought safe to keep all parts used for Rb analyses separated from parts used for Sr analyses, but because of the possibility of contaminating the isotope ratio parts with spike Rb and Sr from the Sr isotope dilution samples this practice was discontinued. The filament was discarded after each Rb analysis, and was cleaned after Sr analyses (isotope dilution and isotope ratio) by increasing the filament current to maximum which resulted in rapid burning off of the Sr. The time for cleaning varies for each sample, and is monitored by scanning the mass 85 through mass 88 range; and is considered clean when no peaks

are observed on the 10 mv scale at a temperature greater than that
reached during the run. Mass 85 and mass 87 commonly appear at the
maximum temperature after the Sr has been burned off because of emis-
sion of Rb from cooler parts of the source, but disappear when the
temperature is lowered. In general, five to seven Sr runs can be
made on the same filament before replacing it. New filaments always
show some Rb upon inspection, and may rarely show Sr also. The fila-
ment is cleaned as described earlier.

It was found to be sufficiently precise and considerably
quicker to record peak heights directly from a lined recorder chart
rather than wait until the end of the run and then construct baselines
and measure each peak with an engineering scale. Baseline by the di-
rect recording method was made as follows: The mass 86 and mass 87
peaks were recorded on the same scale, and the zero of this scale
was adjusted to the zero line on the chart. Due to noise and drift,
baseline was checked often to insure that it remained at the zero
chart position, and when a deviation was found, corrections were ap-
plied to each set of six peaks. The mass 88 peak was recorded on a
higher scale and thus the baseline falls below the zero chart reading.
These peaks were, however, also recorded directly and the distance
below the zero chart position to the true baseline was measured with

an engineering scale and added to the recorded peak height. The baseline for the mass 88 peak is quite stable, and need only be checked at infrequent intervals during the run.

Errors in the Mass Spectrometry

(1) Ion emission

As Mayne (1960) has pointed out, "there is no convenient method of directly stabilizing the ion emission, and it is liable to drift". However, erratic emission may be due to several factors, some of which are: (a) diluents in the sample which evaporate at different rates and alter the ion beam, (b) improper positioning of the sample on the filament such that the main focus of emission varies, (c) filament current too high, causing vaporization so rapid that it cannot be readily measured, (d) reaction between the sample and the filament surface (may occur especially in old filaments) such that the work function of the filament changes and thus changes the efficiency of ionization, (e) filament exhaustion. (a) can be largely prevented by careful chemical procedures, (b) by checking filament alignment in the source and by making sure that the sample is placed directly in the center of the filament, (c) by careful control of current increase and conditioning, (d) and (e) by checking that the amperage

recorded during the previous cleaning process is sufficiently higher than that needed during the run. When erratic emission is still observed after these precautions, a statistical approach is necessary (e.g. 90 or more scans). Possible mass discrimination and fractionation will be discussed later.

(2) Source Alignment

The ion source must be properly aligned because the ion beam must be of constant intensity and be representative of the sample in the source region. Errors in alignment usually result from manual carelessness in spot-welding the filament to the posts (without checking alignment) and improper installation of source parts such that slits are not parallel, etc. When the sample in the source is not aligned properly the run will tend to be erratic because the signal received is not complete, and constant re-focusing during the run is often necessary to obtain even meager statistics.

(3) Peak Shape and Resolution

When the peak measured is flat on top and when resolution between the peaks is equal to baseline, then the height of the peak shape gives

a direct measure of isotopic abundance. However, if the peaks are not flat on top, this indicates that the whole profile of the beam is not viewed, and the resulting sharp peaks must be integrated graphically to measure their total intensity. The sharp peaks may be due to too narrow an exit slit, improper focusing, magnet position, improper sample and/or source alignment, and other factors. To insure that the recorded peak height may be truly indicative of the intensity of the ion beam for a rounded peak, the automatic magnet sweep may be turned off and the mass range scanned by changing the accelerating voltage. If, for a stable emission, the same peak height is reached, then the automatically scanned peaks are probably accurate. Poor resolution between peaks may be caused by several factors, among which are (a) beam broadening due to molecular collisions of gas molecules, (b) too wide a spread in the energy of the ion beam recorded for a single (direction) focusing spectrometer, (c) non-linearity in the detecting circuit (to be discussed). (a) is controlled by running at sufficiently low operating pressures, and (b) by careful alignment and conditioning.

(4) Non-linearities in the Detecting Circuits

It has been observed that the mass range investigated (85-88) commonly shows some type of systematic drift for an individual scan

which is random for a large number of scans. Riley (1961) has

considered this problem and checked the circuit thoroughly with the

following observations:

(i)	Recorder	-	linear to 0.1%
(ii)	V.R.E.	-	Linearity for both feedback line and output voltage better than 0.1 per cent.
(iii)	Input Resistance	-	For a well resolved mass 85 ion beam measured at varying magnitudes, the mean ratio remained constant to within 0.25 per cent over the range 10^{-13} to 8×10^{-12}a. This also included other effects such as fractionation.

The emphasis of this thesis has been on application of results

from the mass spectrometer, and not on the mass spectrometry itself.

It is realized that this approach may lead to serious errors, but,

continuing the approach used by Faure (1961), Powell (1962), Whitney

(1962) and other workers in the laboratory, replication was used to

check precision, and a standard (Eimer and Amend lot no. 492327)

$SrCO_3$ to check the accuracy.

Errors in Measurement

The errors resulting from inaccurate measurements may be either random or systematic, but are probably random over the length of the entire run. These errors may result from improper baseline construction (systematic) for those runs not recorded directly during the run or by baseline drift between zero checks in the direct reading method, as well as by error in engineering scale or chart readings. These errors are best compensated for by double-checking every measurement recorded, especially in the direct reading method.

Precision

The precision (reproducibility) of analyses depends on the random errors involved during the mass spectrometry, and was monitored by replicate analyses on most samples (see Table 3.1). Faure (1961) has suggested that the precision of any single $Sr(87/86)$ ratio is 0.002, and is 0.001 from the mean for replicate analyses.

Absolute Accuracy

The absolute accuracy depends on the total of all the systematic errors affecting a series of measurements, and was monitored during this investigation by periodically analyzing a laboratory standard throughout the course of the work. A $SrCO_3$ Standard (Eimer and Amend lot # 492327) was used, and although the exact isotopic composition is

not known, it is used as a reference standard against which work of
different laboratories may be compared. Table 3.2 shows the results
of the analyses of this standard during the course of this investi-
gation on Snagtooth.

TABLE 3.2

SrCO$_3$ Runs on Snagtooth for the Period 2/11/62 to 11/8/62

date 1962	average Sr(86/88)	average Sr(87/86)	corrected[1] Sr(87/86)	$\bar{E}\%$[2]	no.scans	analyst[3]
2/11	0.1194	0.7117	0.7117	0.05	90	DGB
3/14	0.1200	0.7089	0.7107	0.09	90	WHP
3/28	0.1192	0.7125	0.7116	0.05	92	WHP
5/8	0.1191	0.7094	0.7086	0.07	90	DGB
5/15	0.1196	0.7113	0.7118	0.10	72	DGB
6/15	0.1218	0.7035	0.7106	0.12	96	MLB
6/18	0.1185	0.7104	0.7076	0.05	42	DGB
8/8	0.1207	0.7069	0.7107	0.09	84	MLB
9/12	0.1195	0.7114	0.7117	0.07	84	MLB,DGB
11/8	0.1199	0.7092	0.7107	0.11	90	DGB,MLB
6/22	0.1207	0.7074	0.7113	0.09	84	MLB
mean=	0.1199	0.7093	0.7106	-		

1. based on Sr(86/88) = 0.1194 (see discussion to follow).

2. $\bar{E}\% = (\bar{s}/ x)100$ where x = average Sr(87/86), and $\bar{s} = \sqrt{\dfrac{\Sigma d^2}{n(n-1)}}$

3. DGB = Brookins, MLB = Bottino, WHP = Pinson

The runs on 6/15/62 and 6/18/62 should probably be discarded, because
they were run during a period when Snagtooth was under repair and when
new components were being tested and all other runs during the period
were discarded. The mean values for the remaining runs are:

$Sr(86/88)_{av} = 0.1198$, $Sr(87/86)_{av} = 0.7099$, and $Sr(87/86)_{cor.} = 0.7110$.

Sr (86/88) Correction

The $Sr(86/88)$ ratio in natural systems is assumed to be constant as cases of natural isotopic fractionation for heavy (e.g. atomic number greater than 10) isotopes has not yet been demonstrated. Nier (1938) has suggested that this value is 0.1194, and this value is commonly used by many workers as the standard reference point for normalization. Nier (ibid.) decided that deviations from this value were probably due to fractionation, in the mass spectrometric measurements. This wroter has also used 0.1194 as a reference value, but recent laboratory work indicates a higher value may be more accurate. The difference in mass between 87 and 86 is one-half that between 86 and 88, hence the average 87/86 ratio is corrected by one-half the deviation of 86/88 from 0.1194. For example, if $Sr(86/88)_{av} = 0.1190$, $Sr(87/86)_{av} = 0.7100$ for a run, then the correction is applied by:

$$Sr(87/86)_{cor} = \frac{0.7100}{(0.1194/0.1192)} = 0.7088.$$

As mentioned above, $Sr(86/88) = 0.1194$ is used for normalization, but this value is probably wrong.

Sr(86/88) Variations during This Investigation

Figure 3.1 shows the frequency distribution of 64 Sr(86/88)

ratios measured from isotope ratio analyses during the course of the

investigation. The mean of the values is 0.11946, which is close to

the 0.1194 value of Nier (op. cit.). However, the distribution shown

in Figure 3.1 indicates that the true standard value should be taken

as greater than0.1194. The deviations from any standard value of

Sr(86/88) are not due to fractionation in the mass spectrometer be-

cause (a) the ionization is not mass dependent, (b) no runs were re-

corded in which a continual systematic change of Sr(86/88) occurred,

and (c) mass discrimination by fringe field effects and electrostatic

repulsions is probably negligible (Riley, 1961). It is possible,

however, that material from cooler parts of the filament may evaporate

while the ionization is occurring, and, as evaporation is a mass-

dependent variable, this could cause a fractionation. This would be

especially true if evaporation continued from the cooler parts of the

filament while new material is diffusing to the site of emission of

ions. This is similar to gas mass spectrometric fractionation (e.g.

fed from a solution reservoir) and should be very evident from the re-

sultant mass spectrometric record, but evidence of solid source frac-

tionation has not been yet proven. It is more reasonable to assume

that Sr(86/88) variations are random and due to non-linearity in the

Figure 3.1

Frequency Distribution of Sr(86/88) Ratios
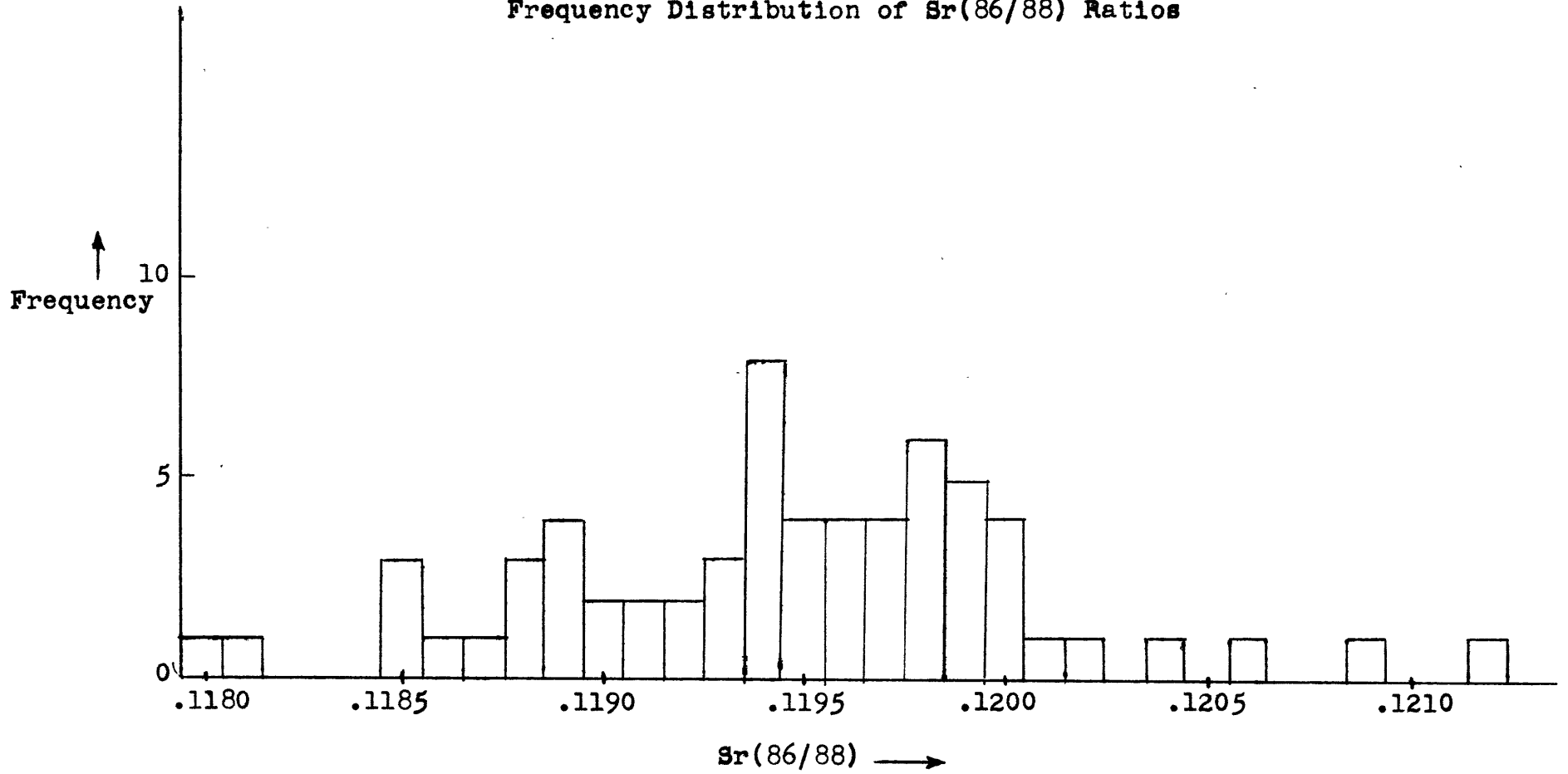
detecting circuit or some other unknown factor.

Discussion of Isotope Dilution Calculations

This section will not attempt to deal with the intrinsic theory of isotope dilution, and the reader is referred to Webster (1960) and Riley (1961) for detailed descriptions. Faure (1961) has discussed the techniques in use at the Massachusetts Institute of Technology, and these are only slightly varied in the discussion to follow.

Formulae

For Rb isotope dilution analyses, the formula is based on the constant $Rb(85/87)$ ratio = 2.59, which is determined from the physical atomic weights, such that Rb^{85} = 0.7215, and Rb^{87} = 0.2785. By careful calibration, the Rb^{87}-rich spike yields Rb^{85} = 0.175 and Rb^{87}=0.9825. Thus, if x = the measured $Rb(85/87)$ ratio (see Webster, 1960), then:

$$x = \frac{0.7215 \ N \ + \ 0.0175 \ S}{0.2785 \ N \ + \ 0.9825 \ S}$$

where N designates normal Rb and S spike Rb and:

$$\frac{N}{S} = \frac{(\ 0.9825) \ (x) \ - \ 0.0175}{(\ 0.7215) \ - \ (0.2785) \ (x)}$$

but this equation must be multiplied by a weight factor, which is equal to: Atomic Weight Normal Rb/Atomic Weight Spike Rb or: 85.557/86.965 = 0.9838. S is given by S = (ml spike) (conc. of spike in microgms./ml). Thus N may be obtained in p.p.m. As the

long half life of Rb^{87} does not affect the abundance of Rb^{87} to any

appreciable degree, no correction need be applied for normal Rb.

Similarly (see Faure, 1961, p. 157), the formula for a spiked

sample yielding a $Sr(86/88)$ ratio $= y$ is:

$$y = \frac{0.0986 \text{ N} + 0.8373 \text{ S}}{0.8256 \text{ N} + 0.0674 \text{ S}}$$

and the weight factor is 1.0172. However, the above formula is rigid

only for $Sr(87/86) = 0.712$, but the change in this isotopic ratio does

not appreciably affect the answer for samples with relatively little

$^{*}Sr^{87}$ (e.g. $Sr(87/86)$ less than 0.800). When $^{*}Sr^{87}$ is significant, it

is necessary to insert the proper isotopic abundances into the Sr spike

formula. For example, consider sample no. R5058aII, and the analysis

for Sr by isotope dilution. The data are presented in Chapter 5, but

in essence are:

$$Sr(87/86)_{cor.mean} = 1.0090$$

Sample weight $= 1.2776$ gms

Spike added $= 1$ ml of $21.6\,\mu$g/ml Sr^{86} -rich sol'n.

$$Sr(86/88)_{meas.,I.D.} = 1.749$$

Using the formula based on normal Sr isotopic composition, a value

of 9.2 p.p.m. was obtained. Now consider the compared compositions for

normal Sr and Sample No. R5058aII:

Normal Sr	Ratio	Sample R5058aII
1.0000	88/88	1.0000
0.0825	87/88	=(1.009)(.1194) = 0.1205
0.1194	86/88	0.1194
0.0068	84/88	0.0068
1.2087	Tot.Sr	= 1.2467
0.8256	$88/Sr_{tot.}$	= 0.8021
0.0986	$86/Sr_{tot.}$	= 0.0958

hence:

$$y = \frac{0.0958 \text{ N} + 0.8373 \text{ S}}{0.8021 \text{ N} + 0.0674 \text{ S}}$$

and the weight factor is 1.045, and calculation of Sr now yields

9.5 p.p.m. This value is over three per cent greater than the value

determined by use of the normal Sr formula and stresses the importance

of allowance for proper isotopic abundances in the formula for samples

with relatively large amounts of $^*Sr^{87}$, and though the error may seem

small, it can change a Rb/Sr ratio by a larger amount.

Spike Release

Figures 3.2a, b show the variation of N/S for measured 85/87 and

86/88 values, and the figures show that the least error will result in

Figure 3.2a

Figure 3.2b

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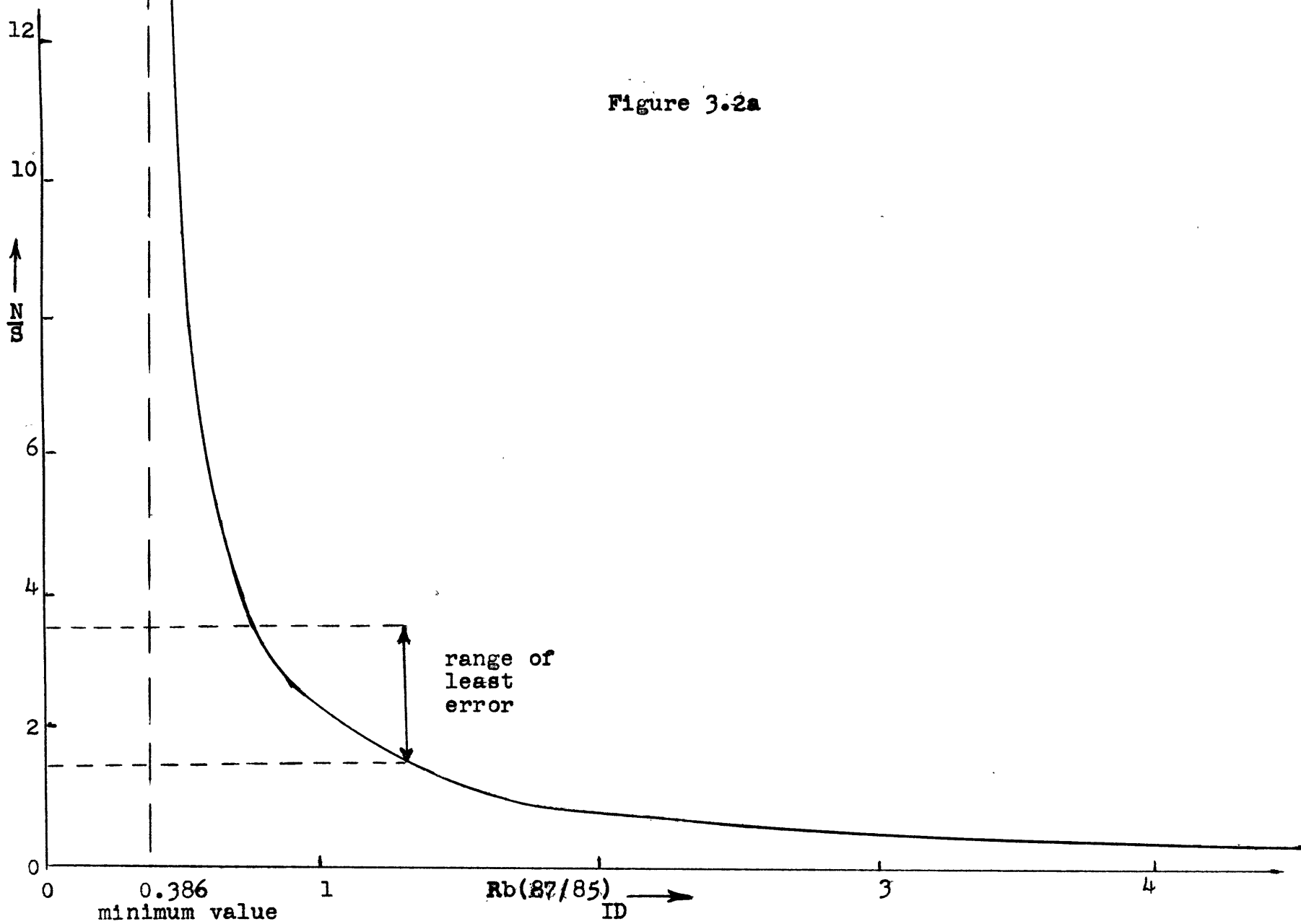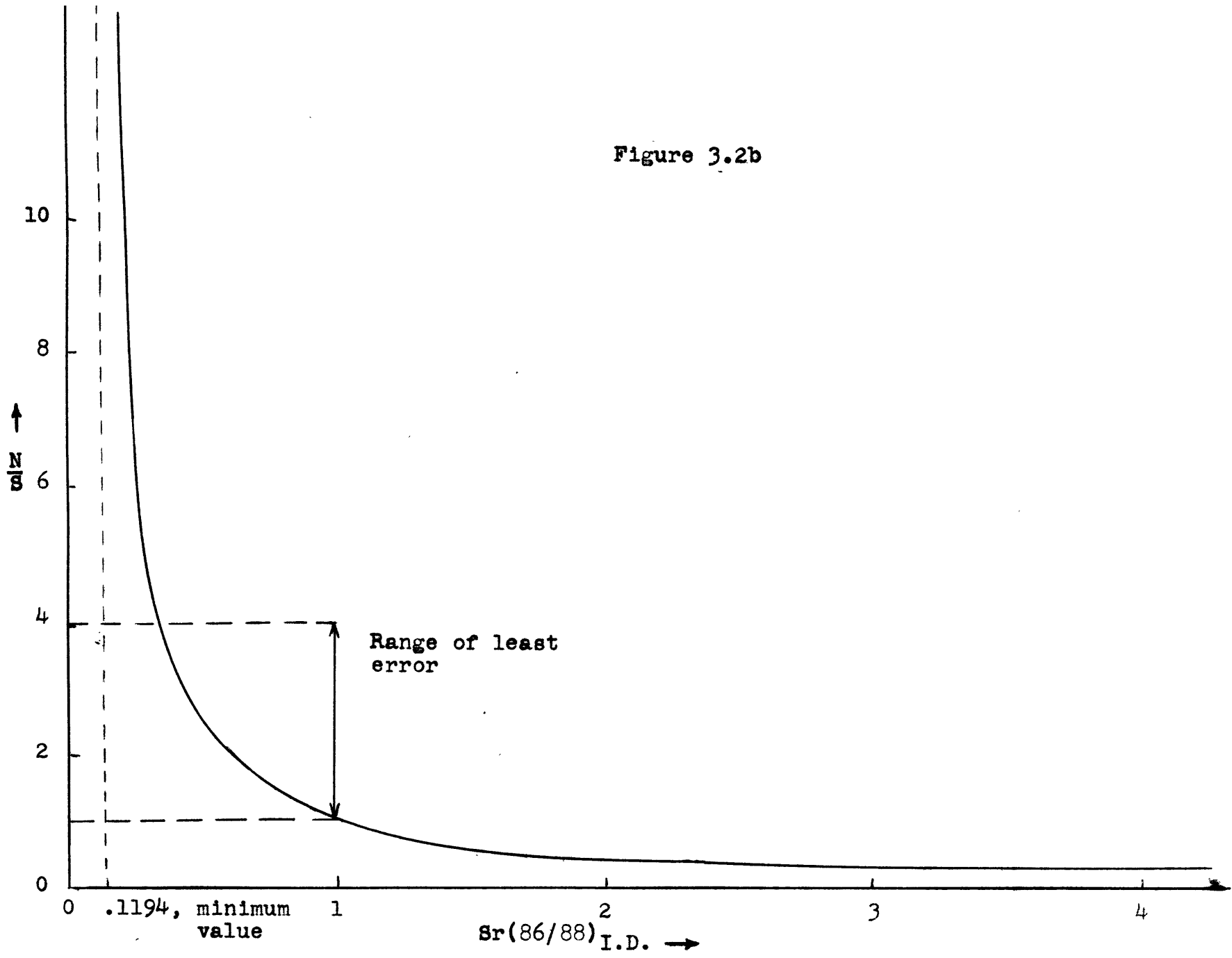
the blocked off areas. The volume of spike added to each sample is released with the intent that the resultant ratios will fall in such an area, and this volume is determined after rough estimation of the amounts of Rb and Sr in the sample by quick-scan X-Ray Spectography or emission spectography or other means. The volume of spike released is extremely critical, and in cases where only one ml of spike was used the precision was found to be good so that errors in volume are probably negligible. All deliveries of spikes were made in calibrated pipettes.

Sr and Rb Blanks

Checks for analytical contamination are made by analyzing known amounts of spike which has been subjected to the same chemistry as a spiked sample. All blanks run in the Massachusetts Institute of Technology Geochronology Laboratory showed a maximum upper limit of less than 0.3 μgms. Sr and less than 0.08 μgms. Rb. These correction limits are so low that they were not applied to the calculated results.

Shelf Solutions

Shelf solutions are carefully prepared solutions containing a known concentration of an element of normal isotopic composition. Typical Sr and Rb salts are very carefully weighed and then dissolved

in a known amount of solvent. Corrections for temperature, etc. are dilligently applied during these processes. Pinson (in 10th Annual Progress Report for 1962, NYO-3943) has discussed in great detail the preparation and isotopic measurements of these shelf solutions, and their subsequent use in spike calibration. All of the shelf solutions in the laboratory are of different isotopic composition, and thus emphasize the need to standardize to only one reference reagent (e.g. Eimer and Amend $SrCO_3$).

CHAPTER FOUR: Previous Absolute Age Measurements

Introduction

Many very accurate absolute age measurements by U-Pb, Th-Pb, K-Ar, and Rb-Sr methods have been reported from this area. Most of these analyses have been reported for pegmatite minerals and thus do not date the surrounding rocks, but a few absolute ages have been reported for the country rocks. No attempt will be made here to describe the analytical techniques in the various methods, and the interested reader is referred to the references cited in this chapter for discussion of K-Ar, U-Pb, and Th-Pb methods, and elsewhere in this thesis for discussion of the Rb-Sr method.

U-Pb and Th-Pb Investigations

Until the classic work of Nier (1939 a,b) the only Pb ages in the area were determined by simple chemical analysis for Pb, U, and Th; with resultant large errors. Nier (ibid.) allowed for correction for nonradiogenic lead and used very accurate isotopic analyses, and obtained a 260 m.y. age for samarskite for the Spinelli Prospect Pegmatite. This age is used by Holmes (1946) in his discussion of the Absolute Time Scale. Rodgers (1952) has summarized most of the early work and has proposed an age of 260 $\pm$ 50 m.y. for pegmatite emplacement in the area. The large error results from incorporation

of many of the early ages which have since been disproven.

Wasserburg et al. (1956) report Pb^{206}/U^{238} and Pb^{207}/U^{235} ages on

K-feldspar from the Spinelli Quarry of 251 m.y. and 255 m.y., and

total Pb/U ages on muscovite from the Strickland Quarry, Toll Gate

Quarry, and Spinelli Quarry of 267 m.y., 267 m.y., and 254 m.y. These

and other results are tabulated in Table 4.1, and it is interesting to

note that the Pb ages from the nine analyses listed give an average

age of 259 m.y., which agrees exactly with the age of emplacement

suggested by Rodgers (op. cit.) but with far less error.

TABLE 4.1

RECENT ABSOLUTE AGE DETERMINATIONS BY THE U-Pb AND Th-Pb METHODS

Quarry	Mineral	Method	Age	Reference
Spinelli	samarskite	Pb^{207}/Pb^{206}	260	Holmes (1946)
do.	K-feldspar	Pb^{206}/U^{238}	251	Wasserburg et al. (1955)
do.	do.	Pb^{207}/U^{235}	255	do.
do.	muscovite	Pb^{207}/Pb^{206}	254	do.
Strickland	do.	do.	267	do.
Toll Gate	do.	do.	267	do.
Strickland	uraninite	Pb^{206}/U^{238}	268	Wasserburg and Hayden(1955)
do.	do.	Pb^{207}/U^{235}	266	do.
do.	do.	Pb^{208}/Th^{232}	239	do.

K-Ar and Rb-Sr Investigations

Tables 4.2 and 4.3 show K-Ar and Rb-Sr ages for the pegmatite

minerals from some of the quarries in the area and from some country

rock minerals. Except where noted, all the data are taken from the

Ninth Annual Progress Report for 1961 (NYO-3942, U.S.A.E.C., Contract

AT(30-1)-1381, pp. 234, 243). The initial Sr(87/86) ratios used in

Table 4.3 are subject to large error because of the lack of samples

with low Rb/Sr ratios.

TABLE 4.2

RECENT ABSOLUTE AGE DETERMINATIONS BY THE K-Ar METHOD

Locality and Rock Type	Mineral	K-Ar Age[4]	K-Ar - Other Laboratories
Strickland Quarry	Muscovite	243 ± 10	252 ± 8[1]
	Microcline		245 ± 8[2]
			252 ± 8[1]
	Lepidolite		252 ± 8[3]
Collins Hill Formation	Biotite	231 ± 9	
Spinelli Quarry	Muscovite		249 ± 8[1]
Glastonbury Gneiss	Biotite	230 ± 9	

1. Wasserburg et al. (1956)

2. Baadsgaard et al. (1957)

3. Wetherill et al. (1956)

4. $\lambda_{\beta K}{}^{40} = 5.3 \times 10^{-10} \mathrm{yr}^{-1}$

5. $\lambda_{e K}{}^{40} = .585 \times 10^{-10} \mathrm{yr}^{-1}$

TABLE 4.3

RECENT ABSOLUTE AGE DETERMINATIONS BY THE Rb-Sr METHOD[2]

Sample Number, Mineral + Locality	$(Rb/Sr)_{wt.}$	(Sr^{87}/Sr^{86}) measured	(Sr^{87}/Sr^{86}) initial	Rb-Sr[1] Age
Spinelli Pegmatite				
M 3370 (muscovite)	290.6	3.76	0.730	240 ± 8
F 3371 (microcline) (a)	19.55	0.9344	0.730	240 ± 8
(b)	18.1	0.9214	0.730	240 ± 8
Strickland Pegmatite				
M 3373 (muscovite)	349.2	4.3864	0.730	240 ± 8
F 3374 (microcline)	33.29	1.0720	0.730	240 ± 8
L 3375 (lepidolite) (a)	776.8	8.223	0.730	227 ± 5
(b)	700.3	7.370	0.730	227 ± 5
Glastonbury Gneiss				
B 3372 (biotite)	124.0	1.907	0.76 max.	217 - 223
B 3372 (whole rock)	9.51	0.8478	0.76 max.	217 - 223
Collins Hill Formation				
B 3376 (biotite)	38.71	1.0888	0.735	208 ± 5
M 3376 (muscovite)	207.4	2.580	0.735	208 ± 5
R 3376 (whole rock)	0.709	0.7303	0.735	208 ± 5

1. $\lambda_{Rb^{87}} = 1.47 \times 10^{-11} \, yr^{-1}$

2. Ref: Ninth Ann. Prog. Rpt., 1961, U.S.A.E.C., NYO-3942.

The values for the initial Sr(87/86) ratios were determined by the isochron plots shown in Figures 4.1a, b, c. The pegmatite

Figure 4.1a

Pegmatite Mineral Isochron
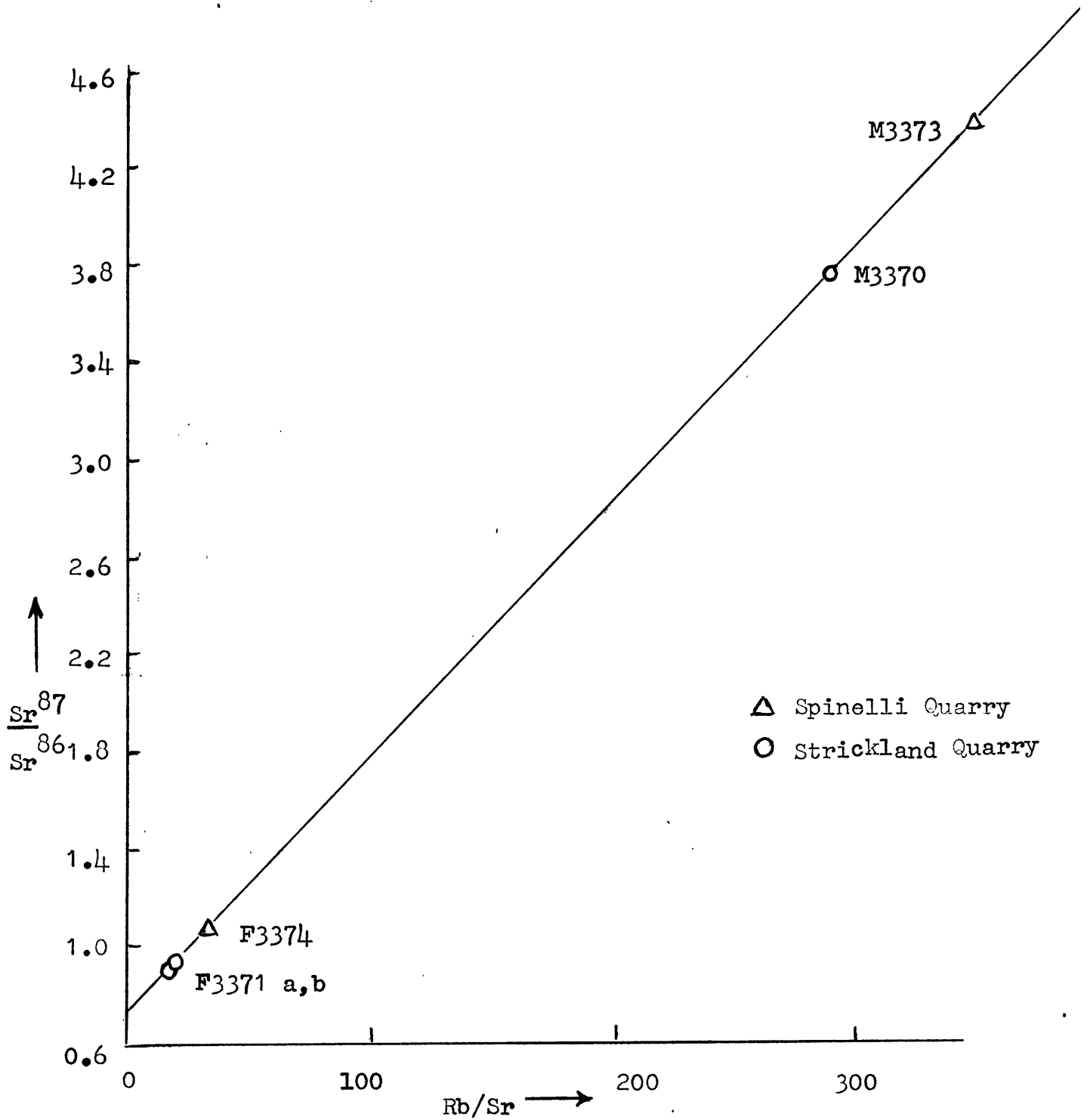
Ref: Ninth Ann. Prog. Rpt., 1961, U.S.A.E.C., NYO-3942.

Figure 4.1b

Glastonbury Gneiss
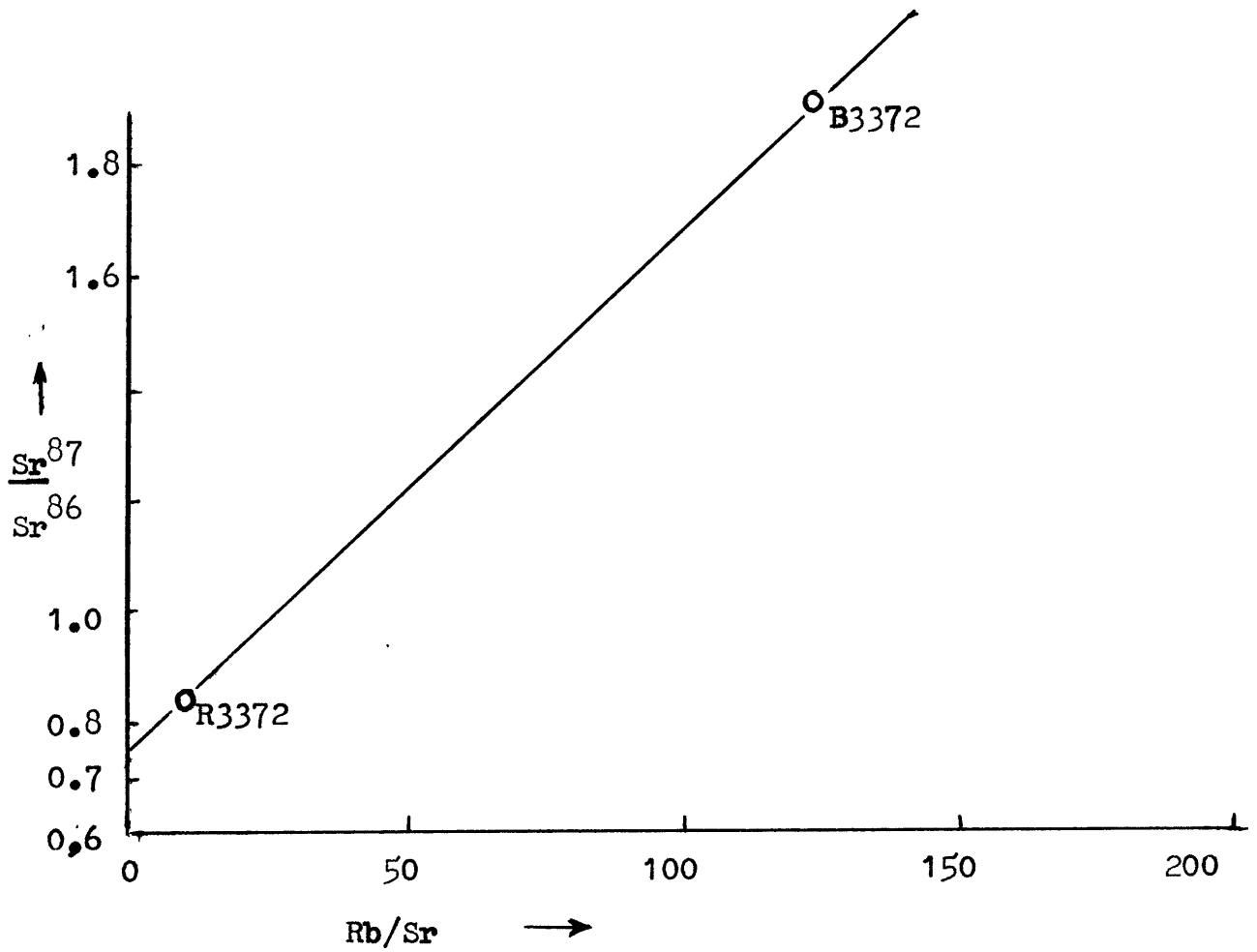
Ref: Ninth Ann. Progress Rpt., 1961, U.S.A.E.C.,
NYO-3942

Figure 4.1c

Collins Hill Formation
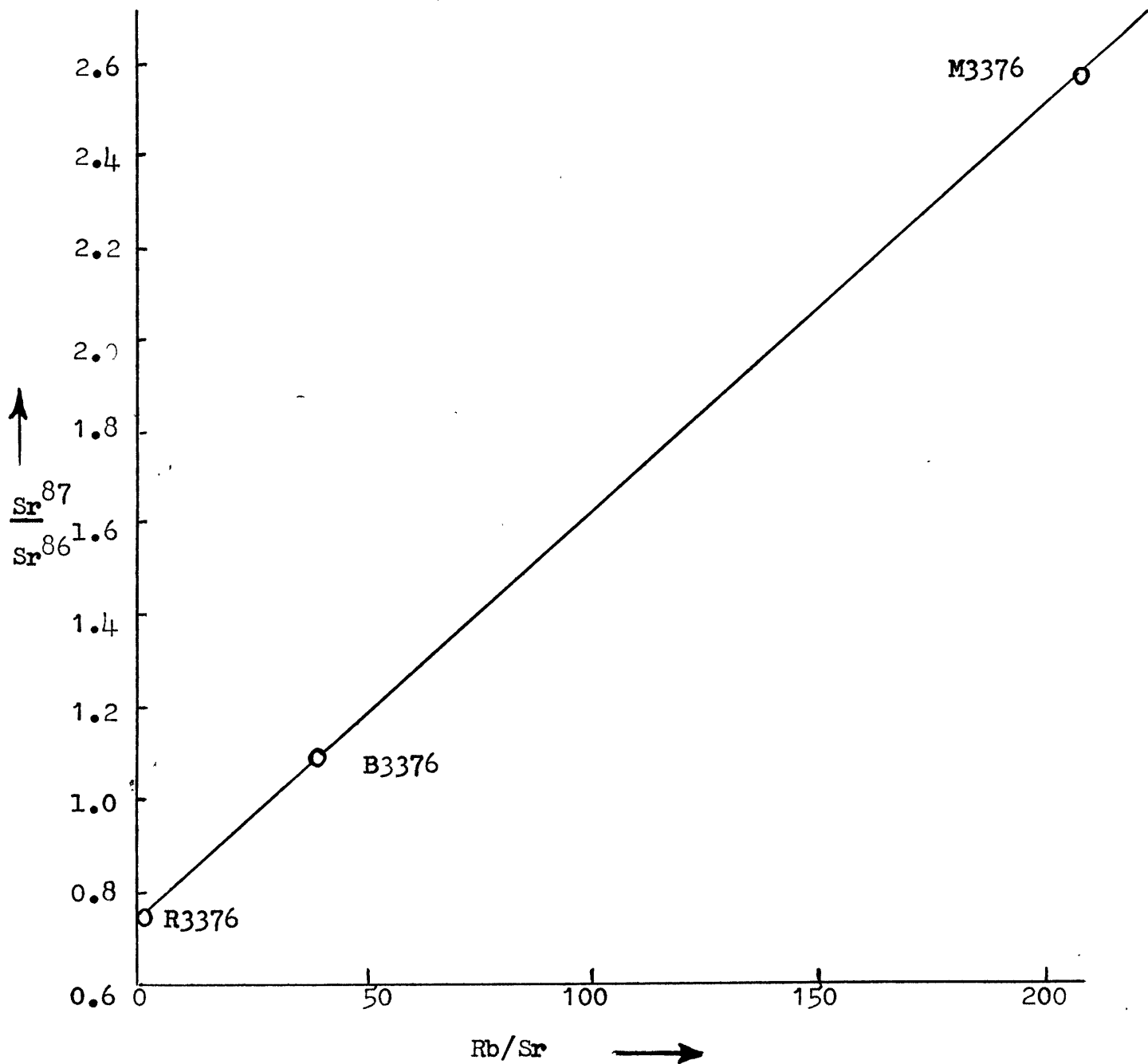
Ref: Ninth Ann. Progress Rpt., 1961, U.S.A.E.C., NYO-3942/

mineral isochron (Figure 4.1a) is defined by at least four points, and that the lepidolites do not fall on this isochron may either be due to experimental error or due to an actual curvature of the isochron as discussed in Chapter Two. The initial $Sr(87/86)$ ratios for both the Glastonbury Gneiss and the Collins Hill Formation were derived from the isochrons of Figures 4.1b and 4.1c, and these plots are based on the assumption that some type of rehomogenization occurred about the time of pegmatite emplacement such that the mineral separates and whole rocks define a unique isochron for each formation. This will be discussed in later sections of this thesis. For the data presented in Table 4.3, recalculation of the ages based on

$$\lambda_{Rb^{87}} = 1.39 \times 10^{-11} yr^{-1}$$ yields an average age for the pegmatite minerals of 251 m.y. and 220 m.y. for the minerals of the Collins Hill Formation. Both of these recalculated ages are in good agreement with the K-Ar ages given in Table 4.2, and the pegmatite mineral ages in Table 4.1. The 220 m.y. recalculated age for the Collins Hill Formation minerals may be too low, because the initial $Sr(87/86)$ value of 0.735 used may be too high, and a mineral from the same system but with a low Rb^{87}/Sr^{86} ratio must be analyzed to resolve this problem. If a "normal Sr" initial $Sr(87/86)$ ratio of 0.710 is used to calculate whole-rock ages for the Collins Hill Formation and

for the Glastonbury Gneiss, the following ages result (again using

$\lambda_{Rb}87 = 1.39 \times 10^{-11} \text{ yr}^{-1}$): Collins Hill Formation - 990 m.y.,

Glastonbury Formation - 360 m.y. The geologic correlation described

in Chapter One indicates that the Collins Hill Formation is Paleozoic

in age, and the 990 m.y. age listed above is therefore wrong, and in-

dicates that the initial Sr (87/86) ratio is much greater than 0.71.

The Glastonbury age of 360 m.y. for the total rock is in fair agreement

with an earlier published age of 370 m.y. (Stugard, 1958), but the

latter age is considered only fair.

In addition to the data already discussed, Ahrens (1949) reports

a probable age of approximately 270 m.y. for an unspecified pegmatite

near Haddam, Connecticut, but he is careful to point out that no

correction for non-radiogenic Sr was applied, hence the age can be

taken as a maximum at best.

Summary and Tentative Conclusions

The U-Pb and Th-Pb ages for the pegmatite minerals average

259 m.y. The K-Ar ages for the pegmatite minerals average 250 m.y.

If the decay constant, $\lambda_{Rb}87 = 1.39 \times 10^{-11} \text{ yr}^{-1}$, is assumed as in

other chapters of this thesis, then the Rb-Sr ages for the pegmatite

minerals average 251 m.y. Thus it is probably safe to indicate an age

of pegmatite emplacement of 255 $\pm$ 10 m.y. Application of this decay
constant to the minerals of the Collins Hill Formation yields ages of
220 m.y., in good agreement with the K-Ar age of 231 $\pm$ 9 m.y.

The age of the end of the last major metamorphism in the area is
probably 230 $\pm$? m.y., and this age is probably significant despite the
higher 255 $\pm$ 10 age of the pegmatitic emplacement (commonly thought to
date the end of the metamorphism). However, J. L. Rosenfeld (written
and personal communcation) has informed this writer that quartz
porphyry blocks are found in the Triassic rocks west of the border
fault, and, because of limited distribution, are thought to represent
material from the Pre-Triassic basement rocks to the east which has
been eroded away. Subsequent analyses of this material may indicate
that the 255 $\pm$ 10 m.y. age on the pegmatites merely indicates time of
last homogenization and that it does not necessarily mark the end of
orogenic events in the area.

CHAPTER FIVE - Rb-Sr Age Investigations in the Middle Haddam and

Glastonbury Quadrangles, Connecticut

Introduction

This chapter will deal with the Rb-Sr data obtained during the course of the thesis investigation. The analytical data and isochrons for the Maromas Granite Gneiss, Glastonbury Gneiss, Middletown Formation, Ammonoosuc Volcanics, Monson Gneiss, Collins Hill Formation, and pegmatites are presented. Samples are described fully in Chapter Seven, and only brief descriptions are mentioned in this chapter.

The limits of error on each isochron presented have been determined by previously constructing maximum and minimum isochrons through the error in $Sr(87/86)$ and Rb^{87}/Sr^{86} about each point, but are not shown for clarity of presentation. The isochrons shown are best-fit lines for the points shown.

Presentation of Data

Table 5.1 shows the data from the isotope ratio measurements determined during this investigation. The average Sr (86/88) and $Sr(87/86)$ ratios are determined from the mean of averages from every six scans, and the $Sr(87/86)$ corrected ratio is determined from normalization of $Sr(86/88) = 0.1194$. $^{o}/o$ $\bar{E}$ is the standard deviation

of the mean, and is determined by the formula $\bar{E} = \dfrac{\bar{\sigma}}{x}$, $\bar{\sigma} = \sqrt{\dfrac{\Sigma d^2}{(n-1)n}}$

where n = number of sets of six scans and d = $\pm$ deviation from the

mean. The quality of the runs is generally based on $\%\,\bar{E}$, unless ob-

servation during the run indicates it to be very steady and good

despite a high $\%\,\bar{E}$. Replicate analyses have been determined for most

points, and it is noteworthy that fair runs and good runs are

experimentally identical.

Table 3.2 shows the determination of the $Rb/Sr_{wt.}$ ratio, the

mean isotope ratio used to determine k (see Chapter Two for curve),

and the subsequently determined Rb^{87}/Sr^{86} ratio. The $(Rb/Sr)_{wt.}$

ratios have been determined both by isotope dilution and by X-Ray

spectography techniques described in Chapter Three. For the former

method, the absolute amounts of Rb and Sr are also presented.

TABLE 5.1

TABULATION OF ISOTOPE RATIO MEASUREMENTS

Sample	Record	1962 Date	Average Sr(86/88)	Average Sr(87/86)	Corrected Sr(87/86)	$\%\ \bar{E}$ [1]	Quality
----------------Table 5.1a, Maromas Granite Gneiss----------------------------							
R4791aI [2]	2531	7/16	0.11958	0.7363	0.7369	0.051	good
do. II	2503	7/9	0.11946	0.7369	0.7371	0.097	fair
R4791bI	2119	3/5	0.11949	0.7334	0.7335	0.13	fair
do. II	2451	6/17	0.12192	0.7269	0.7336	0.076	fair
do. III	2764	10/2	0.11998	0.7314	0.7332	0.096	good
R4791dI	2637	8/14	0.11932	0.7307	0.7305	0.14	fair
do. II	2766	10/2	0.11866	0.7316	0.7293	0.090	good
R5059aI	2784	10/10	0.11977	0.8547	0.8560	0.053	good
R5059bI	2828	10/22	0.11875	0.8308	0.8285	0.11	fair
----------------Table 5.1b, Glastonbury Gneiss----------------------------							
R4792aI	2307	5/1	0.11978	0.7757	0.7763	0.12	fair
R4792b	2492	7/2	0.11915	0.7998	0.7992	0.050	good
do. II	2507	7/9	0.12000	0.7978	0.7998	0.057	good
do. III	2527	7/14	0.11975	0.8009	0.8021	0.059	good
R4792cI	2478	6/27	0.11978	0.7448	0.7460	0.041	good
do. II	2517	7/11	0.12088	0.7414	0.7470	0.12	fair
R4998 I-1 [3]	2488	7/2	0.11979	0.7185	0.7197	0.030	good
do. -2	2495	7/5	0.11993	0.7184	0.7199	0.070	fair
do. II	2636	8/13	0.11948	0.7189	0.7191	0.043	good
R4999 I	2476	6/26	0.11934	0.7119	0.7117	0.076	good
do. II	2521	7/12	0.11992	0.7086	0.7101	0.12	fair
----------------Table 5.1c, Middletown Formation---------------------							
R5052 I	2627	8/10	0.11942	0.7070	0.7071	0.056	good
do. II	2631	8/12	0.11889	0.7084	0.7069	0.12	fair
R5053aI	2658	8/21	0.11935	0.7230	0.7228	0.045	good
do. II	2754	9/26	0.11907	0.7243	0.7233	0.047	good
R5053bI	2678	8/29	0.11904	0.7265	0.7254	0.051	good
R5053cI	2655	8/20	0.11890	0.7384	0.7368	0.059	good
do. II	2749	9/22	0.11925	0.7335	0.7333	0.041	good

1. $\%\ \bar{E} = 100\ \dfrac{\bar{\delta}}{x}$, where $\bar{\delta} = \sqrt{\dfrac{\Sigma\ d^2}{m(m-1)}}$, x = mean Sr(87/86).

2. Roman numeral indicates separate aliquot of sample.

3. Arabic numeral indicates re-run of the same aliquot.

TABLE 5.1 (CONTINUED)

Sample	Record	1962 Date	Average Sr(86/88)	Average Sr(87/86)	Corrected Sr(87/86)	$\%\bar{o}E$	Quality
---------------------------Table 5.1d, Ammonoosuc Volcanics---------------------							
R5069	2866	11/7	0.11892	0.7430	0.7415	0.074	good
R5070	2864	11/6	0.11964	0.7210	0.7217	0.100	good
R5071	2900	11/18	0.11901	0.7132	0.7120	0.079	good
R5072	2870	11/8	0.11937	0.7082	0.7081	0.052	good
---------------------------Table 5.1e, Monson Gneiss[4]---------------------							
R5056bI	2716	9/11	0.11888	0.7132	0.7116	0.094	good
do. II	2752	9/25	0.11943	0.7122	0.7123	0.056	good
R5056cI	2694	9/6	0.11850	0.7196	0.7169	0.090	fair
do. II	2731	9/17	0.11796	0.7217	0.7173	0.052	good
R5058aI	2713	9/11	0.11951	1.0093	1.0099	0.067	good
do. II	2750	9/24	0.11987	1.0060	1.0081	0.050	good
R5058dI	2733	9/18	0.11918	0.7215	0.7208	0.12	fair
R5058eI	2780	10/8	0.11862	0.7087	0.7066	0.100	good
do. II	2770	10/3	0.11882	0.7114	0.7096	0.14	fair
R5058fI	2862	11/6	0.11852	0.9623	0.9587	0.086	fair
---------------------------Table 5.1f, Pegmatites---------------------							
R4722I	2122	3/6	0.11987	0.7265	0.7280	0.12	fair
A4774I	2167	3/20	0.12124	0.7356	0.7411	0.062	good
A4992I	2311	5/2	0.12044	0.8817	0.8855	0.068	good
R5030I	2557	7/23	0.11954	0.8038	0.8043	0.100	good
R5031aI	2611	8/6	0.11950	0.7479	0.7482	0.135	fair
---------------------------Table 5.1g, Collins Hill Formation---------------------							
R4717II	2226	4/4	0.11982	0.7279	0.7291	0.061	good
R4718I	2303	4/29	0.11944	0.7461	0.7462	0.050	good
R4719I	2216	4/2	0.12087	0.7324	0.7369	0.11	fair
do.II	2514	7/10	0.12005	0.7352	0.7372	0.084	good
R4720bI	2096	2/26	0.11966	0.7420	0.7429	0.084	good
do.II	2344	5/14	0.12016	0.7425	0.7449	0.087	good
R4721I	2070	2/18	0.11881	0.7289	0.7271	0.11	fair
do.II	2386	5/29	0.11968	0.7251	0.7257	0.14	fair
R4723I	2146	3/12	0.12000	0.8268	0.8280	0.11	fair
R3376I	2356	5/21	0.11940	0.7348	0.7348	0.100	good
do.II	2360	5/22	0.11967	0.7351	0.7359	0.025	good
R4788I	2148	3/14	0.11966	0.7279	0.7280	0.084	good
do.II	2389	5/30	0.11805	0.7327	0.7286	0.095	good

4. Includes granite dikes cutting other rocks.

TABLE 5.2

$$(Rb/Sr)_{wt.} \quad \text{and} \quad (Rb^{87}/Sr^{86})_{at.} \text{ Determinationa}$$

Sample	Rb p.p.m.	Sr p.p.m.	$(Rb/Sr)_{wt.}$	Corrected Sr(87/86)	k	(Rb^{87}/Sr^{86})
----------------------------------Maromas Granite Gneiss----------------------------------						
R4791a	120.2	59.7	2.01	0.7370	2.9030	5.84
R4791b	116	72.1	1.62	0.7334	2.9020	4.70
R4791d	-	-	1.35	0.7299	2.9010	3.92
R5059a	133.8	10.9	12.50	0.8560	2.936	36.70
do.	132.2	10.4				
R5059b	118.0	12.2	9.63	0.8285	2.9285	28.20
do.		12.3				
----------------------------------Glastonbury Gneiss----------------------------------						
R4792a	301.0	64.3	4.55	0.7763	2.9142	13.26
R4792b	-	-	5.97	0.7995	2.9207	17.44
R4792c	-	-	2.33	0.7460	2.9058	6.77
R3372*			9.51	0.8478	2.934	27.85
R4998	-	-	0.45	0.7194	2.8980	1.30
R4999	-	-	0.15	0.7109	2.8956	0.43
----------------------------------Middletown Formation----------------------------------						
R5052	-	-	0.04	0.7070	2.8945	0.12
R5053a	122.8	148.9	0.82	0.7230	2.8990	2.38
R5053b	97.7	102.5	0.95	0.7254	2.8997	2.75
R5053c	**211.6**	**131.6**	**1.62**	**0.7350**	**2.9025**	**4.67**
----------------------------------Ammonoosuc Volcanics----------------------------------						
R5069	-	-	1.80	0.7415	2.9043	5.24
R5070	-	-	0.63	0.7217	2.8987	1.83
R5071	-	-	0.12	0.7120	2.8960	0.35
R5072	-	-	0.03	0.7081	2.8948	0.09
----------------------------------Monson Gneiss----------------------------------						
R5056b	-	-	0.17	0.7120	2.8960	0.49
R5056c	27.9	75.0	0.37	0.7171	2.8974	1.07
R5058a	167.4	9.5	17.40	1.0090	2.9795	51.84
do.	173.9	10.1				
R5058d	-	-	0.61	0.7208	2.8984	1.77
R5058e	-	-	0.01	0.7081	2.8948	0.03
R5058f	-	-	15.10	0.9587	2.965	44.77

TABLE 5.2

(Continued)

--Pegmatites------------------------------------

R4722	69.5	326.1	0.21	0.7280	2.9005	0.61
do.		317.7				
A4774	-	-	0.50	0.7411	2.9042	1.45
A4992	-	-	2.10	0.8855	2.945	6.18
R5030	-	-	5.76	0.8043	2.9221	16.83
R5031a	-	-	2.05	0.7482	2.9062	5.96

------------------------------Collins Hill Formation--------------------------

R4717	71.0	124.5	0.57	0.7291	2.9009	1.65
R4718	214.2	88.5	2.42	0.7462	2.9056	7.03
R4719	181.4	186.7	0.99	0.7370	2.9030	2.87
do.		179.4				
R4720a	567.8	12.4	44.60	1.1580	3.0225	134.80
R4720b	319.1	196.7	1.62	0.7439	2.9050	4.71
R4721	129.4	251.0	0.51	0.7264	2.9000	1.48
do.		254.2				
R4723*	1456.6	124.5	12.00	0.8280	2.928	35.14
R3376			0.71	0.7352	2.9025	2.06
R4788	52.9	124.6	0.42	0.7283	2.9006	1.22

*   data from Ninth Ann. Prog. Rpt., 1961

** where absolute amounts of Rb and Sr are not given, the Rb/Sr ratio

has been determined by X-Ray Spectrography.

Maromas Granite Gneiss

Samples R4791a,b, and d were taken from the northernmost occurrence of the Maromas, an elliptical lens which occurs between the Collins Hill and Middletown Formations on the west side of Collins Hill near the Strickland Pegmatite Quarry. The spread of $(Rb/Sr)_{wt.}$ ratios for these samples is too narrow to allow an accurate isochron to be constructed. This is in part due to the large samples which it was necessary to take because of the fine- to coarse-grained texture. Samples R5059a,b are from the type locality near Middletown, and were kindly donated by Dr. J. W. Peoples of Wesleyan University. Analyses of these two samples, with high $(Rb/Sr)_{wt.}$ ratios, has allowed construction of the isochron shown in Figure 5.1.

The absolute age of the Maromas Granite Gneiss is given a 287 ± 10 m.y. based on the isochron of Figure 5.1. As the spread of $(Rb/Sr)_{wt.}$ ratios ranges from 1.35 to 12.50, it is suggested that the Maromas Granite Gneiss has remained a closed megasystem since 287 ± 10 m.y. ago. Extrapolation of the isochron below R4791d yields an initial $Sr(87/86)$ ratio of 0.714 ± 0.002, but the error in 0.714 is probably less than 0.002 because of the excellent control on the isochron by the other points.
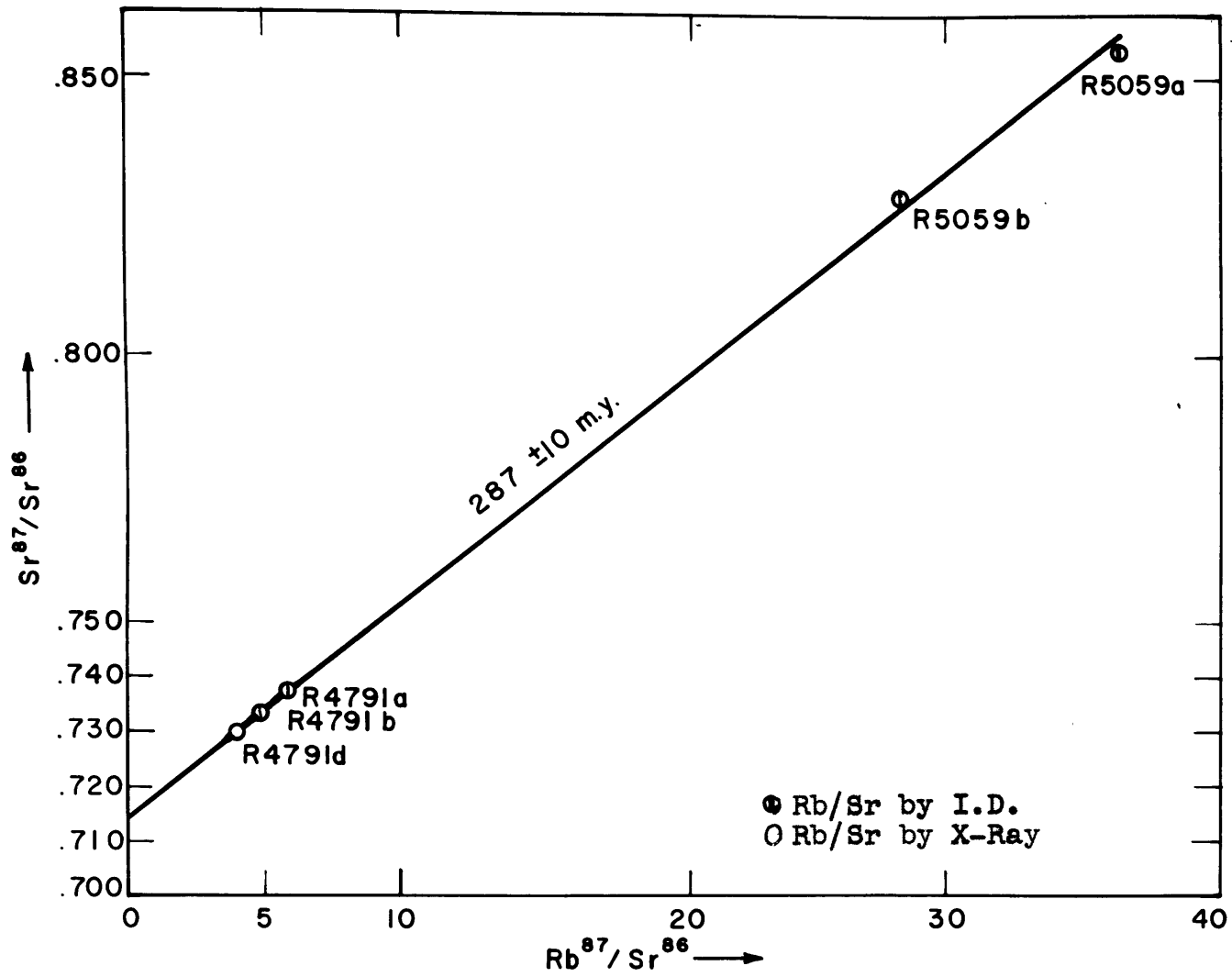
FIG. 5.I MAROMAS GRANITE GNEISS WHOLE-ROCK ISOCHRON

Glastonbury Gneiss

Samples for the Glastonbury Gneiss were all taken from the porphyroblastic facies of Herz (1955). R4792a,b,c were taken from the near-contact east of the Strickland Quarry between the Collins Hill Formation and the Glastonbury Gneiss. R3372 and R4998 were taken in the vicinity of the Spinelli Prospect, and R4999 was taken east of the Hale Quarry. This areal distribution of samples covers several miles and is thus a good sampling of the porphyroblastic facies.

The whole-rock isochron is shown in Figure 5.2, and defines an age of 360 ± 10 m.y. The spread of $(Rb/Sr)_{wt.}$ ratios is excellent, varying from 0.15 to 9.51, for testing the closure of the megasystem. The initial $Sr(87/86)$ ratio determined from this isochron is 0.710 $\pm$ 0.001.

Middletown Formation and Ammonoosuc Volcanics

These two formations are discussed together because of their correlation to each other along the Bronson Hill Anticline from Connecticut to New Hampshire. The samples are described fully in Chapter Seven, and the samples for each formation have a wide areal distribution. The samples of the Ammonoosuc Volcanics were contributed by Dr. M. P. Billings of Harvard University. Unfortunately, the more
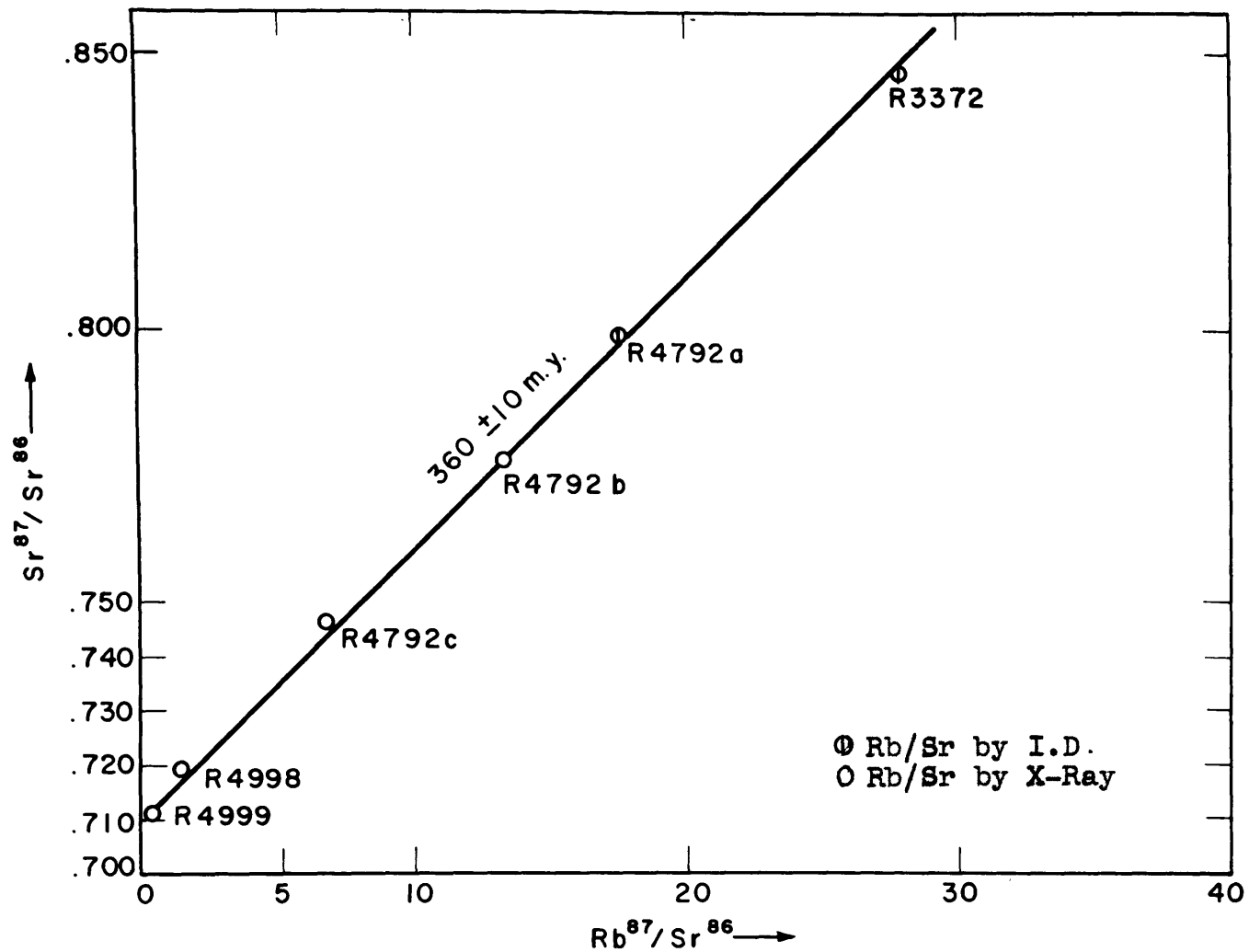
FIG. 5.2 GLASTONBURY GNEISS   WHOLE-ROCK ISOCHRON
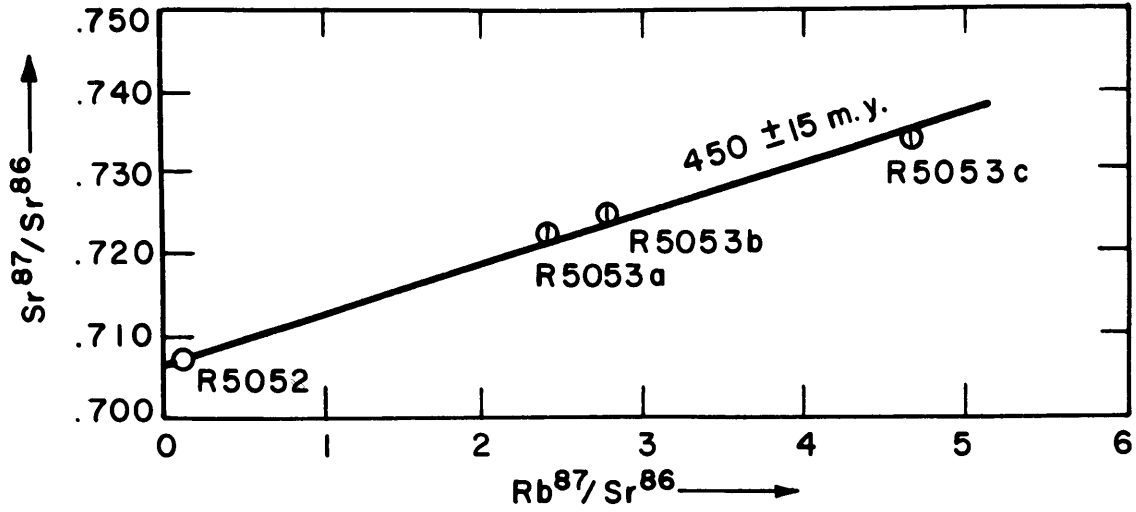
FIG. 5.3   MIDDLETOWN   FORMATION
WHOLE-ROCK ISOCHRON
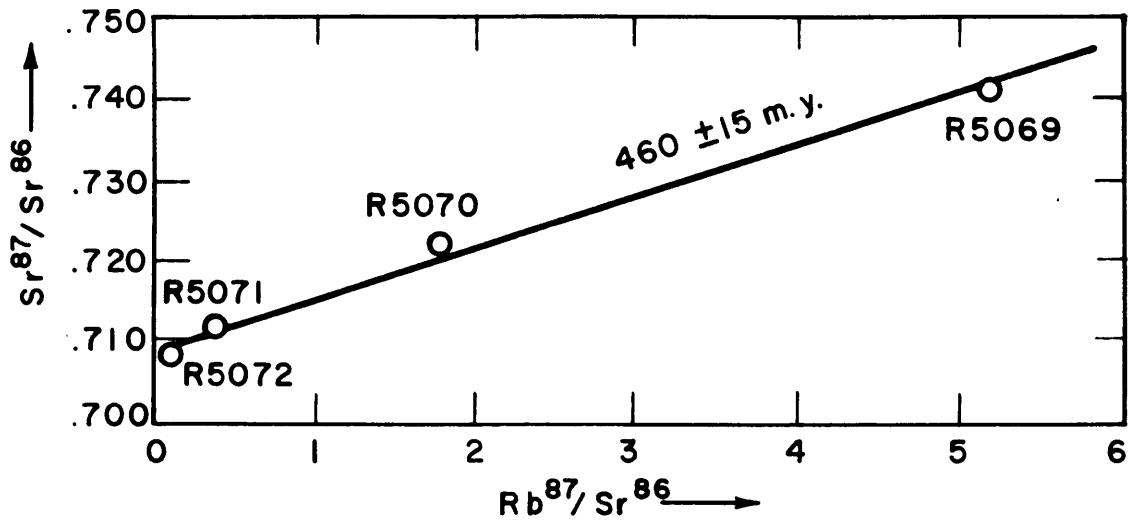
FIG. 5.4   AMMONOOSUC   VOLCANICS
WHOLE-ROCK ISOCHRON

⦶ Rb/Sr by I.D.

O Rb/Sr by X-Ray

acid members of both formations are Na-rich rather than K- (and Rb-) rich; hence the whole-rock isochrons shown in Figures 5.3 and 5.4 are not defined by a wide range of $(Rb/Sr)_{wt.}$ ratios, but the initial $Sr(87/86)$ ratios for each are well defined because of the low $(Rb/Sr)_{wt.}$ ratios. The isochron for the Ammonoosuc Volcanics yields an age of 460 ± 15 m.y., and that for the Middletown Formation yields an age of 450 ± 15 m.y. The $(Rb/Sr)_{wt.}$ ratios for the Ammonoosuc samples have all been determined by X-Ray spectrography; but because this ratio is low, the $\pm$ five per cent deviation from each point does not seriously affect the isochron. The initial $Sr(87/86)$ ratio for the Middletown Formation is 0.7065 ± 0.001, and the initial $Sr(87/86)$ ratio for the Ammonoosuc Volcanics is 0.708 ± 0.001.

Monson Gneiss

Samples R5058a and R5058f represent granitic dikes which cut the Monson Gneiss in the Killingworth Dome, and the other samples represent typical plagioclase-mafic gneisses, from both the Killingworth Dome and the elongated anticlinal belt which continues into Massachusetts. Two isochrons are shown in Figures 5.5a and 5.5b because there is some uncertainty regarding the relationship of the granitic dikes to the remainder of the Monson. The $(Rb/Sr)_{wt.}$ ratios
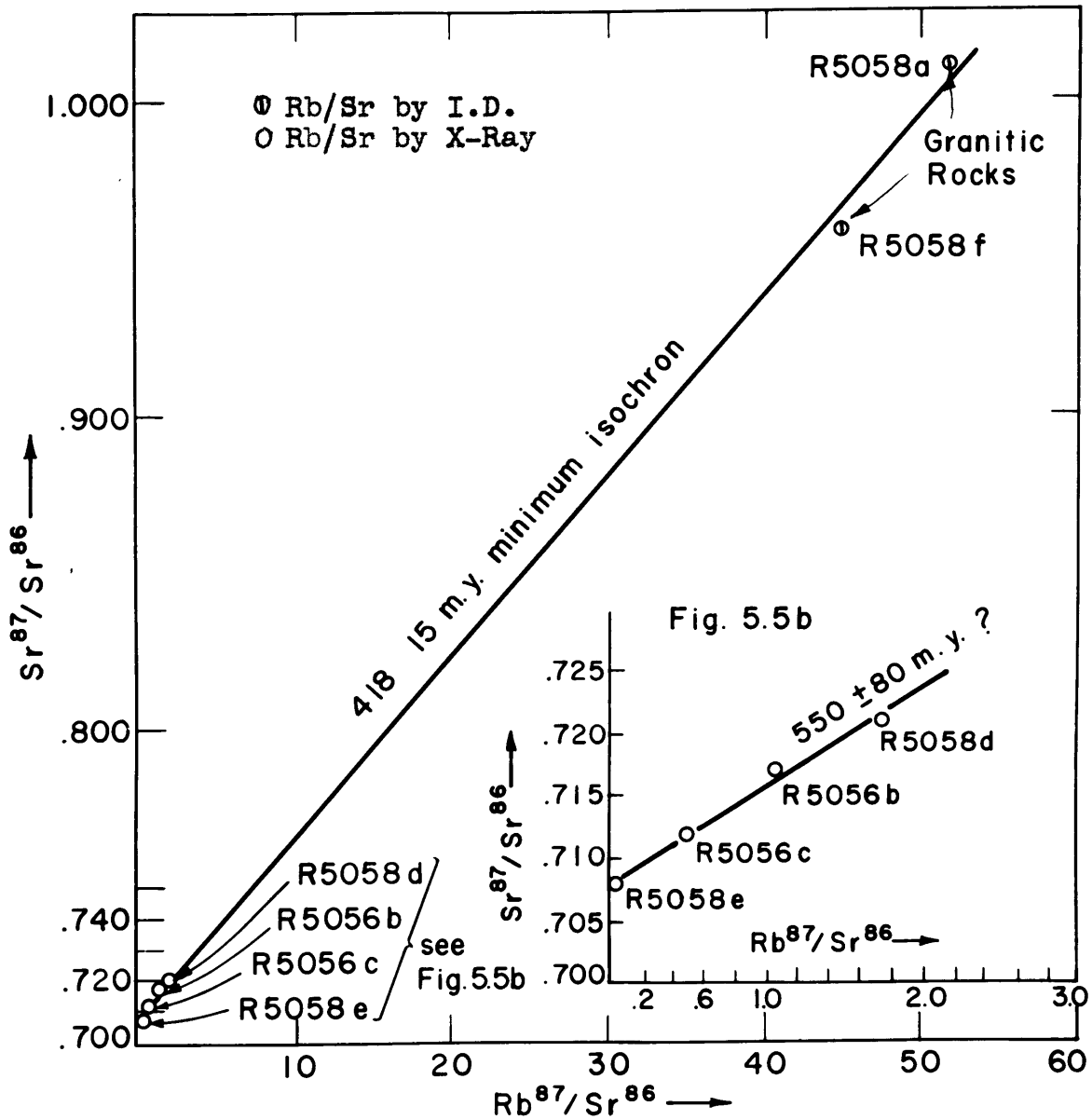
FIG. 5.5a MONSON GNEISS MINIMUM WHOLE – ROCK
ISOCHRON $\lambda = 1.39 \times 10^{-11}$ yr^{-1}

for the granitic dike samples are very high relative to the plagioclase gneisses, and thus influence the isochron of Figure 5.5a to a great degree. Figure 5.5b shows just the plagioclase gneisses plotted alone and a significantly different isochron results. Figure 5.5a shows the granitic dike - influenced isochron as yielding an age of 418 ± 15 m.y., but Figure 5.5b shows that the plagioclase gneisses yield an age of 550 ± 80 m.y. In either case, the initial $Sr(87/86)$ ratio is 0.708 ± 0.001, because R5058e anchors both isochrons.

Collins Hill Formation

All of the samples of the Collins Hill Formation were taken normal to the regional strike across the width of the formation in the vicinity of the Strickland Quarry. Figure 5.6 shows a possible isochron through most of the whole-rock points, but as the formation is a metasediment, the exact meaning of this apparent age is not clear. Samples R4718, R4720a, and R4723 have all been contaminated or infiltrated by reworked (pegmatitic?) material and define an entirely different slope shown with the whole-rock curve in Figure 5.7. The age of the isochron in Figure 5.7 is 210 ± 15 m.y., with an initial ratio of approximately 0.726. The aplite, R4722, which presumably intrudes R4723 also falls on this plot. The genetic implications will
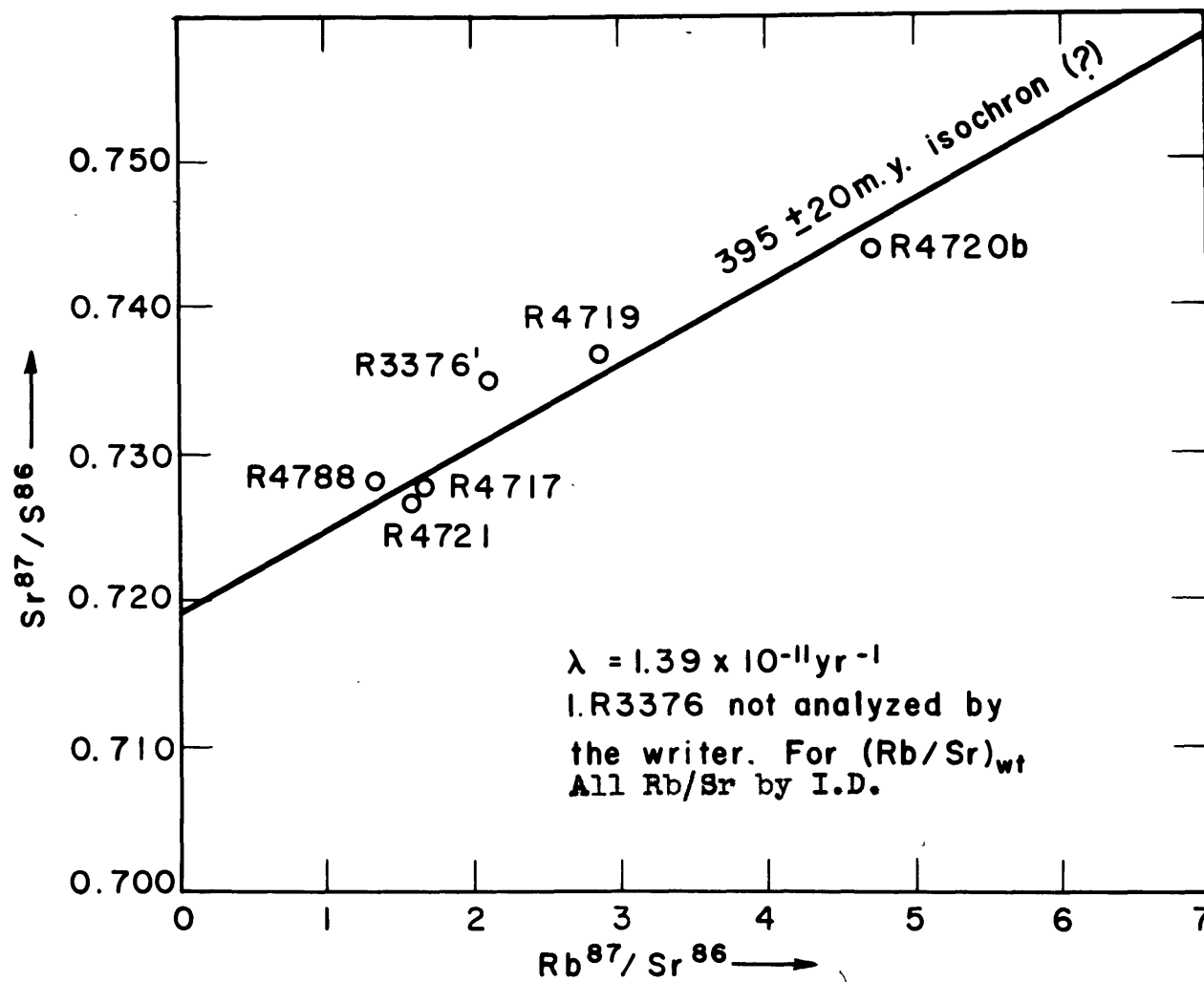
FIG. 5.6 COLLINS HILL FORMATION
POSSIBLE WHOLE-ROCK ISOCHRON
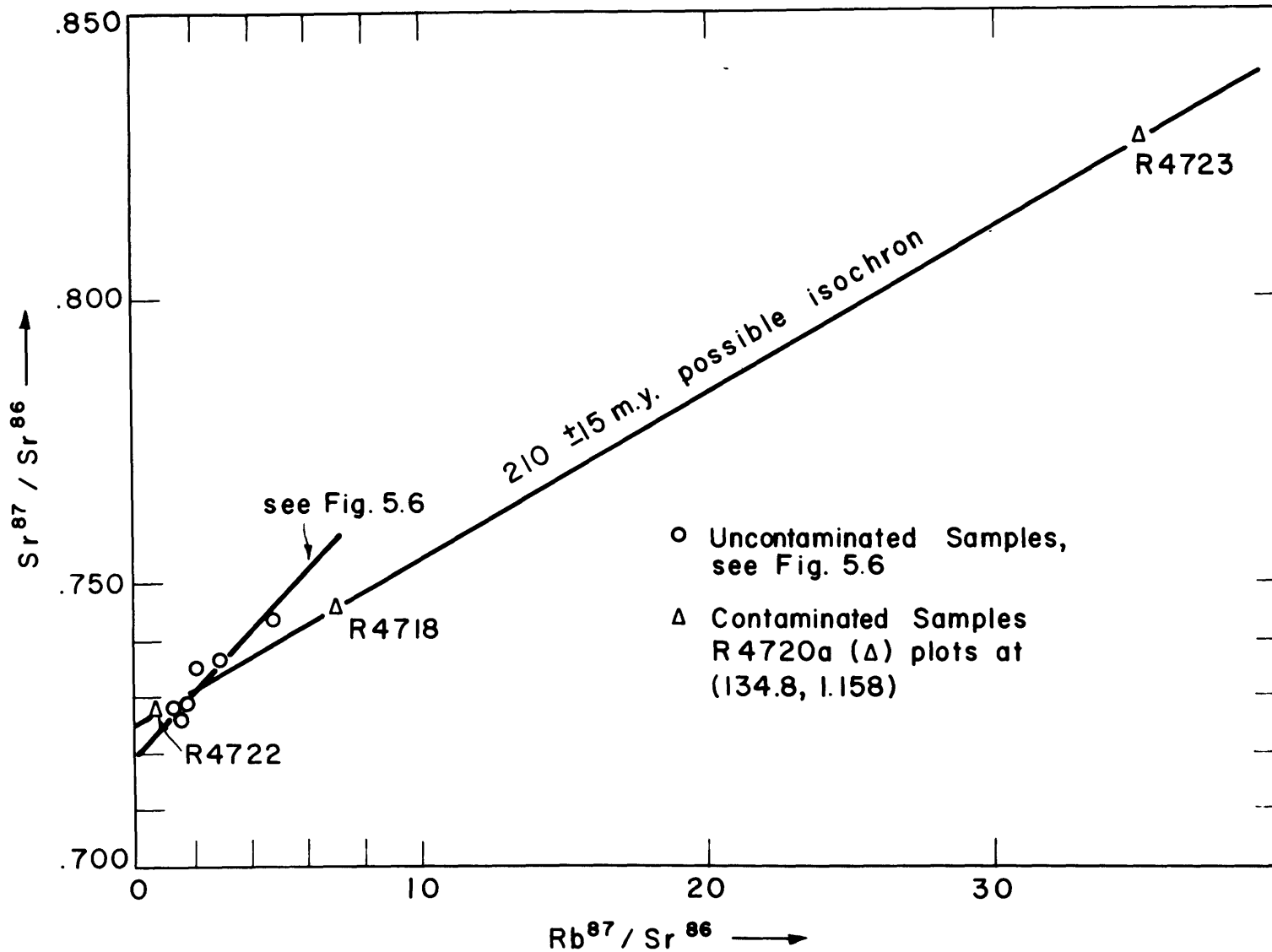
FIG. 5.7 COLLINS HILL FORMATION

All Rb/Sr by I.D.

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be discussed below for both these figures (see Chapter Six).

Pegmatites

Figure 5.8 shows an isochron for the primary minerals of the Strickland and Spinelli Pegmatites, and is taken from Figure 4.1a with the exception of A4774, a primary massive plagioclase from the Strickland Quarry. A secondary cleavandite from the Strickland Quarry, A4992, does not fall on this isochron, and shows an apparent enrichment of $*Sr^{87}$. Two whole-rock samples from the Hale Quarry, R5030 and R5031a, also do not fall on the mineral isochron, but lie close enough to it to be within experimental error. Sample A4774 allows the initial Sr(87/86) ratio to be placed at 0.735 $\pm$ 0.002, and the isochron age is 250 $\pm$ 10 m.y. As mentioned in Chapter Four, the mineral isochron of Figure 5.8 (= 4.1a) is defined by samples from both the Spinelli and the Strickland Quarries and thus confirms cogenesis of the two pegmatites, and that the Hale Quarry samples occur near this isochron suggests that all three pegmatites are cogenetic.

Discussion of the Data and Isochrons

The Maromas Granite Gneiss and the Glastonbury Gneiss show isochrons (Figures 5.2, 5.1) which suggest closure of both systems after emplacement (e.g. 287 and 360 m.y.). However, the initial Sr(87/86)
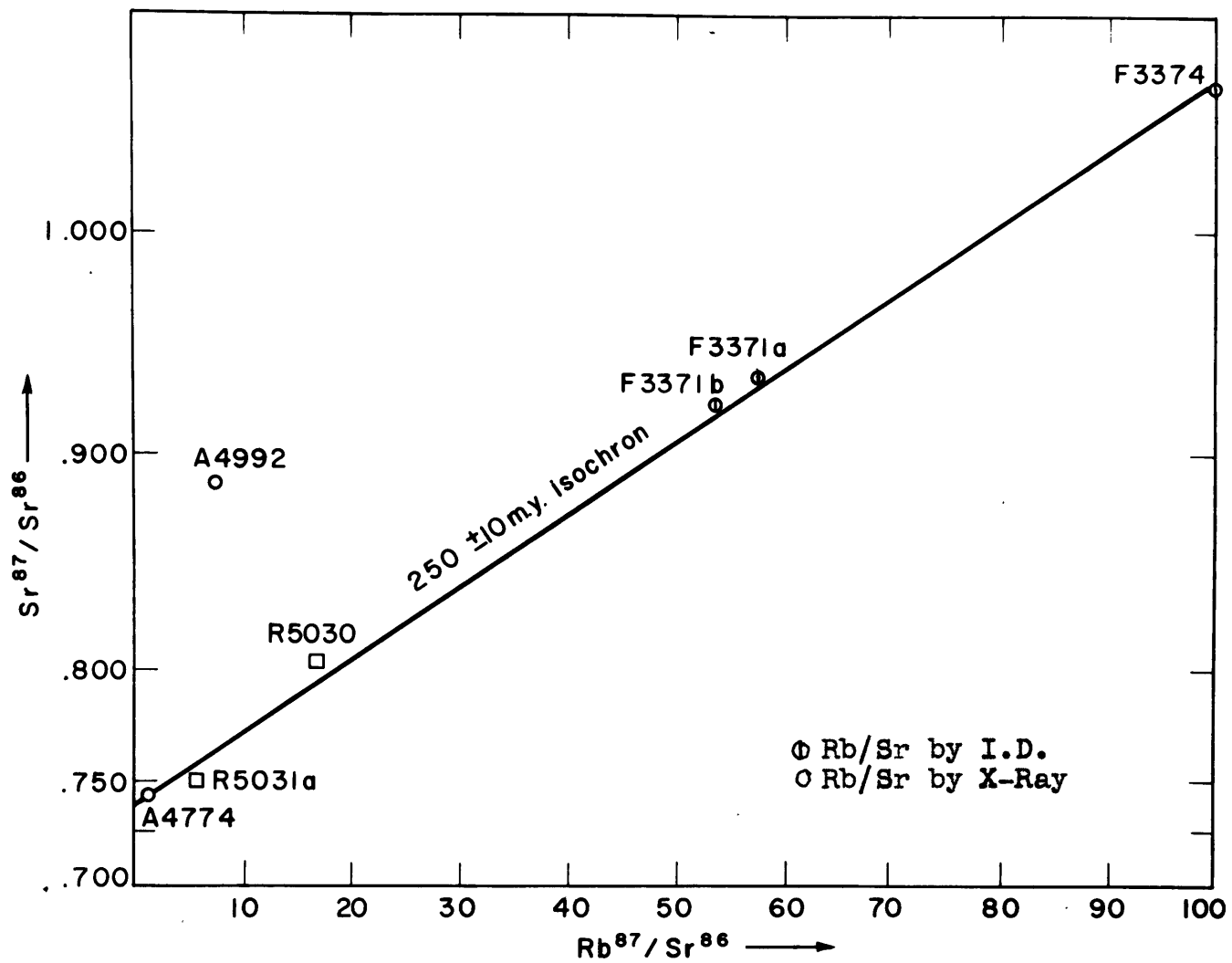
FIG. 5.8 PEGMATITES

ratios for the two gneisses are significantly different. The initial ratio of the Glastonbury Gneiss is 0.710, which is close to that of basalts and suggests little or no pre-history in a crustal reservoir before emplacement, but the initial ratio of the Maromas Granite Gneiss is 0.714, which strongly indicates a lengthy crustal pre-history before homogenization at 287 m.y. ago. The agreement in age between the 460 ± 15 m.y. Ammonoosuc Volcanics and the $450 \pm$ Middletown Formation confirms their correlation, and their initial ratios of 0.708 and 0.7065 respectively are within experimental error of each other. This in turn implies that much of the Middletown Formation is derived from volcanic material, as is the case for the Ammonoosuc Volcanics.

The Monson Gneiss presents more of a problem, as the relation of the granitic dikes which cut the basic gneisses that dominate the Monson is not known. If, as proposed by Mikami and Digman, the granite dikes are late-stage differentiation products of the cooling tonalitic magma which now occupies the Killingworth Dome, then the age of the Monson Gneiss is 418 ± 15 m.y. However, if these dikes are post-Monson, the 418 ± 15 is an absolute minimum age for the Monson, and the isochron defined by just the basic gneisses yields an age of 550 ± 80 m.y. This problem will be discussed in detail in

Chapter Six.

The pegmatite mineral isochron, Figure 5.8, defines an age of
250 $\overset{+}{-}$ 10 m.y., which is the same age as that reported by earlier
workers (see Chapter Four). That the two whole-rock samples from the
Hale Quarry fall near, but not on, the mineral isochron are probably
due to either experimental error or lack of closure with respect to
Rb and/or Sr in each sample.

How to interpret the Collins Hill Formation data is not clear,
although it is obvious that some of the whole-rock samples yield
mineral ages near 210 $\overset{+}{-}$ 15 m.y., and these samples have been subjected
to infiltration of pegmatitic tourmaline and/or aplite. The re-
mainder of the whole-rock samples, Figure 5.6, show a scatter about a
possible isochron, but the apparent 395 $\overset{+}{-}$ 15 m.y. age is difficult to
interpret because scatter of points above a hypothetical isochron
based on pure authigenic Sr and Rb is to be expected (see Chapter
Two) and false apparent ages are common. However, the high initial
ratio of this possible isochron does imply significant detrital
$^*Sr^{87}$ in the metasedimentary system.

The above discussion and results will be expanded in the next
chapter, and are presented here merely as a brief review.

Least Squares Treatment of Data

The application of any rigid, statistical formulae to natural system data is open to criticism because of unknown parameters. For whole-rock Rb-Sr analyses there is no certainty that the system(s) in question are (1) closed, and (2) that the weight of each point on a scattergram can be properly stated due to the uncertainties in the standard deviation of both the X and Y parameters about each point. Thus the method of constructing maximum and minimum isochrons through assumed error limits about each analytical point is probably more realistic. However, any least squares slope or intercept must fall within the error limits of the visually-constructed isochron. To test the data presented in Tables 5.1 and 5.2, least squares ages and initial Sr(87/86) ratios have been determined for the Maromas, Glastonbury, Middletown, Ammonoosuc, and Monson formations. Table 5.3a shows the results of these calculations assuming equal weights for all the samples of each megasystem, and Table 5.3b shows the calculated results for those megasystems in which different weights have been assigned to the various local system analyses. The formulae employed have been discussed by Youden (1951), and, in brief, state that for the straight-line equation of the type Y = A + BX:

$$A = \frac{(\Sigma X)(\Sigma XY) - (\Sigma Y)(\Sigma X^2)}{(\Sigma X)^2 - N(\Sigma X^2)}$$

$$B = \frac{N(\Sigma XY) - \Sigma X \Sigma Y}{N \Sigma X^2 - (\Sigma X)^2}$$

These formulae allow for both X and Y errors in calculating the slope and intercept.

TABLE 5.3a

Formation	Least Squares Age	Least Squares Intercept
Middletown	444	0.7073
Ammonoosuc	452	0.7090
Monson	530	0.7083
Maromas	281	0.7149
Glastonbury	355	0.7100

TABLE 5.3b

Formation[4]	Least Squares Age	Least Squares Intercept
Middletown[1]	443	0.7072
Monson[2]	536	0.7084
Maromas[3]	279	0.7149

1. Sample R5053b weighted once, all other samples weighted twice.
2. Sample R5056c weighted twice, all other samples weighted once.
3. Samples R4791d, R5059b weighted once, all others twice.
4. See Table 5.3a for Ammonoosuc and Glastonbury results, as all samples for both formations were weighted equally.

Whitney (1962) has used other formulae of Youden (op. cit.) to determine the standard deviation of both A and B, but the formulae considered do not allow for any X-parameter error for A_A and presume equal weight of all analytical points for B. For example, if we consider A as a Rb-free point on an isochron, Faure (1961) has shown that the standard deviation should be $\pm$ 0.002, but use of the formulae employed by Whitney (op. cit.) yield $\pm$ 0.0015 for the Middletown Formation and $\pm$ 0.0018 for the Maromas Gneiss .

CHAPTER SIX: Discussion and Conclusions

Relationships Between the Various Formations

(I)   Great Hill Quartzite - Collins Hill Formation

An angular unconformity exists between the Great Hill Quartzite

and the overlying Collins Hill Formation (see Rodgers and Rosenfeld,

1959), and the Great Hill is in part conglomeratic in its basal members.

(II) Great Hill Quartzite - Glastonbury Gneiss

The Great Hill Quartzite is probably younger than the

Glastonbury Gneiss because of a basal conglomerate in the former, and

lack of field evidence to support intrusion of the Glastonbury into

the Great Hill.

(III) Glastonbury Gneiss - Collins Hill Formation

Rodgers and Rosenfeld (1959) mention that the Glastonbury may

be intrusive into the Middletown, but that the Collins Hill Formation

probably lies unconformably over both. However, the Glastonbury -

Collins Hill contact is obscure and difficult to interpret. Westgate

(1902) suggested an intrusive contact based on inclusions of Collins

Hill (called Bolton) schist within the Glastonbury near the Strickland

Quarry, but these exposures were later covered by dump material.

Similarly, the schlieren present in the Glastonbury may also be

interpreted as incompletely digested remnants of schist, and the
presence of diopside in the Collins Hill near the Glastonbury contact
may also indicate intrusion. Stugard (1958, p. 629) suggests that
the Collins Hill (called Bolton) and the Middletown (called Mafic
Gneisses) Formations are cut off at depth by the Glastonbury, based
on comparison of dips of foliation.

(IV) Maromas Granite Gneiss - Middletown Formation

The Maromas Granite Gneiss is observed to cut the Middletown
Formation in three major areas (see Figure 1.3), and has been noted
as intimate dikes and sills cutting the Middletown in numerous other
places (Rosenfeld and Eaton, 1958). It is generally accepted that the
Maromas is intrusive into the Middletown, although Westgate (1899)
and Stugard (1958) have suggested the possible derivation of the
Maromas from the Middletown because of their intimate relationship,
and Rosenfeld and Eaton (op. cit.) have also suggested a hybrid origin
for the Maromas based on similar observations.

(V) Collins Hill Formation - Middletown Formation

Rice and Gregory (1906/7) proposed that the Middletown Formation
represents a contact zone between the intrusive Monson Gneiss and the
intruded Collins Hill Formation, and Mikami and Digman (1957, p. 47)

have also suggested a conformable sequence upwards from Middletown into Collins Hill because of formational parallelism and localized inter-fingering of the formations along their contact. However, careful mapping by Rosenfeld and Eaton (in Rodgers and Rosenfeld, 1959) has shown an unconformity to exist.

(VI) Maromas Granite Gneiss - Collins Hill Formation

The northernmost of the major Maromas lenses occurs on the west side of Collins Hill near the Strickland Quarry and has been studied by this writer in some detail, and although the contact relations are obscure, the following generalizations can be made: (1) there are schlieren-type inclusions of Collins Hill Schist within the Maromas Granite Gneiss near the contact; (2) Although there are no distinct dikes or apophyses of Maromas which cut the Collins Hill, there are Maromas-derived aplites which appear to cut the Collins Hill; (3) Near the Maromas contact, the Collins Hill still shows the regional NW strike, but it is not as well defined as more distant parts removed from the Maromas contact. Thin section shows that the biotite in the Collins Hill near the Maromas is randomly oriented, whereas biotite away from the contact is well-oriented. This lack of orientation of the biotite near the contact may indicate intrusion, as others have noted this effect (Hart, 1960).

(VII) Maromas Granite Gneiss - Monson Gneiss

There is no exposure of the Maromas - Monson contact in the area, and it is probable that the Maromas has transected the Monson at depth. Future gravity work may substantiate this.

(VIII) Maromas Granite Gneiss - Glastonbury Gneiss

There also are no exposures of the Maromas - Glastonbury contact. However, due to several similar features (see Chapter One) many workers in the area have placed these two gneisses in close proximity on the geologic column (see Foye, 1949, Lundgren, 1962, Eaton and Rosenfeld, 1959). Both of these gneisses are characterized by a large amount of quartz and by a granitic appearance in large, but other correlative points are few. Some of the salient features of the Glastonbury are: (1) Well developed foliation striking NW, plus evidences of earlier foliations. (2) Herz (1955) was able to map at least four distinct facies within the Glastonbury, which illustrates its well defined structure. (3) Abundant pegmatites, commonly of the cross-cutting variety. However, the Maromas Granite Gneiss exhibits the following features: (1) A fair foliation striking to the NW, but no positive evidence of any earlier foliation. (2) Sub-divisions of the Maromas are vague, probably due to emplacement (suggested earlier) during the early stages of the last major metamorphism of the area. (3) Paucity

of pegmatites within the Maromas (Stugard, 1958, lists only one

pegmatite which definitely occurs in the Maromas). (4) Aplites, which

can be traced as grading into the Maromas, show the same intrusive

nature against the Collins Hill Formation as do the aplites associated

with the pegmatites which occur within the Collins Hill, but the

Glastonbury exhibits no such aplites. Thus it may be inferred from

the above arguments alone that the Maromas is of a significantly

later age than the Glastonbury. This is borne out by the current work

(Chapter Five).

(IX) Middletown Formation - Monson Gneiss

The relation of the Middletown Formation to the Monson Gneiss

has been reported in Chapter One. A gradational contact from younger

Middletown to older Monson has been advocated by Lundgren (1962) and

Eaton and Rosenfeld (1960), but Mikami and Digman (1957) have argued

that the Middletown Formation is intruded by the Monson and that the

so-called gradation between the two is actually a mixed zone, possibly

due to incomplete digestion of the Middletown by the tonalitic Monson

magma.

Conclusions

(I) Maromas Granite Gneiss

The Maromas Granite Gneiss became a separate multiplex chemical system 287 $\pm$ 10 m.y. ago, at the probable time of intrusion of the Maromas into the Collins Hill and Middletown Formations. The scatter of points about the whole-rock isochron is limited and indicates that the Maromas was derived from a homogeneous parent source and has remained a closed system after emplacement. The initial Sr(87/86) ratio is 0.714, which suggests that the intruded material had a high Rb/Sr pre-history before emplacement; but the nature of this pre-history is unknown. The time interval between the 287 Maromas age of emplacement and the 250 age of emplacement of the pegmatites was sufficient for some regional structures to develop within the Maromas megasystem. The pegmatites do not represent late-stage differentiation products of the crystallizing Maromas because the initial Sr(87/86) ratio of the Maromas is 0.714, which is too low to allow a mineral isochron with a 0.735 initial ratio to develop in a span of 30 to 40 my.

(II) Glastonbury Gneiss

The absolute Rb-Sr age of the Glastonbury Gneiss is $360 \pm$
10 m.y., but this age does not resolve the problem of the Collins
Hill - Glastonbury relationship because of the uncertainties in-
volved in the interpretation of the Collins Hill "age". The 360 m.y.
age for the Glastonbury is defined by a six point isochron and in-
dicates closure of at least the porphyroblastic facies since that
time, and that this facies was probably homogeneous. The initial
ratio of the Glastonbury is 0.710, which is close to the subsialic
source region-derived rocks (see Chapter Two); but to therefore as-
sume an intrusive history of the Glastonbury may be erroneous because
careful mapping by Herz (1955) and others suggests derivation in part
from non-intrusive rocks. The absolute age of 360 m.y. does, however,
explain the more advanced degree of foliation within the Glastonbury
relative to the Maromas, and probably lack of any direct genetic re-
lationship to the pegmatites in the area (of a 250 m.y. age). The
difference in the initial $Sr(87/86)$ ratios between the Glastonbury
and the pegmatites (e.g. 0.710 as opposed to 0.737) also disproves
any direct cogenetic relationship.

(III) Correlation of the Ammonoosuc Volcanics of New Hampshire with
the Middletown Formation of Connecticut

The data presented in Chapter Five show good agreement between
the ages for the Ammonoosuc Volcanics and the Middletown Formation
and thus confirms their contemporaneity. Both the Ammonoosuc and
Middletown groups of samples show a narrow spread of Rb/Sr values,
leading to the error limits of $\pm$ 15 m.y. for both the 450 m.y.
Middletown and the 460 m.y. Ammonoosuc. The Ammonoosuc Volcanics
occur in four distinct belts in New Hampshire and show no clear doming
effects or relationship to any one dome, and thus the suggestion of
Lundgren (1962) that the Middletown may be a facies of the dome-
(or anticline-) forming Monson Gneiss is inconsistent with regional
evidence. The mean age of 455 $\pm$ 10 m.y. for both the Middletown
and the Ammonoosuc is proposed, but the relationship of this absolute
age to the time scale problem is tenuous because the Geologic Age is
open to some question and the decay constant is in doubt. The ini-
tial Sr(87/86) ratios for the Middletown and Ammonoosuc Formations
are respectively 0.707 $\pm$ 0.001 and 0.708 $\pm$ 0.001 and confirm their
derivation (at least in part) from basic volcanics.

(IV) Monson Gneiss

A minimum age of 418 ± 15 m.y. may be placed on the Monson Gneiss, but is largely controlled by samples from a granitic dike which cuts part of the formation, and until further evidence either proves or disproves the cogenesis of these dikes with the more basic gneisses, only the above minimum age can be given. If the granitic dikes are not considered as part of the Monson, an entirely different age results as shown in Figure 5.5b of 550 m.y., but with a large ± 80 m.y. error. The large error results from the low $(Rb/Sr)_{wt.}$ ratios of the basic gneisses which allow very different maximum and minimum isochrons to be drawn through the limits of error about each point. The initial $Sr(87/86)$ ratio of the Monson Gneiss is 0.708 ± 0.001, which again is close to that suggestive of derivation of parent material from the subsialic source region. Because of the differing opinions as to the relation of the above-mentioned granitic dikes (see earlier dis-cussion) the Monson-Middletown relationship cannot be resolved; but it is interesting to note that the Monson does not cut the Collins Hill Formation in the area, which may suggest that the doming in the area took place after the emplacement and/or deposition of Monson-Middletown-Collins Hill in normal stratigraphic order. That the

Collins Hill Formation is younger than the Monson is indisputable from this argument, and is supported by the fact that the granitic dikes which cut the Monson do not apparently cut the Collins Hill.

(V) Collins Hill Formation

Samples from the Collins Hill Formation which have not been contaminated by pegmatitic material define a series of points through which an apparent isochron can be constructed. Although the age of this possible isochron is 395 ± 15 m.y., this age does not help interpret the relationship of the Collins Hill Formation to the other basement rocks because of the problems of detrital phases rich in $^{*}Sr^{87}$ in the original material at the time of deposition, which would lead to scatter of points when there is an unequal distribution of authigenic versus allogenic Sr and Rb in the megasystem among the various local systems. Therefore the importance of the 395-apparent age yielding isochron is only two-fold: (1) Samples defining this possible isochron have been taken at, near, and removed from the Strickland pegmatites, and thus indicate that local systems are too restrictive for widespread migration of material to take place, and

(2) the high initial Sr(87/86) ratio of this apparent isochron of 0.719-$^+$0.002 definitely shows influence of $^*87^{87}$ enrichment in the allogenic components of the original sedimentary material. There has been some type of exchange system set up between pegmatitic aplites and their immediate host rocks, as evidenced by the samples R4722, an aplite, and R4723, Collins Hill Formation plus some aplite. The isochron for the pegmatites in the area is well established as having an initial Sr(87/86) ratio of 0.737 $^+$ 0.002, and the aplite yields 0.7280 $^+$ 0.002, but the host rock to the aplite (R4723) yields 0.8280 for a Rb/Sr ratio of 12.0, which falls well below the possible Collins Hill Isochron. An isochron constructed between R4722 and R4723 yields an absolute age of approximately 210 m.y., and thus indicates that there has been a local re-homogenization in restriced contact zones between the pegmatite and the host rock. As seen in Figure 5.7, two other samples also fall on this isochron, R4720a and R4718, both of which have been contaminated by some pegmatitic material. The exchange of pegmatitic and host rock material is limited to those local systems adjacent to the pegmatite, and the only when structural conditions are favorable. The uncontaminated whole-rock samples represent

the complete stratigraphic section of the Collins Hill Formation in the vicinity of the Strickland Quarry, but may not be representative of the Collins Hill over the entirety of the outcroppings.

Mantled Gneiss Domes

This writer has not engaged in field investigations on the problem of mantled gneiss domes. However, it is felt that the Rb-Sr information on the Monson, Glastonbury, and Maromas domes is of genetic significance and places severe limits on the various interpretations presented in the literature.

(I) Glastonbury Dome

The 360 ± 10 m.y. age for the Glastonbury Gneiss does not resolve the Glastonbury - Collins Hill problem because of the previously mentioned uncertainties concerning the apparent 395 ± 15 m.y. age of the Collins Hill, but the Glastonbury whole-rock isochron does indicate that the porphyroblastic facies of the gneiss to be of an orthogneissic origin, and a closed system since 360 ± 10 m.y. ago.

If the Glastonbury Gneiss is intrusive into the Collins Hill Formation, then assimilation of the Collins Hill by the Glastonbury

near their contact has been negligible, as evidenced by the low

initial Sr(87/86) ratio of the Glastonbury (0.710) as opposed to the

high initial ratio (0.719) of the Collins Hill. If assimilation

played any significant role, one would expect the initial ratio of

the Glastonbury to be higher than 0.710 because of inherited excess

$*Sr^{87}$ from the Collins Hill schists.

(II) Maromas Dome

The Maromas Granite Gneiss yields a whole-rock isochron which
defines an age of 287 $\pm$ 10 m.y., and this age is much less than that
of any of the other domes or pre-pegmatite country rocks in the area.
This age confirms the fact that it was emplaced during the beginning
of the Appalachian Oregeny, and the poor- to fair-foliation developed
is explained by the length of the orogeny (e.g. pegmatites emplaced
at about 250 m.y., metamorphism of country rocks ended at about 220 -
230 m.y.).

The high initial Sr(87/86) ratio of the Maromas Granite Gneiss
can originate in several different ways as discussed in Chapter Two.
Assimilation of K-rich border facies of host rock is probably not
significant. because the Maromas is not in contact with the same
Collins Hill members in all exposures from which samples have been
taken, and thus the well-defined isochron (Figure 5.1) would not be
expected in this case. It is more logical to assume that the Maromas
represents material derived from a homogenized parent which has under-
gone a previous crustal history. Whether the parent material re-
presents a continually rehomogenizing magma chamber (see Model VIII,
Chapter Two) or another form of remobilized material cannot be
decided from this study, as both cases yield a high initial Sr(87/86)

ratio.

It is also suggested that, because the Maromas is the youngest
of these domes, and because it shows the clearest intrusive contacts
into the other country rocks, the repeated regional metamorphisms
(Acadian (?), Appalachian (?)) could have destroyed the contact
features of the Glastonbury and the Monson with their host rocks.

(III) Killingworth Dome

A minimum age of 418 ± 15 m.y. can be placed on the Monson Gneiss
from Figures 5.5a and 5.5b, but this age is controlled by the granitic
dikes which cut the formation. There is scant evidence that these
dikes are genetically related to the more basic plagioclase gneisses
and thus the age is probably not valid, and if the dikes are unrelated
to the plagioclase gneisses then a false minimum age is represented by
Figure 5.5a, and the plagioclase gneisses define a possible older iso-
chron of 550 ± 80 m.y. (Figure 5.5b). In either case, the Monson Gneiss
is of a significantly different age than the Maromas or the Glastonbury
Gneisses. The relationship of the Monson to the Middletown cannot be
resolved from these ages and the initial $Sr(87/86)$ ratio of 0.708 is
consistent with either hypothesis. However, Peter Robinson, of Harvard
University, (Personal Communication) has shown that the Middletown-
equivalent (Ammonoosuc) overlies the Monson in Massachusetts.

(IV) Tentative Conclusions

The gneissic rocks which now occupy the Maromas, Glastonbury

and Killingworth (Monson) domes are of three significantly different

ages, and thus the proposed similarity in age of the gneissic domes

in the New Hampshire part of the Bronson Hill Anticline (see

Billings, 1956) is probably not warranted. It is possible that the

doming mentioned above represents intrusions of three different

orogenic periods: the Taconic, Acadian, and Appalachian. It is

interesting to note that the data for the three domes fit theoretical

model VIII (Chapter Two), the case for repeated removal of material

periodically from a continually homogenizing reservoir. Thus

$R_{mr} > R_{gl} > R_{mo}$ but $t_{mo} > t_{gl} > t_{mr}$, but more statistics are needed to

substantiate this hypothesis. There are enough indications, however,

to demonstrate that the Rb-Sr whole-rock method can aid in inter-

preting the geologic relationships and genesis of gneiss domes, and

this is the real value of the investigation.

Pegmatite Investigations

The geology of the pegmatites studied has been described in Chapter One, and the age work on these pegmatites in Chapters Four and Five. This section will attempt to summarize features of these pegmatites and discuss theories of genesis.

Three different theories for genesis of the pegmatites in the area have been proposed: (1) magmatic injection from an unexposed parent source, which has been discussed by Chadwick (1958), Stugard (1958), Jenks (1935), and Cameron et al. (1949, 1954). (2) Magmatic injections of late-stage segregations of the Glastonbury and/or Maromas gneisses, which has been discussed by Westgate (1899) and Foye (1949). (3) Metamorphic theories, including metasomatism of the country rocks (Collins, 1954), partial fusion of country rocks (see general discussion in Turner and Verhoogen, 1960), and secretional theories (as in Rosenfeld and Eaton, 1958). These theories will be discussed below.

(I) Relation of the Strickland Quarry Pegmatite to the Collins Hill Formation

Rosenfeld and Eaton (1958) have suggested that the abundance of pegmatites within the Collins Hill Formation may be due to lateral secretion of material "sweated out of the Collins Hill during metamorphism, aided by the fluxing action of CO_2 and H_2O,

which were undoubtedly driven off in large quantities during the
event. The current geochronological investigations are not sufficient
to answer this theory, but some restrictions can be placed on this
source by considering the theoretical models for pegmatite genesis
which have been described in Chapter Two. Case VII-A (magmatic in-
jection from an unexposed source material) can be discarded because the
initial $Sr(87/86)$ ratio of the pegmatite mineral (and whole-rock ?)
isochron is 0.737, which is much greater than that of any known acid
igneous rock (see Hurley et al., 1962). The initial ratio of the
Collins Hill Formation is 0.719, so this is a good case to test the
primary magmatic melt theory, but it does not apply to the Strickland
Pegmatite. Riley (196) has proposed that possibly one pegmatite in
the Western Australian Shield may be of a near-mantle derivation be-
cause of a possible low initial ratio, but the isochron is poorly de-
fined and inconclusive to warrant the statement.

Case VII-B (In Situ diffusional theory) may be discarded because
(1) there is every evidence for forceful injection of the pegmatite
into its host rock, (2) the abundance of Sr^{87} in the pegmatite is in-
consistent with any diffusional model as Sr should migrate parallel
to Ca and not K and Na, (3) the apparent Collins Hill Isochron,
Figure 5.6, for uncontaminated samples is defined from specimens taken

both near and removed from the pegmatite, and thus the local systems
are too restrictive to have allowed any widespread migration of
material in situ, and (4) any such model must of necessity be a slow
continuous one, and thus the earliest formed parts of the pegmatite
would be expected to show effects of the regional foliation, but this
is not observed.

Case VII-C (injection of re-mobilized material) is the most
applicable of the theoretical models for the Strickland Quarry
Pegmatite because it suggests injection of a homogeneous pegmatitic
material into its present site as evidenced by lack of influence of
the pegmatite on the Collins Hill (isochron) except in the immediate
contact zone, and because of its very high initial $Sr(87/86)$ ratio.
It is interesting to note that an excess of Sr^{87} has been observed in
pegmatites which occur in regionally metamorphosed areas in other
parts of the world. Giletti et al. (1961) have reported excess $^*Sr^{87}$
from the Knoydart Pegmatite in Scotland, and Riley (1961) has also
found such an excess in the Harts Range and Bindoon pegmatites in the
Western Australian Shield area. From the same area, Compston and
Martin (in press) have presented evidence of excess $^*Sr^{87}$ in the
Donneybrook pegmatite, which, unlike the others, is a small (less than

one foot in width) pod-like pegmatite occurring in granite gneiss,
and which they can demonstrate by Rb-Sr work, to have been derived
from the surrounding rocks by some secretional (possibly anatectic)
process. It is difficult to apply their results to a large pegmatite
such as the Strickland, however.

(II) Relation of the Pegmatites of the Area to the Maromas Granite
      Gneiss and/or the Glastonbury Gneiss

Because of their close relationship in age (e.g. 250 as opposed
to 287 m.y.) it is tempting to suggest a genetic relationship between
the Maromas Granite Gneiss and the pegmatites of the area. However,
the vast difference in initial $Sr(87/86)$ ratios for the two suggest a
complete lack of direct genetic relationships, as the Maromas yields
0.714 and the pegmatites 0.735. Riley (1961) found that the York
pegmatite was related to its petrographically-indicated parent granite,
and found agreement in initial ratios. Vlasov (1961), Jahns (1955),
and Orville (1961) have discussed such petrographic guides, but they
have not been applied to the Maromas.

By similar reasoning, the initial ratio of 0.710 for the
Glastonbury and its 360 $\pm$ 10 m.y. age suggests lack of any genetic
relationship with the pegmatites of the area. The two whole-rock samples

from the Hale Quarry, R 5030 and R5031a, fall near the mineral isochron, and their departure from this isochron may be due to either experimental error or inadequate sampling. A line can be constructed through the two points which has a steeper slope than the mineral isochron and which yields an age of approximately 350 - 360 m.y. This age is inconsistent with field evidence, because there is no evidence of regional foliation developed on any significant scale in the pegmatite which would be present if the above ages were real.

(III) Conclusions for Genesis of Pegmatites in the Area

The probable age of emplacement of the pegmatites is 255 ± 10 m.y. based on concordance between U-Pb, Th-Pb, K-Ar and Rb-Sr ages, but this age probably does not mark the end of the Appalachian Orogeny as mineral ages for the Collins Hill Formation and Glastonbury Gneiss are lower (e.g. 220 ± 10). Further evidence that the 255 ± 10 age merely represents the closure of the pegmatite systems is indicated by the excess of $^*Sr^{87}$ in a secondary cleavandite, A4992, in the Strickland Pegmatite. The Spinelli Prospect Pegmatite and the Strickland Quarry Pegmatite are cogenetic with the Hale Quarry Pegmatite.

The pegmatites are not genetically related to either the Maromas or the Glastonbury Gneisses, and the parent material is unknown, although it must represent re-mobilized material.

Stratigraphy of the Pre-Triassic Rocks of the Middle Haddam and Glastonbury

Quadrangles, Connecticut

Figure 6.1 shows the suggested stratigraphic relations among the pre-Triassic rocks of the area, and incorporated the uncertainties concerning the Collins Hill and Monson ages.

FIGURE 6.1

Formation	Probable Geologic Age	Rb-Sr Age
Pegmatites	Mississipian (?)	255 ± 10
Maromas Granite Gneiss	(?)	287 ± 10
Bolton Group	Siluro-Devonian	(?)
Glastonbury Gneiss	(?)	360 ± 10
Collins Hill Formation	Middle to Late Ordovician (?)	395 ± 15 (?)[*]
Granite Dikes in Monson	(?)	418 ± 15[**]
Middletown Gneiss	Early to Middle Ordovician (?)	455 ± 10[***]
Monson Gneiss	(?)	550 ± 80

[*] absolute age uncertain, see Chapter Five and Chapter Six.

[**] minimum age, real age may be older.

[***] age based on average of 460 ± 15 m.y. Ammonoosuc Volcanics.

and 450 ± 15 m.y. Middletown Formation.

CHAPTER SEVEN: Sample Descriptions

(I) Collins Hill Formation (all samples normal to regional strike,
         from near the Strickland Quarry)

R4717   -   Biotite-quartz-(plagioclase) schist, taken 150 feet from
            the HW contact of the Strickland Pegmatite.

R4718   -   Tourmalinized biotite-quartz-garnet schist, taken less than
            2 feet from HW contact of pegmatite.

R4719   -   Biotite-quartz-(plagioclase)-(garnet) schist, 5 inches from
            FW contact of pegmatite.

R4720a -   Biotite-quartz-(pyritiferous) schist; coarse grained contact
            facies, FW side.

R4720b -   Biotite-quartz-sericitized feldspar-(garnet) schist, slightly
            mylonized, cut by quartz veins, contact facies, FW side.

R4721   -   Biotite-quartz-(garnet)-plagioclase schist, 15 feet from FW
            contact with pegmatite.

R4722   -   Quartz-albite-(muscovite) aplite; in contact with R4723.

R4723   -   Biotite-quartz-(garnet) schist, cut by numerous stringers
            of R4722. Contact zone.

R4788   -   Biotite-quartz-(plagioclase schist, approximately 20 feet
            from Maromas contact.

(II) Pegmatites

A4774   -   Massive plagioclase, some quartz, from Strickland Quarry dump.

A4992   -   Cleavandite, with minor quartz and light blue tourmaline,
            probably from transitional zone, Strickland Quarry dump.

R5030   - Pegmatite, Hale Quarry. Whole-rock sample showing both graphic granite and muscovite-bearing aplite.

R5031a   - Pegmatite, Hale Quarry. Musvocite bearing aplite.

(III) Maromas Granite Gneiss

R4791a,b,d   - Microcline-plagioclase (An_{14})-quartz-biotite gneiss with minor garnet. From the west side of Collins Hill near the Strickland Quarry. Samples a,b,c showed varying amounts of microcline and garnet in hand specimen

R5059a,b   - Microcline-quartz-plagioclase(An_{15})-biotite) gneiss, from near the main Maromas Dome, samples donated by Dr. J. W. Peoples, Wesleyan University.

(IV) Middletown Formation

R5052   - Amphibolite (Hdbe 70 percent, quartz 10 percent, plag(An_{33}) 20 percent), from west side of State Highway 17 south of intersection with Isinglass Hill Road.

R5053a,b,c   - Biotite-quartz-microcline-plagioclase gneiss (some epidote), from road cut on State Highway 15 approximately one-half mile past the turnoff to Vernon. Samples a,b,c represent the same outcrop, but with different amounts of biotite and microcline.

(V) Ammonoosuc Volcanics

R5069   - Rhyolite porphyry, from the Moosilaukee Quadrangle, north central ninth, 200 feet SW of highway bridge at Salmon Hole School. Donated by Dr. M. P. Billings of Harvard University (Harvard No. L-70).

R5070   - Quartz bearing soda rhyolite, from the Littleton Quadrangle, south central ninth, one-third mile NW of N. Lisbon School. Donated by Dr. M. P. Billings, Harvard University, (Harvard No. L-H56).

R5071   - Biotite gneiss, from Moosilaukee Quadrangle, south central ninth, two-thirds of a mile NW of Long Pond. Donated by Dr. M. P. Billings of Harvard University (Harvard No. L-H48).

R5072   - Chlorite-epidote schist, from Littleton Quadrangle, south central ninth, site of Slate Ledge School. Donated by Dr. M. P. Billings of Harvard University, (Harvard No. L-490).

(VI)   Glastonbury Gneiss

R4792a,b,c   - Granite gneiss, from contact zone near Collins Hill contact east of Strickland Quarry. Sample a,b,c selected only after quick scan X-Ray spectrographic study.

R4998   - Chloritized biotite-quartz-plagioclase gneiss, taken from outcrop south of Spinelli Prospect in which no microcline was visible in hand specimen.

R4999   - Chloritized biotite-quartz-plagioclase gneiss, taken just east of contact with Hale Quarry Pegmatite.

(VII)   Monson Gneiss

R5056,b,c   - Plagioclase-quartz-hornblende gneiss, from outcrop on State Highway 2 approximately 2 miles NW of Marlborough.

R5058   - (Mafic)-plagioclase gneiss and granitic dikes, taken south of Higganum from various exposures. R5058a,f represent granitic material, presumed to be related to the more basic rocks; and R5058d is a biotite-plagioclase-quartz gneiss, and R5058e is a hornblende-plagioclase-quartz gneiss.

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Biography

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