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WHOLE-ROCK RUBIDIUM-STRONTIUM AGE OF THE SILURIAN-DEVONIAN BOUNDARY IN NORTHEASTERN NORTH AMERICA

by

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Captions for Figures and Tables

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Table 1. Analyses of Eimer and Amend $SrCO_3$. Lot #492327.

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Figure 4. Plot of data which yielded 413 ± 5 M.Y. age for the Silurian-Devonian boundary. Hedgehog Formation sample numbers are on left side of lines, and the Eastport Formation sample numbers on right.

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ABSTRACT

Nine whole rock samples of the Skala (post-Ludlow, pre-Gedinnian) age volcanics from the Eastport Formation, Eastport, Maine, and nine whole rock samples of Lower Devonian (New Scotland age) volcanics from the Hedgehog Formation, Presque Isle, Maine, have been analyzed for their rubidium, strontium and strontium isotopic composition. The analyses of the Eastport volcanics produced an isochron age of 412 ± 5 M.Y. ($\lambda_{Rb^{87}} = 1.39 \times 10^{-11}$ year^{-1}) with an initial ratio of 0.707 ± 0.001. The Hedgehog Formation volcanics yielded an isochron age of 413 ± 10 M.Y. with an initial ratio of 0.706 ± 0.002. Combining the results gives an age of 413 ± 5 M.Y. for the Silurian-Devonian boundary; this age is based on the average of the age values of the individual samples, and the precision assigned is two standard deviations of the mean of the individual ages. This age is a precise measurement of the Silurian-Devonian boundary in northeastern North America and is in reasonable agreement with recent time scale estimates considering the uncertainty of the Rb^{87} decay constant.

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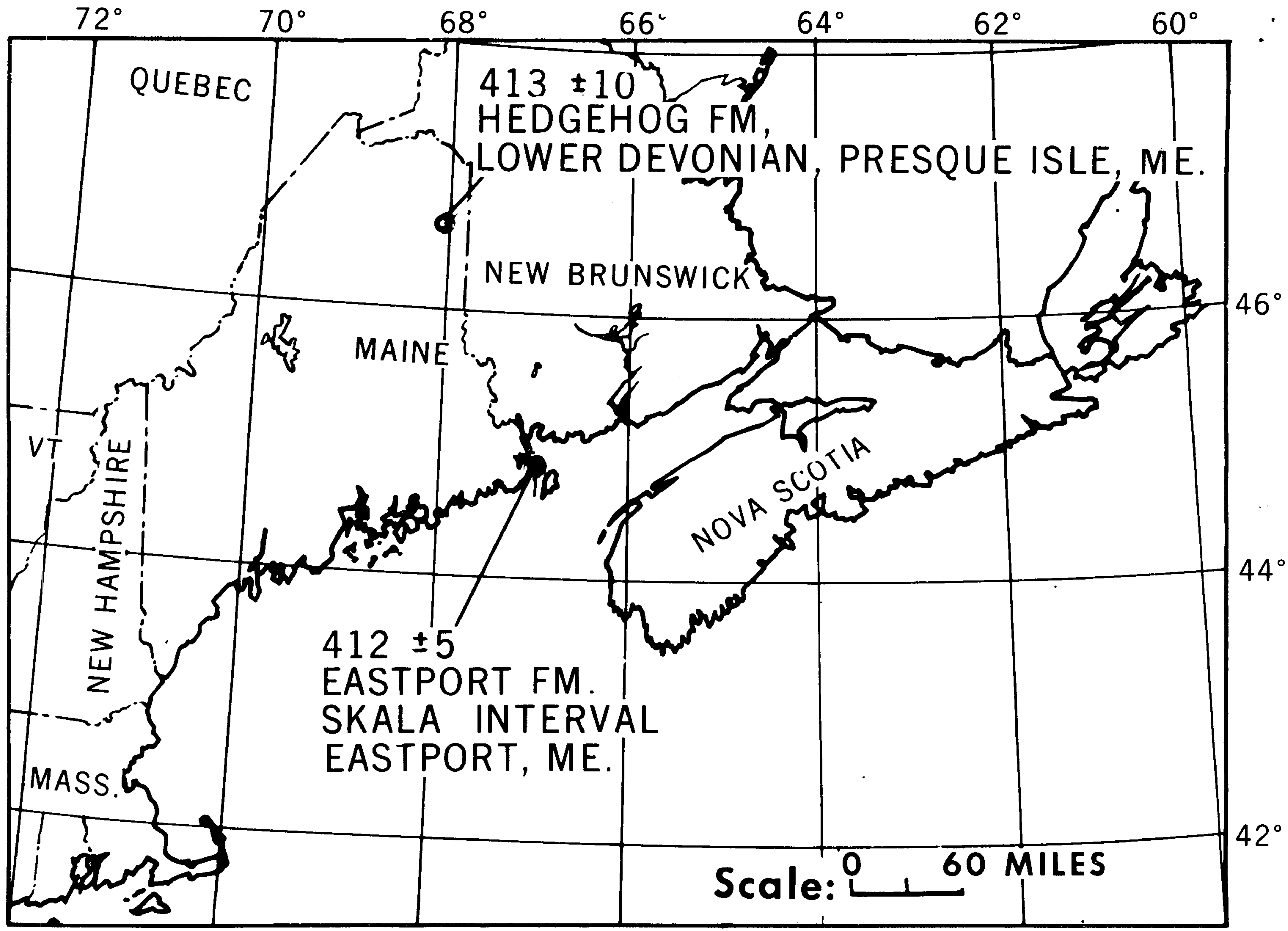
INTRODUCTION

Whole rock Rb-Sr age determinations were made on volcanics from the Eastport Formation, Eastport, Maine, and the Hedgehog Formation, Presque Isle, Maine (Fig. 1). In general, whole rocks are less susceptible than minerals to the loss of radiogenic strontium and thus a representative whole rock sample will yield the age of crystallization or solidification of an igneous rock. The volcanic rocks analyzed in this study are conformably interbedded with fossiliferous sediments which allows a precise determination of their geological age. The rocks studied sharply limit the Silurian-Devonian boundary (Bastin and Williams, 1914; Boucot, et. al., 1964, p. 45; Naylor and Boucot, 1965, p. 165; Berry and Boucot, in press); the Rb-Sr analyses of these rocks produced isochrons which yield a radiometric age for this boundary.

ANALYTICAL PROCEDURES

The laboratory procedures followed in this investigation were essentially the same as those described by Herzog and Pinson (1956), Herzog, et. al. (1958), and Faure and Hurley (1963). The only change in procedure was the elimination of pyrex glass from the chemical separation techniques and the use of vycor glass, teflon and polyethylene. The rubidium, strontium and strontium isotopic analyses were made with a solid source, 12 inch radius of curvature, 60^{o} sector, single-focusing mass spectrometer.

The whole rock samples were prepared by powdering a block of rock sufficiently large to yield 20-50 grams. The powders were dissolved with a mixture of reagent grade hydrofluoric and doubly vycor distilled sulfuric acids. Separation and purification of the Rb and Sr was



72°
70°
68°
66°
64°
62°
60°
46°
44°
42°
QUEBEC
413 ±10
HEDGEHOG FM,
LOWER DEVONIAN, PRESQUE ISLE, ME.
NEW BRUNSWICK
MAINE
VT
NEW HAMPSHIRE
NOVA SCOTIA
412 ±5
EASTPORT FM.
SKALA INTERVAL
EASTPORT, ME.
MASS.
Scale: 0 60 MILES

accomplished by cation exchange using Dowex 50W-X8 resin with vycor distilled 2N HCl as the eluant. Rubidium and strontium concentrations were determined by isotopic dilution analyses. Separate, unspiked samples were analyzed to measure the strontium isotopic composition.

The Rb^{87} spike which was used for the Rb analyses was calibrated eight times during this work. Both the Goddard Space Flight Center Rb shelf solution and the M.I.T. Rb shelf solution, which was distributed to assist in inter-laboratory comparison of analyses, were used to calibrate the Rb spike. The Rb shelf solutions were prepared from Johnson-Mathey spec-pure RbCl. Analyses with both shelf solutions yielded the same results for the concentration of the Rb^{87} spike. The standard deviation of the mean for the Rb^{87} spike calibrations was ± 0.86%. The Sr^{86} spike was calibrated six times during this work using both the G.S.F.C. and the M.I.T. Sr shelf solutions. The Sr shelf solutions were prepared from Johnson-Mathey spec-pure $Sr(NO_3)_2$. Analyses using both shelf solutions produced the same results for the concentration of the Sr^{86} spike. The standard deviation of the mean for the Sr^{86} spike calibrations was ± 0.29%.

Blanks were determined for both Sr and Rb. Four Sr blank determinations averaged 0.1 μgSr. This quantity was subtracted from all Sr isotope dilution analyses. The Rb blank was measured twice and averaged 0.01 μg Rb. This quantity was not subtracted from the results of the isotope dilution analyses as it is insignificant compared to the amounts of Rb in the analyzed samples.

The average Sr^{87}/Sr^{86} ratio of the M.I.T. standard strontium carbonate, Eimer and Amend lot #492327, was 0.7076 when normalized to $Sr^{86}/Sr^{88} = 0.1194$ (see Faure and Hurley, 1963, for a discussion of normalization procedures). This normalized Sr^{87}/Sr^{86} value of 0.7076 is in good agreement with results obtained in other laboratories. The standard deviation of a single isotopic ratio analysis of the standard strontium carbonate is ± 0.0012, or ± 0.17 per cent of the average $(Sr^{87}/Sr^{86})_N$ ratio, where $(Sr^{87}/Sr^{86})_N$ is the normalized Sr^{87}/Sr^{86} ratio. The individual analyses are given in Table 1. The precision of the Rb and Sr isotope dilution analyses was estimated from duplicate determinations by calculating the standard deviation of the per cent difference between duplicate Rb analyses and duplicate Sr analyses. The standard deviation of a single analysis for Rb is ± 1.22% and for Sr is ± 1.32%.

Based on these results, the error for individual isochron points was plotted as ± 5% for Rb^{87}/Sr^{86} and ± 0.25% for $(Sr^{87}/Sr^{86})_N$. These estimates of error are considered to be conservative.

TABLE 1

ANALYSES OF EIMER AND AMEND
$SrCO_3$. LOT #492327

Date	Sr^{86}/Sr^{88}	Sr^{87}/Sr^{86}	$(Sr^{87}/Sr^{86})_N$
14 April, 1964	0.1195	0.7063	0.7066
10 June, 1964	0.1184	0.7128	0.7098
12 June, 1964	0.1179	0.7136	0.7091
15 June, 1964	0.1201	0.7040	0.7061
18 June, 1964	0.1206	0.7055	0.7090
2 September, 1964	0.1191	0.7086	0.7078
27 September, 1964	0.1203	0.7045	0.7072
20 March, 1965	0.1202	0.7051	0.7076
2 June, 1965	0.1195	0.7075	0.7078
4 June, 1965	0.1196	0.7051	0.7058
7 June, 1965	0.1205	0.7037	0.7070
12 July, 1965	0.1199	0.7051	0.7066
14 July, 1965	0.1192	0.7085	0.7079
Averages:	0.1196	0.7069	0.7076

$(Sr^{87}/Sr^{86})_N$: $\overline{\sigma} = \pm 0.0003$: $\sigma = \pm 0.0012$

The ages were determined by the equation

$$(Sr^{87}/Sr^{86})\ \text{present} = (Sr^{87}/Sr^{86})\ \text{initial} + (Rb^{87}/Sr^{86})(e^{\lambda t}-1)$$

where $\lambda_{Rb^{87}} = 1.39 \times 10^{-11}$ year^{-1}.

EASTPORT FORMATION

The rocks of the Eastport Formation are located near Eastport, Maine (Fig. 1). The detailed geology of the area is described by Bastin and Williams (1914). This formation is composed of rhyolites, tuffs, limestone and shale. The volcanics are more abundant than the sedimentary rocks and the total thickness of the formation is approximately 8000 feet. The geologic age of this formation is based on fossils found in the sedimentary rocks; Bastin and Williams (1914) date the Eastport Formation as Upper Silurian. Boucot, et. al. (1964) and Naylor and Boucot (1965) date the formation as of Ludlow (Upper Silurian) age but also mention the possibility that the Eastport Formation is earliest Devonian. More recent investigations (Berry and Boucot, in press) indicate that the Eastport Formation is younger than Ludlow age but older than earliest Devonian (Gedinnian): it is assigned to the Skala interval which never has been formally assigned to either the Silurian or Devonian. Thus, this formation is at or close to the Silurian-Devonian boundary.

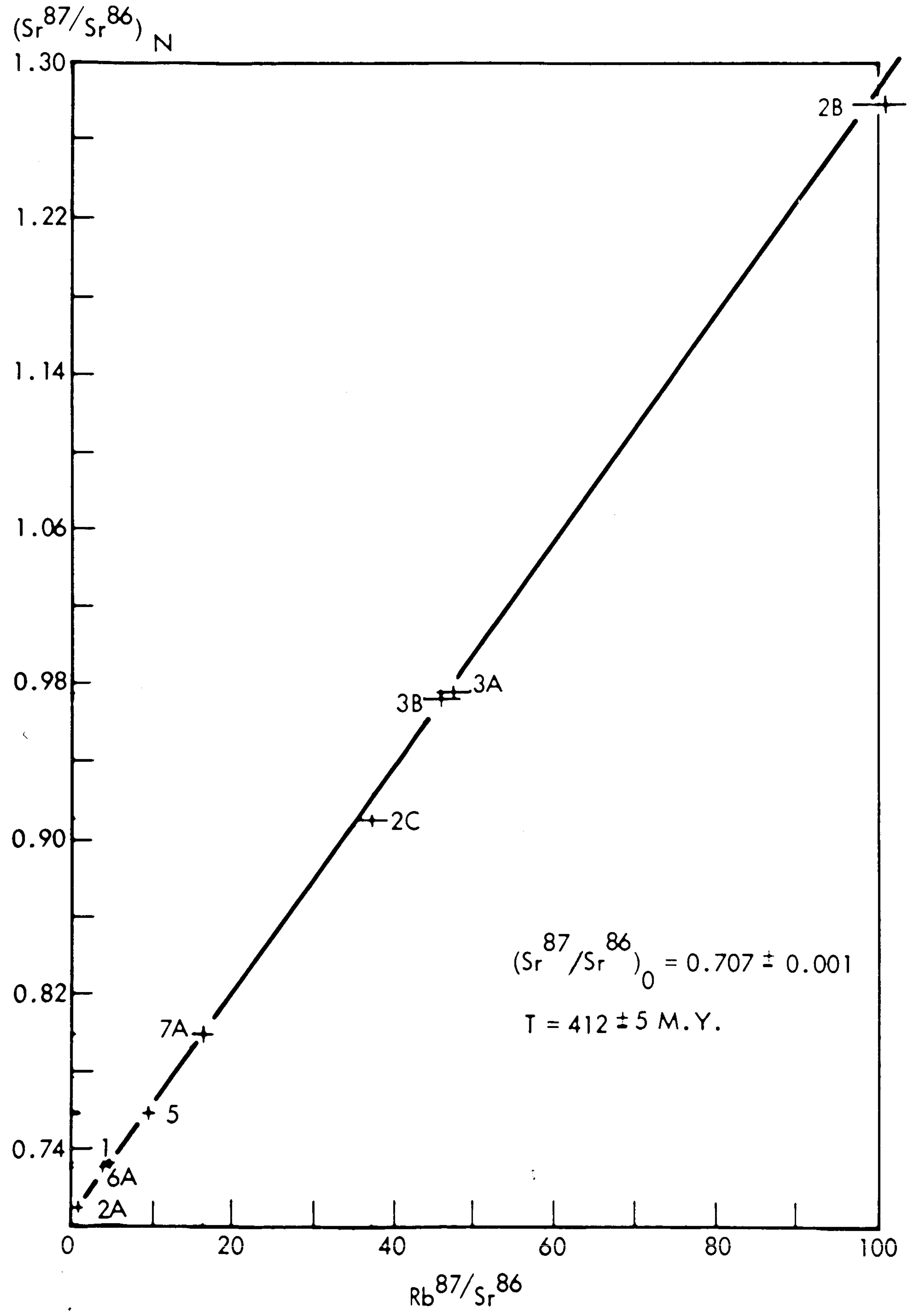
Nine whole rock samples of volcanics from the Eastport Formation were analyzed. These samples were collected within several miles of Eastport, Maine; precise sample localities are given in the Appendix. The analytical results are given in Table 2. The Rb^{87}/Sr^{86} ratios range from 0.54 to

100.3, and the $(Sr^{87}/Sr^{86})_N$ values range from 0.7111 to 1.2819. The isochron obtained from plotting $(Sr^{87}/Sr^{86})_N$ ratios versus Rb^{87}/Sr^{86} ratios and drawing the line of best fit through the points is shown in Figure 2; this isochron yields an age of 412 ± 5 M.Y. and an initial $(Sr^{87}/Sr^{86})_N$ ratio of 0.707 ± 0.001. The estimated error and a confirmation of the age was obtained by calculating the ages of the individual samples using the initial ratio determined by the isochron and then determining the standard deviation of the mean of the ages of all samples except 2A; this sample was excluded from the calculations because of its low radiogenic Sr^{87} content. The age determined by this method was also 412 M.Y. and the calculated standard deviation of the mean equaled ± 2.7 M.Y., thus an error of ± 5 M.Y. represents almost two standard deviations of the mean.

TABLE 2

EASTPORT FORMATION ANALYTICAL DATA

Sample	Rb(ppm)	Sr(ppm)	Rb^{87}/Sr^{86}	Sr^{86}/Sr^{88}	$(Sr^{87}/Sr^{86})_N$
ODC - 1	150	99.3	4.38	0.1197	0.7324
ODC - 2A	63.5	340	0.54	0.1198	0.7111
ODC - 2B	130 128 137	4.08 3.91	100.3	0.1194	1.2819
ODC - 2C	124 123	9.80 9.93	37.0	0.1199	0.9113
ODC - 3A	136 140	8.70 8.80	46.8	0.1195	0.9743
ODC - 3B	168	10.95	45.5	0.1199	0.9724
ODC - 5	257	81.5	9.17	0.1199	0.7603
ODC - 6A	469	323	1.45	0.1201	0.7310
ODC - 7A	99.4	18.1	16.0	0.1204	0.8006



$(Sr^{87}/Sr^{86})_N$
1.30
1.22
1.14
1.06
0.98
0.90
0.82
0.74
2B
3A
3B
2C
7A
5
1
6A
2A
$(Sr^{87}/Sr^{86})_0 = 0.707 \pm 0.001$
T = 412 ± 5 M.Y.
0
20
40
60
80
100
Rb^{87}/Sr^{86}

HEDGEHOG FORMATION

The Hedgehog Formation volcanics were collected near Presque Isle, Maine (Fig. 1). This formation is the lower part of the Dockendorff Group which is Lower Devonian (New Scotland) in age. Boucot, et. al., 1964, p. 40-41, state that the Hedgehog Formation consists of many small lenses composed essentially of andesite, trachyte, tuff, and rhyolite with minor units of intercalated sedimentary rocks; this formation has an average thickness of 4000 feet. The New Scotland age of this formation is based on brachiopods and corals from tuffaceous material and a calcareous ash bed (Boucot, et. al., 1964, p. 45).

All but two of the samples collected for this study came from the north half of Green Mountain from outcrops at the base of radio beacon number 3. The two andesite samples analyzed were collected from the same mountain but from outcrops at the base of the site of radio beacon number 2. The exact position of these radio beacons is shown on the geologic map included in the paper on this area by Boucot, et. al., 1964. Precise sample localities are given in the Appendix.

Nine whole rock samples were analyzed. The Rb^{87}/Sr^{86} values range from 0.45 to 80.9 and the $(Sr^{87}/Sr^{86})_N$ values range from 0.7069 to 1.1720. The analytical results are given in Table 3. The isochron for the Hedgehog Formation is shown in Figure 3; this isochron was obtained by drawing the line of best fit through the points and gives an age of 413 ± 10 M.Y. with an initial ratio of 0.706 ± 0.002. As was done for the age of the Eastport Formation, the estimated error and a confirmation of the age of the Hedgehog Formation was obtained by calculating the individual sample ages using the initial ratio determined by the isochron and then determining the standard deviation of the mean of the ages of the samples; two samples, ODC - 9 and ODC - 10 were excluded from these calculations because of low radiogenic Sr^{87} content. The calculated age was identical to the 413 M.Y. age obtained directly from the isochron. The standard deviation of the mean equaled ± 4.6 M.Y.; thus, ± 10 M.Y. represents slightly more than two standard deviations of the mean.

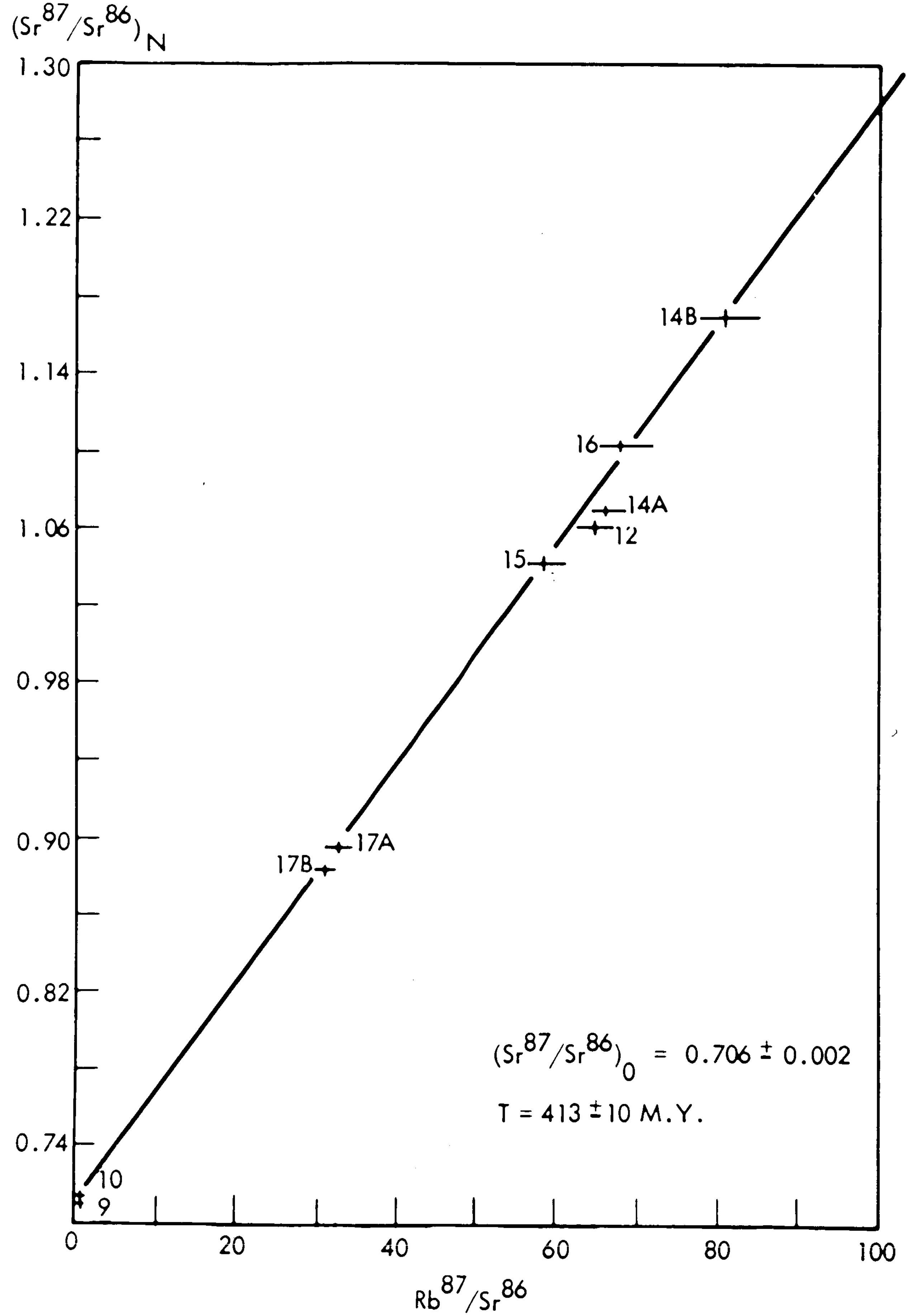
TABLE 3

HEDGEHOG FORMATION ANALYTICAL DATA

Sample	Rb(ppm)	Sr(ppm)	Rb^{87}/Sr^{86}	Sr^{86}/Sr^{88}	$(Sr^{87}/Sr^{86})_N$
ODC - 9	56.1	362	0.45	0.1196	0.7069
ODC - 10	57.7	323	0.52	0.1201	0.7089
ODC - 12	131	5.94 6.28	64.1	0.1199	1.0615
ODC - 14A	145	6.43 6.71	66.3	0.1200	1.0706
ODC - 14B	154	5.66 5.84	80.9	0.1198	1.1720
ODC - 15	149	7.68 7.78	57.6	0.1201	1.0438
ODC - 16	137	6.11 6.09	67.7	0.1208	1.1074
ODC - 17A	123	10.81 11.97	32.0	0.1195	0.8953
ODC - 17B	117	11.34 11.38	30.3	0.1210	0.8829

DISCUSSION AND CONCLUSIONS

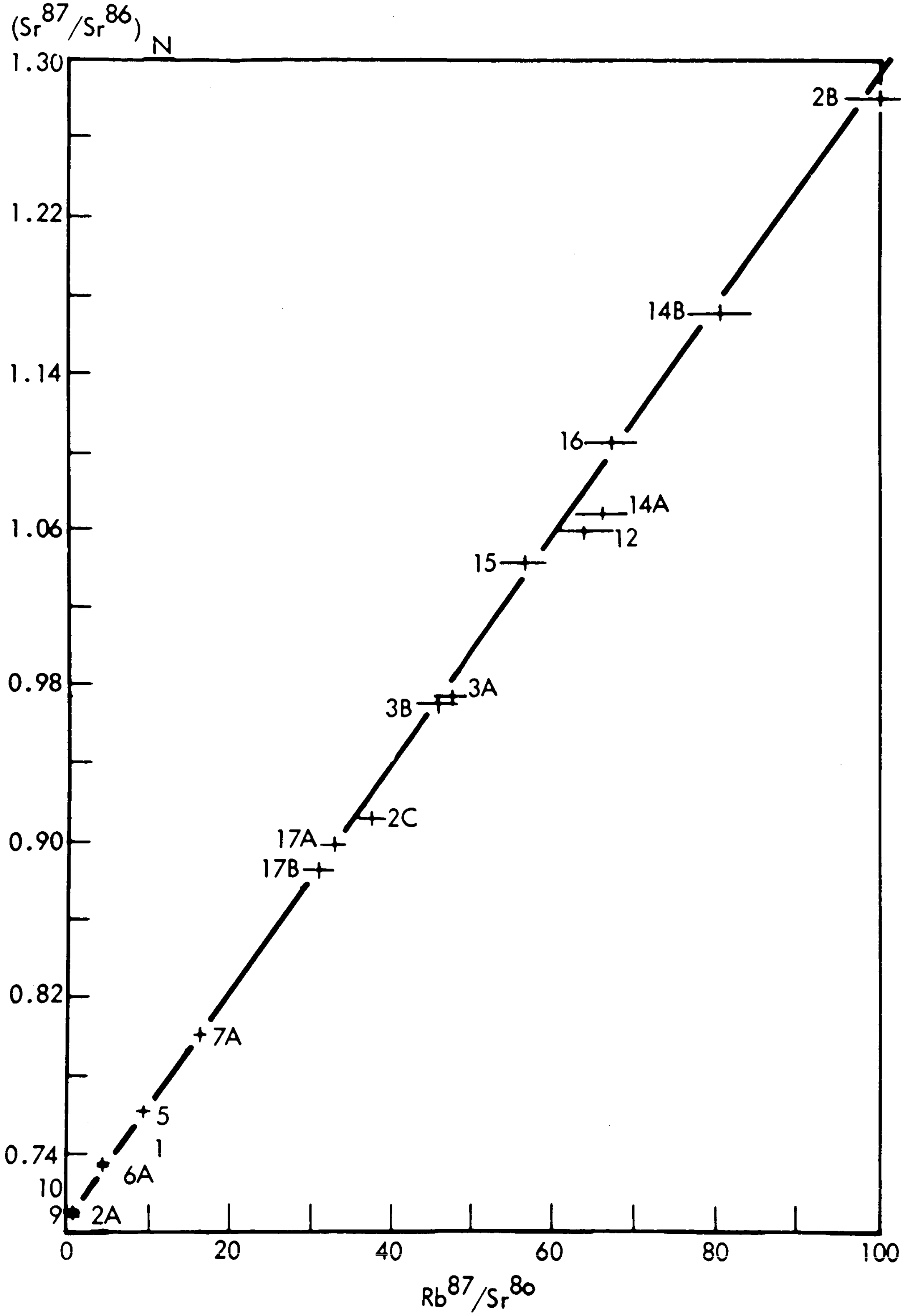
The results of the analyses of the Eastport and Hedgehog Formation volcanics were plotted on one diagram, Figure 4. Although this figure is not, strictly speaking, an isochron, it does show the agreement of the results



(Sr87/Sr86)N
1.30
1.22
1.14
1.06
0.98
0.90
0.82
0.74
14B
16
14A
12
15
17A
17B
10
9
(Sr87/Sr86)0 = 0.706 ± 0.002
T = 413 ± 10 M.Y.
0
20
40
60
80
100
Rb87/Sr86

for the two areas as the two isochrons are superimposed. The combined results from the two areas yielded an age of 413 ± 5 M.Y. for the Silurian-Devonian boundary. The age of 413 M.Y. and the error of ± 5 M.Y. were obtained by determining the mean and the standard deviation of the mean of the ages of the 15 samples that were used to calculate the individual formation ages. The standard deviation of the mean was ± 2.5 M.Y., and the error of ± 5 M.Y. represents two standard deviations of the mean. This precision is far better than the knowledge of the value for the Rb^{87} decay constant. Nonetheless, it is of value to obtain Rb-Sr ages which are as precise as possible in order to be able to compare ages determined by this method. In addition, refinement of the Rb^{87} decay constant will allow more precise comparisons of these ages to ages determined with other decay schemes.

Several conclusions may be drawn from this study. First, the age determined for the Silurian-Devonian boundary is consistent with ages on biotites from granites which intrude the Eastport Formation; Faul, et. al., 1963, determined several K-Ar biotite ages which averaged 405 M.Y., and a Rb-Sr biotite age of 414 M.Y. ($\lambda_{Rb}87 = 1.39 \times 10^{-11}$ year^{-1}). Second, this age is in good agreement with the Kulp (1961) and the Holmes (1960) time scale estimates considering the uncertainty of the Rb^{87} decay constant; it should be pointed out that this conclusion is somewhat redundant as the Kulp and the Holmes time scale estimates for the age of the Silurian-Devonian boundary are based to a large extent on the above data obtained by Faul. Third, due to the relatively large number of samples analyzed, the good isochrons which were obtained, and the close paleontological control of the rocks involved, it is believed that this work represents as precise a



$(Sr^{87}/Sr^{86})_N$
1.30
1.22
1.14
1.06
0.98
0.90
0.82
0.74
2B
14B
16
14A
12
15
3A
3B
2C
17A
17B
7A
5
1
6A
10
9
2A
0
20
40
60
80
100
Rb^{87}/Sr^{86}

measurement of the radiometric age for the Silurian-Devonian boundary as has yet been determined.

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APPENDIX: SAMPLE LOCALITIES

The samples of the Eastport Formation were collected along Maine highway 190 and U. S. highway 1, between Perry and Eastport, Maine, by M. L. Bottino during the summer of 1962. Except where otherwise noted, distances are measured along the highways.

Sample	Locality
ODC-1	Outcrop on Carlow Island, on southwest side of Maine highway 190, 2.8 miles southeast of the intersection of U. S. highway 1 and Maine highway 190, which is near Perry, Maine.
ODC-2A ODC-2B ODC-2C	Outcrops near Pleasant Point, along Maine highway 190, 1.8 miles southeast of the intersection of U. S. highway 1 and Maine highway 190.
ODC-3A ODC-3B	Outcrops on west side of U. S. highway 1, near intersection of U.S. 1 and Maine highway 190.
ODC-5 ODC-6A	Outcrops on hill near Johnson Cove and Carryingplace Cove, 0.2 miles north of Maine highway 190, 4.0 miles southeast of the intersection of U. S. highway 1 and Maine highway 190.
ODC-7A	Outcrop on the southwest side of Maine highway 190, 1.2 miles southeast of the intersection of Maine highway 190 and U. S. highway 1.

The samples of the Hedgehog Formation volcanics were collected on the north half of Green Mountain, approximately 5 miles south of Presque Isle, Maine, by M. L. Bottino and P. D. Fullagar during the summer of 1964.

Sample	Locality
ODC-9 ODC-10	Outcrops at the base of the site of beacon 2, approximately 0.8 miles west of Spragneville, Maine, which is at the north end of Echo Lake.

ODC-12	Outcrop on top of Green Mountain, 100 feet north of radio beacon 3, which is less than 0.1 miles east of the Aroostook State Park boundary, and approximately 0.6 miles south of Echo Lake.
ODC-14A ODC-14B	Outcrops on top of Green Mountain, 25 feet east of beacon 3.
ODC-15	Outcrop on top of Green Mountain, 50 feet west of beacon 3.
ODC-16	Outcrop on top of Green Mountain, 100 feet southwest of beacon 3.
ODC-17A ODC-17B	Outcrops down trail on northeast side of Green Mountain, approximately 0.1 miles north of beacon 3.