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THE Sr^{87}/Sr^{86} RATIO IN OCEANIC AND CONTINENTAL BASALTS AND THE ORIGIN OF IGNEOUS ROCKS

by

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B.Sc., University of Western Ontario
(1957)

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by Gunter Faure

Submitted to the Department of Geology and Geophysics on May 15, 1961, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Abstract.

The isotopic compositions of strontium in 25 basalts and related volcanic rocks from oceanic and continental localities have been determined. The results indicate that the abundance of Sr^{87} in basalts, expressed as the Sr^{87}/Sr^{86} ratio, is constant within narrow limits. The average values of the Sr^{87}/Sr^{86} ratios of eleven oceanic basalts and fourteen continental basalts are 0.7072 ± 0.0003 and 0.7082 ± 0.0003, respectively. The difference in the abundance of Sr^{87} is not consistent and is not believed to be significant. The overall average Sr^{87}/Sr^{86} ratio for all 25 basalts is $0.7078^{+0.002}_{-0.003}$. A reproducibility of ± 0.001(.14%) for the Sr^{87}/Sr^{86} ratio was achieved by making an instrumental isotope fractionation correction. The accuracy of the measurements was monitored by periodic analyses of a $SrCO_3$ standard.

The concentrations of rubidium and strontium in a representative number of basalts were determined by isotope dilution. Five olivine basalts averaged: Rb = 17 ± 6 ppm, Sr = 390 ± 55 ppm, Rb/Sr = 0.044 ± 0.018 whereas six tholeeitic basalts were found to contain 30 ± 7 ppm Rb, 504 ± 167 ppm Sr, Rb/Sr = 0.060 ± 0.024. The reproducibility of the rubidium and strontium analyses is $\pm$ 2%.

The small, but statistically significant, differences in the abundance of Sr^{87} in basalts from different localities are interpreted as evidence of small lateral and/or vertical variations in the Rb/Sr ratios of the source material of basalt magma. Numerical values of the Rb/Sr ratio were calculated with the assumption that the initial Sr^{87}/Sr^{86} ratio was 0.7004 ± 0.002 and that the age of the source material is 4.5×10^9 years. The average value and its limits of variation was found to be Rb/Sr = $0.039^{+0.012}_{-0.017}$. The relative abundance of rubidium in the source regions of basalt magma is therefore approximately identical to that of olivine basalt, eclogite or ultrabasic igneous rocks. The low value of the Rb/Sr ratio as well as other geophysical and geochemical evidence suggest that basalt magma is generated in the upper mantle.

The abundance of Sr^{87} in the sialic crust was estimated by making reasonable assumptions about its Rb/Sr ratio, its age and its initial Sr^{87}/Sr^{86} ratio. On the basis of the most reliable rubidium and strontium analyses available in the geochemical literature and using Poldervaart's crustal model, the Rb/Sr ratio of the sialic crust was estimated to be 0.25. If its age is 2 billion years and its initial Sr^{87}/Sr^{86} ratio was 0.704, the present value would be 0.725. This estimate was substantiated by the results obtained for two composites of Paleozoic shale which averaged $Sr^{87}/Sr^{86} = 0.7215 \pm 0.001$. This value is measurably higher than that in oceanic and continental basalts.

On the basis of this evidence the hypothesis is advanced that the value of the Sr^{87}/Sr^{86} ratio of igneous rocks, at the time of crystallization, can be used as a criterion for the origin of the material. The initial Sr^{87}/Sr^{86} ratio of an igneous rock formed by re-melting or granitization of sialic material is expected to be measurably higher than that of an igneous rock derived from the source regions of basalt magma.

The initial Sr^{87}/Sr^{86} ratio of a complex of intrusive igneous rocks or of a series of lava flows of different compositions is best determined from the coordinates of the point of convergence of the whole-rock strontium development lines. The convergence of the strontium development lines is a test for possible co-magmatic relationships of associated igneous rocks. This test is particularly applicable to the study of alkaline rocks, pegmatites, lamprophyres and carbonatites.

A preliminary investigation of the intrusive igneous rocks of the Monteregian hills, Quebec, indicated that the different rock types were derived from the same source about 115 ± 25 million years ago which at that time had a Sr^{87}/Sr^{86} ratio of 0.7047 ± 0.001. This unusually low value indicates that these rocks originated in the source regions of basalt magma, perhaps well below the base of the crust.

Thesis Supervisor: Patrick M. Hurley
Title: Professor of Geology

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Part 1

(Intended for Publication)

THE Sr^{87}/Sr^{86} RATIO IN OCEANIC AND CONTINENTAL BASALT AND THE ORIGIN OF IGNEOUS ROCKS.

By G. Faure and P. M. Hurley.

Abstract.

The isotopic compositions of strontium in 25 basalts and related volcanic rocks from oceanic and continental localities have been determined. The results indicate that the abundance of Sr^{87} in basalts, expressed as the Sr^{87}/Sr^{86} ratio, is constant within narrow limits. The average values of the Sr^{87}/Sr^{86} ratios of eleven oceanic basalts and fourteen continental basalts are 0.7072 ± 0.0003 and 0.7082 ± 0.0003, respectively. The difference in the abundance of Sr^{87} is not consistent and is not believed to be significant. The overall average Sr^{87}/Sr^{86} ratio is $0.7078 \, {}^{+0.002}_{-0.003}$.

The concentrations of rubidium and strontium in a representative number of basalts were determined by isotope dilution. Five olivine basalts averaged: Rb = 17 ± 6 ppm, Sr = 390 ± 55 ppm, Rb/Sr = 0.044 ± 0.018 whereas six tholeeitic basalts were found to contain 30 ± 7 ppm Rb, 504 ± 167 ppm Sr, Rb/Sr = 0.060 ± 0.024.

The small, but statistically significant, differences in the abundance of Sr^{87} in basalts from different localities are interpreted as evidence of small lateral and/or vertical variations in the Rb/Sr ratios of the source regions. Numerical values of the Rb/Sr ratio were calculated on the assumption that the initial Sr^{87}/Sr^{86} ratio was 0.7004 ± 0.002 and that the age of the upper mantle is 4.5×10^9 years. The average value and its limits of variation was found to be Rb/Sr = $0.039 \, {}^{+0.012}_{-0.017}$. The relative abundance of rubidium in the source regions of basalt magma is therefore approximately identical to that of

olivine basalts or eclogite.

On the basis of the most reliable rubidium and strontium analyses of igneous and sedimentary rocks available from the literature and using Poldervaart's crustal model, the Rb/Sr ratio of the sialic crust was estimated to be 0.25. If the age of the sialic crust is approximately 2 billion years and its initial Sr^{87}/Sr^{86} ratio was 0.704, the present average value would be 0.725. This estimate was substantiated by the results obtained for two composites of Paleozoic shale which averaged $Sr^{87}/Sr^{86} = 0.7215 \pm 0.001$.

On the basis of this evidence the hypothesis is advanced that the value of the Sr^{87}/Sr^{86} ratio of igneous rocks, at the time of crystallization, can be used as a criterion for the origin of the material. The initial Sr^{87}/Sr^{86} ratio of an igneous rock formed by re-melting or granitization of the sialic crust is expected to be measurably higher than that of an igneous rock derived from the sub-crustal source regions of basalt magma.

The initial Sr^{87}/Sr^{86} ratio of a complex of intrusive igneous rocks or of a series of lava flows of different compositions is best determined from the point of convergence of the whole-rock strontium development lines. The convergence of the strontium development lines can also be used to test for possible co-magmatic relationships between associated igneous rocks. It is suggested that this method is particularly applicable to the study of alkaline rocks, pegmatites, lamprophyres and carbonatites.

Introduction:

The abundance of Sr^{87}, expressed as the ratio Sr^{87}/Sr^{86}, has increased by the natural radioactive decay of Rb^{87} to Sr^{87} since the time of formation of the elements. The rate of increase of the Sr^{87}/Sr^{86} ratio of any system which is closed to rubidium and strontium during its life-

time is proportional to its Rb/Sr ratio. Differentiation processes operating since the beginning of geologic time have resulted in an enrichment of rubidium in the upper regions of the continental crust relative to the base of the crust and the upper mantle. As a result it is expected that in the course of geologic time the abundance of Sr^{87} in the sialic crust has increased at a greater rate than in those parts of the upper mantle which are the source regions of basaltic magma. If the difference in the Sr^{87}/Sr^{86} ratios of the two environments is measurable, then the origin of intrusive igneous rocks in the sialic crust can be determined from the values of their Sr^{87}/Sr^{86} ratios at the time of crystallization. Intrusives which were formed by re-melting or granitization of sialic material are expected to have higher Sr^{87}/Sr^{86} ratios than those igneous rocks which originated in the upper mantle or the lower simatic regions of the continental crust.

A very similar suggestion was made by Holmes (1932) who proposed that the abundance of the isotope Ca^{41} could be used to differentiate between granites formed by re-melting of granitic parent material from those which

are derivatives of basalt magma. This proposal was based on the assumption, now disproved, that K^{41} decays to Ca^{41}.

The abundances of the isotopes Sr^{87} and Rb^{87}, both relative to $Sr^{86} = 1$, as a function of time in any system which remained closed to rubidium and strontium during its lifetime can be expressed as follows:

$$a = a_o + b(e^{\lambda t} - 1) \qquad (1)$$

where

a = Sr^{87}/Sr^{86} at time of analysis of the material
b = Rb^{87}/Sr^{86} at time of analysis of the material
a_o = Sr^{87}/Sr^{86} at an initial time t_o
t = time measured backwards from the present
λ = decay constant of Rb^{87}
= 1.47×10^{-11} yrs^{-1} (Flynn and Glendenin, 1959)

Before equation (1) may be used to calculate the abundance of Sr^{87} in the sub-crustal source regions of basalt magma throughout geologic time, appropriate values of a_o and t_o must first be determined by a judicious examination of available data. Moreover, the homogeneity of the source regions with respect to a_o to t_o should be demonstrated.

In this paper the results of isotopic analyses of strontium in 25 basalts and related volcanic rocks of sub-crustal origin are reported. The specimens were

selected from oceanic and continental localities in order to test the lateral homogeneity of the sub-crustal source regions of basalt magma with respect to a, the present Sr^{87}/Sr^{86} ratio. The results will also be examined in order to determine to what extent they indicate homogeneity of the source regions with respect to a_o and t_o.

Concentrations of rubidium and strontium were measured in a representative number of basalts by the method of isotope dilution. These analyses were made not only for their geochemical interest but also in order to compare the measured values of the Rb/Sr ratios in basalts to those of their source regions calculated by means of equation (1). Such comparisons can give evidence of chemical fractionation during the partial melting of the source material to produce magma.

Experimental Errors and Accuracy.

All measurements were made on one 60° sector, 6 inch radius, solid source mass spectrometer using a magnet sweep and a vibrating reed electrometer for amplification of the ion current. The instrument was built at M.I.T. and has been described previously by Herzog et al. (1958) and Herzog and Pinson (1956).

It was desirable for the purpose of this investigation to determine Sr^{87}/Sr^{86} ratios with a reproducibility of 0.1% or better and to maintain a high standard of accuracy of all measurements. The reproducibility of the mass spectrometric measurements was determined from the results of several analyses of a single sample repeated periodically throughout the course of this investigation. It was expressed as the standard deviation for a single analysis calculated from the results of the replicate analyses. The main factors which determine the reproducibility are: variable amounts of contamination during chemical processing of the samples and the mass spectrometric analysis, effects of isotopic fractionation in the instrument, variations of the rate of ion emission from the filament, instability of the magnetic field of the magnetic analyzer and high-frequency electronic noise in the amplification and recording systems. Several of the errors listed above may be systematic for a single analysis but are random for a large number of repeated measurements. They thus affect the reproducibility of a single determination and are included with the truly random errors.

An instrumental fractionation correction was applied to all Sr^{87}/Sr^{86} ratios on the assumption that the Sr^{86}/Sr^{88} ratio is a constant equal to 0.1194(Nier, 1938). All measured Sr^{86}/Sr^{88} ratios were adjusted to this value but only half of this correction was applied to the measured Sr^{87}/Sr^{86} ratio because the mass difference between Sr^{87} and Sr^{86} is only one half that between Sr^{86} and Sr^{88}. This correction resulted in a marked improvement of the reproducibility of the Sr^{87}/Sr^{86} ratio without at the same time affecting the value of the mean. The effect of the fractionation correction and the resulting improvement of the reproducibility are well illustrated by the analyses of an olivine basalt from Kilauea, Hawaii (Table A-1).

Table A-1 Olivine Basalt, Kilauea, Hawaii (R1292).

Date	Sr^{87}/Sr^{86}	$(Sr^{87}/Sr^{86})^{*}_{corr}$	Sr^{86}/Sr^{88}	Sr^{84}/Sr^{88}	No. of scans
6/1/60	0.7062	0.7068	0.1196	0.0070	138
8/3/60	0.7102	0.7072	0.1184	0.0063	84
9/3/60	0.7090	0.7069	0.1187	0.0066	84
1/25/61	0.7040	0.7058	0.1200	--	104
2/8/61	0.7091	0.7061	0.1184	0.0065	90
Average	0.7077	0.7066	0.1190	0.0066	
$\bar{\sigma}$	±0.0011	±0.0003	±0.0003	±0.0001	
σ	±0.0025	±0.0006	±0.0007	±0.0003	

*Corrected by adjusting Sr^{86}/Sr^{88} to 0.1194 and the Sr^{87}/Sr^{86} ratio by half this amount.

In this series of measurements a reproducibility of $\pm$ 0.0006 (0.08%) has been achieved for the corrected Sr^{87}/Sr^{86} ratios. This represents an improvement by a factor of about four over the reproducibility of the uncorrected ratios. The importance of isotopic fractionation in the mass spectrometer is illustrated by the range of variation of the measured values of the uncorrected Sr^{87}/Sr^{86} ratios as well as the Sr^{86}/Sr^{88} and the Sr^{84}/Sr^{88} ratios. A precision error of 0.1% for the Sr^{87}/Sr^{86} ratio can be achieved only by removing the effects of isotopic fractionation in the mass spectrometer .

The accuracy of the measurements was monitored by periodic analyses of a $SrCO_3$ standard (Eimer and Amend, lot 492327) for which isotopic analyses have been reported by Herzog et al. (1953) as well as Aldrich et al. (1953). The average of eight analyses performed during the course of this investigation is in excellent agreement with earlier analyses (Table A-2) as well as the original measurements reported by Nier (1938) for metallic strontium.

Table A-2 Isotopic Composition of Strontium in Strontium Reagents

Analyst	Sr^{87}/Sr^{86}	$(Sr^{87}/Sr^{86})^{*}_{corr}$	Sr^{86}/Sr^{88}	Sr^{84}/Sr^{88}
Nier, 1938, p. 277	0.712 ± 0.007		0.1194 ± 0.0012	0.0068 ± 0.00014
Aldrich et al.,[1] 1953, p.458	0.711 ± 0.0004		0.1195 ± 0.0003	0.0067 ± 0.0005
Herzog et al., 1953, p.462	0.712		0.1196	0.0070
This work[2]	0.7119 ± 0.0006	0.7120 ± 0.0003	0.1195 ± 0.0002	0.0066 ± 0.0001

*Corrected by adjusting Sr^{86}/Sr^{88} to 0.1194 and the Sr^{87}/Sr^{86} ratio by half this amount.

(1) Average of six analyses; (2) Average of eight analyses.

The consistency of our results for the $SrCO_3$ standard with those previously reported is an indication of the reliability of the analyses of the isotopic composition of strontium in basalts. The reproducibility of the corrected Sr^{87}/Sr^{86} ratios achieved in this case is ±0.0009 (0.13%).

On the basis of this evidence single measurements of the Sr^{87}/Sr^{86} ratio, corrected for isotopic fractionation, of good quality are assumed to have a reproducibility of ± 0.001 (0.14%). An analysis is judged to be of good

quality if it is based on 80 or more consecutive scans recorded at pressures of less than 2×10^{-6} mm of Hg and if it is not otherwise affected by instrumental difficulties.

Concentrations of rubidium and strontium were determined by means of isotope dilution using spikes enriched in Rb^{87} and Sr^{86}, respectively. The spike solutions were calibrated by triplicate isotope dilution analyses against shelf solutions containing known amounts of rubidium and strontium of normal isotopic composition. The isotopic compositions of the spikes were confirmed by separate triplicate analyses (Faure, 1961). Four blank analyses for rubidium and strontium were made in the course of this investigation and appropriate contamination corrections (Rb = 0.0674 μgrs. , Sr = 0.250 μgrs.) were applied to all analyses. The reproducibility of the rubidium and strontium analyses was determined by triplicate analyses. The results indicate a reproducibility of ± 2% for both rubidium and strontium analyses when Rb > 15 ppm and Sr > 150 ppm. (Faure, 1961).

Analytical Data.

The results of the isotopic analyses of strontium in basalts together with their concentrations of rubidium and strontium are shown in Table A-3. The figures in brackets after the measured value of the Sr^{87}/Sr^{86} ratio indicates the number of independent analyses performed for that specimen. Averages of the ratios of strontium isotopes were calculated for each locality from which more than one specimen was analyzed. The Sr^{87}/Sr^{86} ratios were weighted in the average by the total number of specimens analyzed whereas the averages for the Sr^{86}/Sr^{88} and Sr^{84}/Sr^{88} ratios were calculated from the total number of analyses performed. All errors are the standard deviations of the mean.

The concentrations of rubidium and strontium in five olivine basalts average Rb = 17±6 ppm, Sr = 390 ± 55 ppm, Rb/Sr = 0.044 ± 0.018. The six tholeeitic basalts were found to contain Rb = 30 ± 7 ppm, Sr = 504 ± 167 ppm and Rb/Sr = 0.060 ± 0.024. One eclogite from a kimberlite pipe in S. Africa was analyzed in duplicate. The results are: Rb = 6.9 ppm, Sr = 149 ppm, Rb/Sr = 0.046. The Rb/Sr ratio of the eclogite is identical to that in the olivine basalts.

Table A-3 Analytical Results for Oceanic and Continental Basalts.

Sample Number	Rock Type and Locality	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})^{*}_{corr}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{84}}{Sr^{88}}$	No. of scans	Rb ppm	Sr ppm	$\frac{Rb}{Sr}$
Oceanic Basalts.									
Hawaiian Islands									
R1292	Olivine basalt, Kilauea Erupted in 1894	.7077(5) ±.001	.7066 ±.0003	.1190 ±.0003	.0066 ±.0001		9.76(3) ±.11	398.6(3) ±2.0	.0245
R1282	Basalt glass, Kilauea Probably erupted in 1921	.7094(1)	.7073	.1187	.0065	48	9.13	380.6	.0240
R2001	Olivine basalt, Kilauea Recent flow	.7084(1)	.7063	.1187	.0064	90	9.78	379.3	.0258
R1993	Basalt, Mauna Kea	.7097(1)	.7073	.1186	.0062	108	46.7	1249	.0375
Average for Hawaii Islands		.7088 ±.0005	.7069 ±.0003	.1189 ±.0002	.0065 ±.0001				
R2002	Basalt, Maui Island	.7059(2) ±.0013	.7047 ±.001	.1190 ±.0001	.0066 ±.0001	84,90			
Samoan Islands									
R2029	Olivine basalt Tutuila, Samoa	.7098(1)	.7077	.1187	.0066	90	41.6	567.6	.0733
R1995	Olivine gabbro from volcanic neck, Ofu	.7093(1)	.7078	.1189	.0066	78	14.1	222.5	.0634
R2030	Basalt, Ofu	.7096(1)	.7075	.1187	.0060	78	20.9	469.3	.0445
Average for Samoa		.7096 ±.0002	.7077 ±.0001	.1188 ±.00002	.0064 ±.0002				

Table A-3, continued

Sample Number	Rock Type and Locality	$\frac{Sr^{87}}{Sr^{86}}$	$\left(\frac{Sr^{87}}{Sr^{86}}\right)^{*}_{corr}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{84}}{Sr^{88}}$	No. of scans	Rb ppm	Sr ppm	$\frac{Rb}{Sr}$
R2031	Basalt, Ascension Island	.7073(1)	.7070	.1193	.0065	90	31.9	643.0	.0496
R4125	Basalt boulder, Mid-Atlantic Ridge, 31°18:8N 40°54.° 3W.	.7078(2)	.7062	.1188	.0066	48,84	9.75	118.3	.0824
R4156	Olivine basalt, Horta Fayal, Azores	.7106(1)	.7088	.1188	.0066	78			
Average for eleven oceanic basalts		.7087 ±.0006	.7072 ±.0003	.1189 ±.0001	.0065 ±.0001				
Continental Basalts.									
Japan									
R4161	Andesite (bomb) Erupted in 1909 at Sakurajima, Kyosho	.7124(1)	.7084	.1181	.0061	60			
R4221	Andesite vitrophyre Erupted in 1914 at Sakurajima, Kyosho	.7086(1)	.7080	.1192	.0066	84			
R4244	Dacite. Erupted in 1888 at Bandai San.	.7098(1)	.7080	.1188	.0069	90			
Average for Japan		.7103 ±.0011	.7081 ±.0001	.1187 ±.0003	.0065 ±.0002				

Table A-3, continued

Sample Number	Rock Type and Locality	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})^{*}_{corr}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{84}}{Sr^{88}}$	No. of scans	Rb ppm	Sr ppm	$\frac{Rb}{Sr}$
Deccan Plateau, India.									
R1864	Basalt, Kogna River, Bombay State, between Pophali (17°26'N, 73°46'E) and Navja (17°26'N, 73°46'E)	.7106(1)	.7085	.1187	--	40	16.1	234.9	.0685
R1865	Basalt " "	.7121(1)	.7091	.1184	.0063	78			
R1868	Basalt " "	.7096(1)	.7090	.1192	.0069	54			
Average for Deccan basalt		.7108 ±.0007	.7089 ±.0002	.1188 ±.0002	.0066 ±.0003				
	Age correction: 0.7089 - 0.0003 = 0.7086, assuming age = 100 m.y., Rb/Sr = .07								
Triassic Diabase of New Jersey and Connecticut.									
R4209	Diabase, Palisades Interstate Park, top of cliff.	.7106(1)	.7079	.1185	.0065	90			
R4210	Diabase, Palisades Interstate Tourist Camp 100 ft. above Hudson R.	.7100(1)	.7070	.1184	.0066	102			
R4211	Diabase, Sleeping Giant Quarry, Mt. Carmel, Connecticut	.7125(2)	.7094	.1184	--	32,48			
Average for Triassic diabase		.7110 ±.0008	.7081 ±.0007	.1185 ±.00004	.0066 ±.0001				
	Age correction: 0.7081 - 0.0009 = 0.7072, assuming age = 200 m.y., Rb/Sr = 0.1								

Table A-3, continued

Sample Number	Rock Type and Locality	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})^{*}_{corr}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{84}}{Sr^{88}}$	No. of scans	Rb ppm	Sr ppm	Rb/Sr
Columbia River Plateau, Oregon.									
R1428	Basalt, Wahkeenah Trail, Rte.US.30 east of Portland, Oregon.	.7080(3) ±.0010	.7067 ±.0001	.1189 ±.0003	.0066 ±.0002	30,84 84			
R1435	Basalt, " "	--	--	--	--	--	54.8	310.6	.176
	Age correction: 0.7067 - 0.0002 = 0.7065, assuming age = 25 m.y., Rb/Sr = 0.18.								
R1574	Basalt, Yellowstone Park	.7108(1)	.7084	.1186	.0064	90			
R4245	Tertiary basalt Squaw Creek, Montana	.7123(1)	.7096	.1185	.0066	90			
	Age correction: 0.7096 - 0.0002 = 0.7094, assuming age = 50 m.y., Rb/Sr = 0.1.								
R4159	Olivine basalt, post-Pleistocene, Iceland.	.7128(1)	.7101	.1185	.0064	78			
R4243	Basalt glass, Mt.Vesuvius, Italy.	.7088(1)	.7082	.1192	.0065	85			
Average for fourteen continental basalts and related rocks.		.7106 ±.0004	.7082(1) ±.0003	.1187 ±.0001	.0065 ±.0001				
Combined average for all twenty-five oceanic and continental volcanic rocks.		.7098 ±.0003	.7078 ±.0002	.1188 ±.0001	.0065 ±.0001				

Table A-3, continued

Sample Number	Rock Type and Locality	$\frac{Sr^{87}}{Sr^{86}}$	$\left(\frac{Sr^{87}}{Sr^{86}}\right)^{*}_{corr}$	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{84}}{Sr^{88}}$	No. of scans	Rb ppm	Sr ppm	$\frac{Rb}{Sr}$
R3111	Eclogite, xenolith in kimberlite pipe at the Robert Victor Mine, S. Africa.	.7095(3) ±.0009	.7088 ±.0008	.1192 ±.0003	.0066 ±.0001	84,78 84	6.90(2) .09	149 ±.7	.0463 ±.0006

* Corrected by adjusting the measured Sr^{86}/Sr^{88} ratio to 0.1194 and the Sr^{87}/Sr^{86} ratio by one half this amount (See text.).

(1) Increase in Sr^{87}/Sr^{86} ratio since the time of crystallization was subtracted as indicated in each case.
(2) All errors are the standard deviation of the mean.

THE ISOTOPIC COMPOSITION OF STRONTIUM IN THE SOURCE REGIONS OF BASALT MAGMA.

The Sr^{87}/Sr^{86} ratios of basalts from different continental and oceanic localities vary between the limits 0.7047 (R2002, Maui Island) and 0.7101 (R4159, Iceland). The eleven oceanic basalts average $Sr^{87}/Sr^{86} = 0.7072 \pm 0.0003$ whereas the fourteen continental basalts have a mean of 0.7082 ± 0.0003. The difference between the abundances of Sr^{87} of continental and oceanic basalts is not consistent and is probably not significant. The combined average Sr^{87}/Sr^{86} ratio for all oceanic and continental basalts is 0.7078 ± 0.0002 with the limits of variation of + 0.002 and -0.003. The results therefore demonstrate homogeneity of the source material of basalt magma with respect to the Sr^{87}/Sr^{86} ratio.

This homogeneity could be the result of fortuitous combinations of the variables a_o, b, and t_o in a multiplicity of source materials or it could be taken as evidence that a_o and t_o are constants for all source regions of basalt magma. The latter interpretation is preferrable. It implies that the small differences in the Sr^{87}/Sr^{86} ratios of basalts from different localities are caused by

corresponding differences in the Rb/Sr ratios of the source regions. The absolute values of the Rb/Sr ratios calculated for the source material of basalt magma depend on the selection of values for a_o and t_o in equation (1).

The value of the initial Sr^{87}/Sr^{86} ratio (a_o) and the time of the differentiation of the earth (t_o) have been determined from analyses of meteorites. Direct measurements of this ratio cannot be made because crustal rocks formed at that time have apparently not been preserved. The use of meteorites to determine values of a_o and t_o for the source regions of basalt magma can be justified by analogy with the results for lead isotopes. Patterson and his associates showed that the abundances of lead isotopes in different stony meteorites and in Recent crustal rocks converge at $t = 4.55 \pm 0.07$ billion years to the primordial abundances preserved in the troilite phase of the iron meteorite Henbury (Patterson, 1956). The uranium and thorium contents of this meteorite are so low that the abundances of the lead isotopes have remained virtually unchanged since t_o. Similarly, the value of the initial Sr^{87}/Sr^{86} ratio can be determined directly from isotopic analyses of strontium in Rb-poor stony meteorites such as the achondrite Pasamonte.

Measurements of the Sr^{87}/Sr^{86} ratio for this meteorite have been reported by Herzog and Pinson (1956), Schumacher (1956), and Gast (1960a). Gast's value of 0.7004 ± 0.002 is based on triplicate analyses on two mass spectrometers and is probably the most precise determination. The error of 0.002 is here considered to be the uncertainty of Gast's value as an estimate of the true value of a_o. Assuming that $a_o = 0.7004 \pm 0.002$ and $t_o = 4.55 \pm 0.07 \times 10^9$ years, equation (1) can be solved for (Rb^{87}/Sr^{86}) which is then transformed to the weight-ratio of Rb/Sr.

Using these values for a_o and t_o the variation of the Sr^{87}/Sr^{86} ratio in basalt from different localities indicates a range of values of the Rb/Sr ratio in the source material of basalt magma from 0.022 to 0.051. The average Rb/Sr ratio is 0.039. A comparison of the calculated values of the Rb/Sr ratios of the source material with the Rb/Sr ratios in basalts indicates an enrichment of Rb (or depletion of Sr) of the basalt magma relative to the source material. The only exception to this are the basalts from Hawaii Island whose Rb/Sr ratio is identical to that calculated for their source regions.

The average of the Sr^{87}/Sr^{86} ratios of four basalts from Hawaii Island is 0.7069 ± 0.0003 whereas the basalt

from the neighboring island of Maui has a value of 0.7047 $\pm$ 0.001. This difference, if real, can be interpreted as evidence that basalt magma was derived from two separate source regions having different Rb/Sr ratios. If the concentration of alkali elements decreases with depth in the source regions, differences of Sr^{87}/Sr^{86} ratios of basalts could also be interpreted in terms of depth of the source material.

A comparison of the calculated values of the Rb/Sr ratios of the source regions of basalt magma with the Rb/Sr ratios of different types of igneous rocks may serve to identify the nature of the source material. Concentrations of rubidium and strontium in different types of igneous and sedimentary rocks were compiled from the literature (Table A-4). The calculated average Rb/Sr ratio of the source regions of basalt magma is 0.039 and thus lies in the range of basalt, eclogite, and pyroxenite. No reliable data exist for peridotites. Neither chondrites nor the achondrites which have been analyzed are suitable materials from which to derive basalt magma. Based on the evidence presented here the conclusion is justified that the source material of basalt magma has an average Rb/Sr

ratio which most closely resembles those observed in ultra-basic igneous rocks and eclogite.

The analytical results and their interpretation are shown in Figure A-1. The initial point is assumed to have the coordinates $a_o = 0.7004 \pm 0.002$, $t_o = 4.55 \pm 0.07 \times 10^9$ years. Differences in the Sr^{87}/Sr^{86} ratios of basalts from different localities are attributed to corresponding differences in the Rb/Sr ratios of the source regions of basalt magma. The basalt from Iceland (R4159) has the highest value of the Sr^{87}/Sr^{86} ratio. The strontium development line of its source material therefore may give an upper limit of the Sr^{87}/Sr^{86} for all source regions throughout geologic time. This limiting upper value will be used in comparisons with initial Sr^{87}/Sr^{86} ratios of intrusive rocks of unknown origin to determine their possible derivation from the source regions of basalt magma. The slope of this strontium development line can be determined independently be measuring the initial Sr^{87}/Sr^{86} ratios of Precambrian basic intrusives.

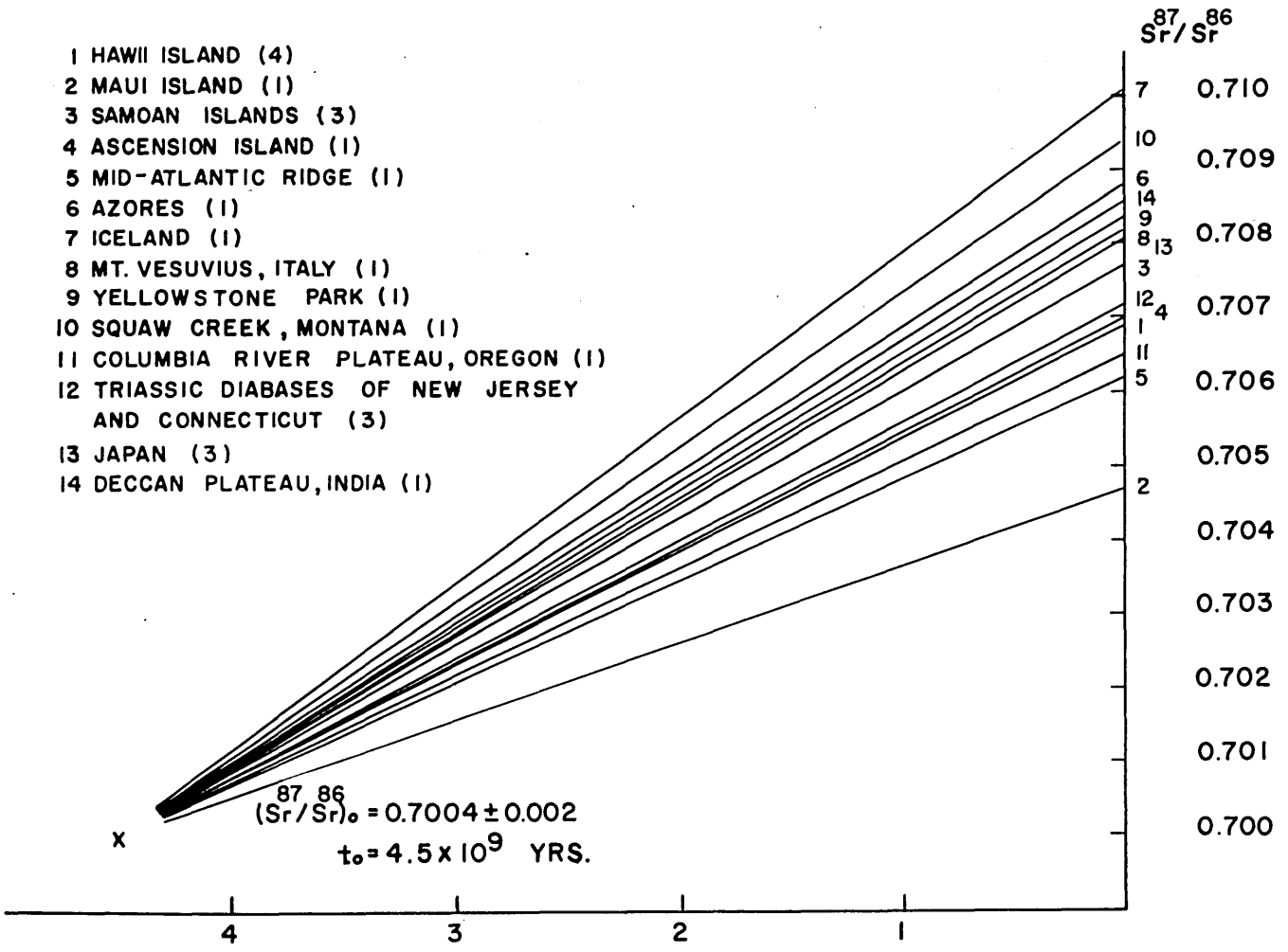

FIGURE A-1 THE Sr^{87}/Sr^{86} RATIO IN THE SOURCE REGIONS OF BASALT

THE ISOTOPIC COMPOSITION OF STRONTIUM IN THE CONTINENTAL CRUST.

The objective is to show that the average Sr^{87}/Sr^{86} ratio of rocks in the upper regions of the continental crust is measurably higher than that of the source regions of basalt magma. To date only a small number of isotopic analyses of strontium in crustal rocks have been reported. Gast (1960a) analyzed ten granitic rocks ranging in age from 200 to more than 2650 million years and found Sr^{87}/Sr^{86} ratios from 0.720 to 1.003, averaging 0.830. Schreiner (1958) reported values ranging from 0.859 to 1.811 for the red granite from the Bushveld Complex. On the other hand Paleozoic limestones are known to have Sr^{87}/Sr^{86} ratios close to 0.712 as does ocean water (Gast, 1960a). It is clear that existing data are not adequate to define the composition of crustal strontium but serve merely to demonstrate the extreme variations which exist. The range of values is large because the crust is composed of a great variety of rock types of different ages whose Rb/Sr ratios vary through several orders of magnitude. In spite of this inhomogeneity meaningful average values can probably be obtained by analyzing the strontium in

those geological environments which are composed of or contain weathering products of a variety of crustal rocks. Such environments are geosynclinal sediments, metamorphic rocks, paragneisses, glacial till, river water and ocean water.

Isotopic analyses of strontium in such rock types are not yet available. It is therefore necessary to estimate the Sr^{87}/Sr^{86} ratio in the crust on the basis of the average Rb/Sr and probable age of the continental crust. Such an estimate will show that it is reasonable to expect that the average Sr^{87}/Sr^{86} ratio of a mass of sialic rocks, which might become granitized during an orogeny, is significantly higher than that of the source regions of basalt magma. The actual value of the initial ratio of an igneous rock of crustal derivation depends, of course, on the geological history of the material. The average Sr^{87}/Sr^{86} ratio of a volume of geosynclinal sediments, for instance, will depend on the proportions of volcanic rocks and limestone on the one hand and detrital sediments derived from weathering of ancient continental rocks on the other.

An extensive survey of the geochemical literature was undertaken in order to obtain the best estimate of

the Rb/Sr ratios in different types of rocks and in the continental crust. Analyses were selected on the basis of a precision error of better than ± 15%. The analyses were weighted in the average for each rock type by the total number of specimens represented by each analysis (Table A-4).

Table A-4 Concentrations of Rubidium and Strontium in Igneous and Sedimentary Rocks.

Rock Type	Rb ppm	Sr ppm	Rb/Sr
Granite	196 (290) 1,4,5,6,7,8	197 (245) 1,2,3,7,9	1.00
Granodiorite	122 (9) 4,8	440 (85) 3	0.28
Syenite	136 (14) 4,5,10,11	156 (2) 10,11	0.87
Diorite andesite	88 (21) 4,5,8	500 (13) 3	0.18
Gabbro basalt	32 (331) 1,4,5, 7,11,12,13	440 (612) 2,3,7,9,11	0.07
Olivine basalt	18 (11) 7,11	440 (11) 7,11	0.04
Eclogite	6.9 (1) 11	149 (1) 11	0.05
Anorthosite	0.6 (1) 11	280 (2) 11,13	0.002
Pyroxenite	0.5 (1) 11	49 (1) 11	0.01
Chondrites	3.17 (12) 13,15,16,17,18	10.6 (2) 16,17,18	0.30
Achondrites	0.37 (6) 13,15,17,18	92.1 (1) 17	0.004
Shale	149 (29) 3,5,19	300 (69) 3	0.50
Limestone	5 (7) 5	610 (160) 3,19	0.008
Sandstone	60 (4) 5	20 ( ) 3	3
Deep sea clay	110 (8) 5	720 (98) 3,20,21,22	0.15
Globigerina ooze	10 (6) 5	800 (3) 22	0.012

(/) Number of specimens.
2 Index to authors.

1. Ahrens et al., 1952
2. Turekian, 1955
3. Turekian and Kulp, 1956
4. Taylor et al., 1956
5. Horstman, 1957
6. Sazhina, 1958
7. Gast, 1960a
8. Demin and Khitarov, 1958
9. Katchenkov & Flegontova, 1958
10. Wager and Mitchell, 1953
11. This work
12. Fairbairn et al., 1953
13. Cabell and Smales, 1957
14. Pinson et al., 1953
15. Gast, 1960b
16. Herzog and Pinson, 1956
17. Schumacher, 1956
18. Webster et al., 1957
19. Heide and Christ, 1953
20. Clarke, 1924
21. Hevesy et al., 1934
22. Goldberg et al., 1958

Values from Table A-4 were used to estimate the concentrations of rubidium and strontium in the crust as defined in Poldervaart's model (Poldervaart, 1955). The results are shown in Table A-5.

Table A-5 Concentrations of Rubidium and Strontium in the Crust as Defined by Poldervaart's Model.

Geological Environment	Rb ppm	Sr ppm	Rb/Sr
Total crust above Moho	74	441	0.17
Continental crust only	87	442	0.20
Igneous rocks in continental shields	90	443	0.20
Sediments on continental shields	88	229	0.39
Sediments in young folded belts	100	352	0.28
Sediments in sub-oceanic regions	114	388	0.29
Deep sea sediments	55	660	0.08

The Rb/Sr ratio of the continental crust is estimated to be 0.20. This includes a layer of basalt which is assumed to exist at the bottom of the continental masses. Because we are primarily concerned with the sialic portion

of the continental crust an average Rb/Sr ratio of 0.25 is arbitrarily accepted as most representative for that region. This value is approximately that of granodiorites shown in Table A-4.

The Sr^{87}/Sr^{86} ratio of a hypothetical geosynclinal assemblage can be estimated on the basis of the data presented in Tables A-4 and A-5. Such an estimate for the volcanic and sedimentary rocks of Poldervaart's young folded belt is shown in Table A-6.

Table A-6 Estimate of the Sr^{87}/Sr^{86} Ratio in a Hypothetical Geosynclinal Assemblage.

Rock Type	Wt.%	Sr ppm	Sr x Wt.% / 100	Sr%	Sr^{87}/Sr^{86}	87/86 x Sr% / 100
Shale	52	300	156	44.3	0.733(1)	0.324
Sandstone	13	20	3	0.9	0.733	0.007
Limestone	22	610	134	38.1	0.712	0.271
Graywacke	5	500	25	7.1	0.708	0.050
Andesite	6	500	30	8.5	0.708	0.060
Rhyolite	2	197	4	1.1	0.708	0.008
Total			352 ppm			0.720

(1) Pure shale and sandstone derived from weathering of granodiorite 2 billion years in age, Rb/Sr = 0.29, $(Sr^{87}/Sr^{86})_o$ = 0.708.

The average Sr^{87}/Sr^{86} ratio for this assemblage might be 0.720 and its Rb/Sr ratio is 0.28. If the average age of the continental crust is 2 billion years and its initial Sr^{87}/Sr^{86} ratio at that time was 0.704, it would now have

an average Sr^{87}/Sr^{86} ratio of 0.725 assuming its Rb/Sr ratio 0.25 as suggested above.

These estimates were confirmed by the isotopic analyses of strontium in two composites of Paleozoic shale. One of these composites is from the Appalachian Province, the other one is from the west coast (Table A-7). The average Sr^{87}/Sr^{86} ratio is 0.7215 which is very close to the value predicted for a geosynclinal assemblage. These shale composites

Table A-7 Isotopic Composition of Strontium in Composites of Paleozoic Shale.

Sample Number	Locality	87/86	$(87/86)_{corr}$	86/88	84/88	No. of scans.
R4184	East Coast	0.7204	0.7204	0.1194	0.0064	44
R4185	West Coast	0.7232	0.7226	0.1192	0.0066	90
Average shale		0.7218	0.7215	0.1193	0.0065	

contain calcite and probably some volcanic material. They therefore resemble more closely the geosynclinal assemblage than a "pure" shale.

Based on the evidence presented above the assumption is justified that the Rb/Sr ratio of the upper regions of the continental crust is approximately 0.25 and that the Sr^{87}/Sr^{86} is of the order of 0.725 ± 0.005.

For age determination purposes by the Rb-Sr method it

is customary to assume an initial Sr^{87}/Sr^{86} ratio of 0.712. This value is based on analyses of the isotopic composition of strontium in sea water and $SrCO_3$ reagents. It gives meaningful ages only when the material is strongly enriched in radiogenic Sr^{87} so that the exact value of the initial abundance of Sr^{87} is not important. An average crustal Sr^{87}/Sr^{86} ratio of 0.712 implies that the continental crust is composed predominantly of basalt or of relatively young acid volcanic rocks. Green and Poldervaart (1958, p.105) found that "... the geochemistry of Na and K is incompatible with a theory of evolution of continents by weathering and sedimentation of basaltic source rocks. On the one hand there is too much sediment, on the other there is not enough Na and K in sea-water". Moreover, the age of the continental masses is known to be of the order of 2 billion years or more. An average Sr^{87}/Sr^{86} ratio of 0.712 therefore does not seem compatible with the chemical compositon of the sialic crust and its probable age. The apparent low abundance of Sr^{87} in sea water may be the result of several causes:

1. Recent and Tertiary volcanism in the circum-oceanic belts and in the oceans makes a major contribution to the total amount of strontium in solution in the oceans. This volcanic strontium was developed in the Rb-poor environment of the source regions of basalt magma.

2. Orogenic belts in which young volcanic rocks predominate form the major topographic features actively undergoing erosion. An important proportion of sediments introduced into the oceans therefore has low Sr^{87}/Sr^{86} ratios.

3. Limestones go rapidly into solution thus recycling oceanic strontium.

4. Rubidium is concentrated in clay minerals and micas by replacement of potassium. These minerals are deposited in sedimentary basins and may prevent accumulated radiogenic Sr^{87} from entering the oceans.

All evidence available at the present time favours the conclusion that rubidium is concentrated in the sialic upper regions of the continental crust and that the average value of its Rb/Sr ratio is sufficiently high to result in a measurable enrichment of the sialic crust in Sr^{87}. The particular value of the average Sr^{87}/Sr^{86} ratio of a volume of crustal rocks depends on its geologic history and the Rb/Sr ratios of its component rock types. It is reasonable to expect that the initial ratio of an igneous rock of crustal derivation is higher than that of a rock which originated in the source regions of basalt magma.

Geological Applications.

The objectives of the study of Sr^{87}/Sr^{86} ratios in geological materials can be stated as follows:

1. To distinguish igneous rocks formed by re-melting of the sialic crust from those originating from the source regions of basalt magma in the upper mantle or the base of the crust.

2. To relate diverse products of magmatic differentiation to a common source.

3. To obtain information about the chemical composition of the source regions of basalt magma.

The use of the initial Sr^{87}/Sr^{86} ratio of igneous rocks as a criterion to determine the origin of the material is illustrated in Figure A-2. The strontium development line for the source regions of basalt magma is drawn from the initial point, based on meteoritic data, to the upper limit of variation of the Sr^{87}/Sr^{86} ratio in basalts. This line, if drawn correctly, therefore represents the maximum value of the Sr^{87}/Sr^{86} ratio in source regions of basalt magma throughout geologic time. It is implied that the Rb/Sr ratio of the source regions has remained constant with time. This assumption may need modification but serves as a first approximation.

The most representative value of the Sr^{87}/Sr^{86} ratio of the sialic crust at the present time is assumed to be 0.725 ± 0.005 with an average Rb/Sr ratio of 0.25 as indicated by the slope of the dashed line in

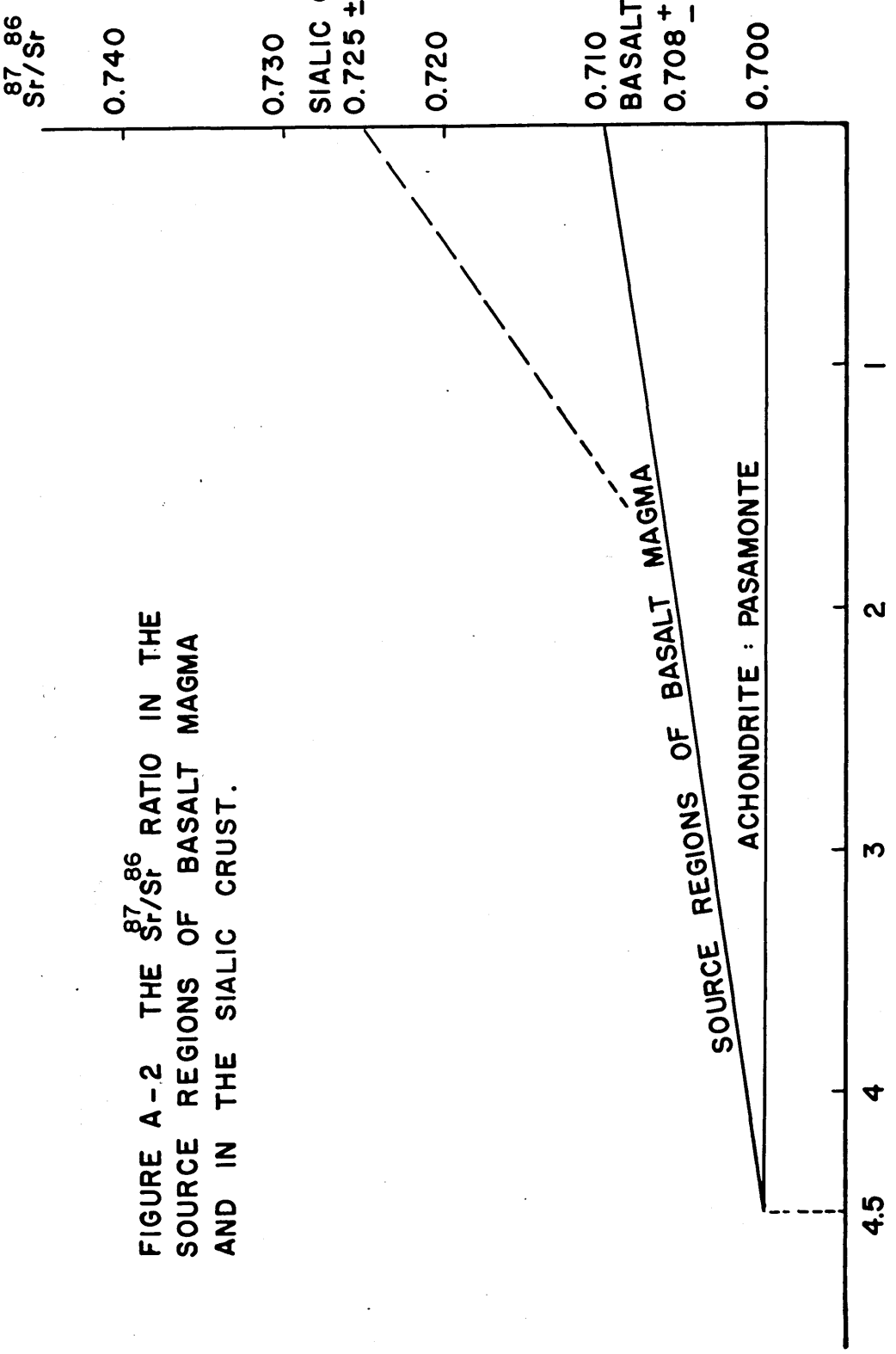

FIGURE A-2 THE Sr^{87}/Sr^{86} RATIO IN THE SOURCE REGIONS OF BASALT MAGMA AND IN THE SIALIC CRUST.

Figure A-2. If the initial Sr^{87}/Sr^{86} ratio of an intrusive or volcanic igneous rock falls on or below the strontium development line of the source regions of basalt magma, a sub-crustal origin is indicated for that rock. On the other hand, if the initial ratio lies significantly above the Sr^{87}/Sr^{86} ratio of the sub-crustal source regions a crustal origin is implied. The actual value of the initial Sr^{87}/Sr^{86} ratio of such a rock will be a measure of the amount of young volcanic rocks of sub-crustal origin mixed with the sialic material.

In order to determine the initial Sr^{87}/Sr^{86} ratio of an igneous rock it is necessary to know its present Sr^{87}/Sr^{86} ratio, its Rb/Sr ratio and its age. The value of the initial ratio and the time of crystallization of the intrusive are also given by the coordinates of the point of convergence of the whole-rock strontium development lines of several co-magmatic rock types having different Rb/Sr ratios. If the rock was not re-heated after its initial time of crystallization, the component minerals may also be used to determine the initial Sr^{87}/Sr^{86} ratio. In general the products of differentiation of a volume of magma initially all have the same

Sr^{87}/Sr^{86} ratio as their parent magma. Thereafter each fraction develops its own value of the Sr^{87}/Sr^{86} ratio in accordance with its particular Rb/Sr ratio. The convergence of the whole-rock strontium development lines of a number of associated igneous rocks is therefore strong evidence for a co-magmatic relationship. The coordinates of the point of convergence are the time of differentiation of the parent magma and the Sr^{87}/Sr^{86} ratio of the magma at that time. The magnitude of this value can then be used to determine the origin of the magma as indicated above.

This convergence test can be applied to the study of the differentiation of magma under different physical conditions as indicated by associated volcanic and intrusive igneous rocks. It can also be used to determine the relationships of pegmatites, lamprophyres, carbonatites, etc. to the igneous intrusives with which they may be associated. A co-magmatic origin is indicated if it can be shown that their strontium development lines converge to the same point as do those of the associated igneous rocks.

In so far as basalt magma is formed by partial

melting of source material in the upper mantle, the abundance of Sr^{87} in basalts and other basic and ultra-basic igneous rocks from different geographic localities can be used to study the homogeneity of the upper mantle with respect to its Rb/Sr ratio. The initial Sr^{87}/Sr^{86} ratios of basic intrusives intruded into the sialic crust at different times record the abundance of Sr^{87} of the upper mantle throughout geologic time. From a plot of these points vs geologic time independent evidence of the history of differentiation of the upper mantle can be obtained.

Evidence of Sub-crustal Origin of the Intrusive Igneous Rocks in the Monteregian Hills, Quebec

The Monteregian "hills" are a series of eight small intrusives of alkali-rich igneous rocks extending from Montreal, Quebec, eastward across the St. Lawrence lowlands for a distance of about 50 miles. These intrusives and their associated dikes and sills are composed of a great variety of rocks ranging in composition from basic essexite to intermediate nepheline syenites. They constitute collectively a distinct petrographic province which is believed to have formed as a result

of crystal fractionation of a single parent magma and multiple injections of the fractionation products. A detailed escription of the intrusives and a complete bibliography were given by Dresser and Denis, (1944, p. 455).

These igneous rocks have intruded Precambrian crystalline rocks of the Grenville Province which are at least 1000 million years in age. Much of the material forming the metamorphic rocks of this region probably came from older Precambrian areas to the North, with ages of 1700 to 2600 million years. The Sr^{87}/Sr^{86} ratio in the host rocks is therefore undoubtedly well up in the range of values for ancient continental crustal regions.

The age of the intrusives is 122 ± 9 million years according to K-Ar age determination on biotite from Brome Mountain (Lowdon, 1960, p.38). This age has been confirmed by the Geochronology Laboratory at M.I.T. (Ann. Progress Report, 1960, p. 283).

Isotopic compositions of strontium in four specimens of igneous rocks from the Monteregian hills and in one sample of calcite from a carbonatite at Oka were

determined. Concentrations of rubidium and strontium were measured in two of the igneous rocks by isotope dilution. The experimental data are shown in TableA-8.

Discussion of Experimental Results.

The average value of the corrected Sr^{87}/Sr^{86} ratio of the essexite, the yamaskite and the tinguate is 0.7049. This value is considerably lower than that for the nordmarkite which is 0.7156. However, when the strontium development lines with their error envelopes are plotted for the nordmarkite and the yamaskite, an intersection is obtained at t = 115 $\pm$ 25 million years and Sr^{87}/Sr^{86} = 0.7047 $\pm$ 0.001 (Figure A-3). This time is identical within experimental error to the age of the biotite from Brome Mountain which was determined by the K-Ar method. The time at which the strontium development lines intersect is therefore also the time at which the different rock types were separated from the parent magma and from each other and began to accumulate radiogenic strontium in accordance with their different Rb/Sr ratios. This is strong evidence that the nordmarkite is a magmatic differentiate of the same parent magma which gave rise to the yamaskite and the

Table A-8 Isotopic Composition of Strontium in Igneous Rocks from the Monteregian Hills.

Sample No. Locality & Rock Type	Date	$\frac{Sr^{87}}{Sr^{86}}$	$(\frac{Sr^{87}}{Sr^{86}})_{corr}$ *	$\frac{Sr^{86}}{Sr^{88}}$	$\frac{Sr^{84}}{Sr^{88}}$	No. of scans	Rb ppm	Sr ppm	$\frac{Rb}{Sr}$
Mt. Johnson, Quebec									
R4180 Essexite	10/28/60	.7050	.7053 ±.001	.1195	.0064	84			
Mt. Yamaska, Quebec									
R4179 Yamaskite	11/4/60	.7040	.7049 ±.001	.1197	.0066	84	59.6 ±2%	1635 ±1%	.0365 ±.0008
Mt. Royal, Quebec									
R3069 Tinguaite(?)	12/17/60	.7048	.7045 ±.001	.1193	.0067	90			
Oka, Quebec									
C3252 Calcite	12/18/60	.7046	.7067	.1201	.0067	84			
" "	1/6/61	.7067	.7057	.1191	.0069	90			
Average Calcite		.7057 ±.0011	.7062 ±.0005	.1196 ±.0005	.0068 ±.0001				
Shefford, Quebec									
R4181 Nordmarkite	11/1/60	.7177	.7156 ±.001	.1187	.0066	84	140.9 ±2%	62.4 ±2%	2.24 ±.06

*Corrected by adjusting the Sr^{86}/Sr^{88} ratio to .1194 and the Sr^{87}/Sr^{86} ratio by half this amount.

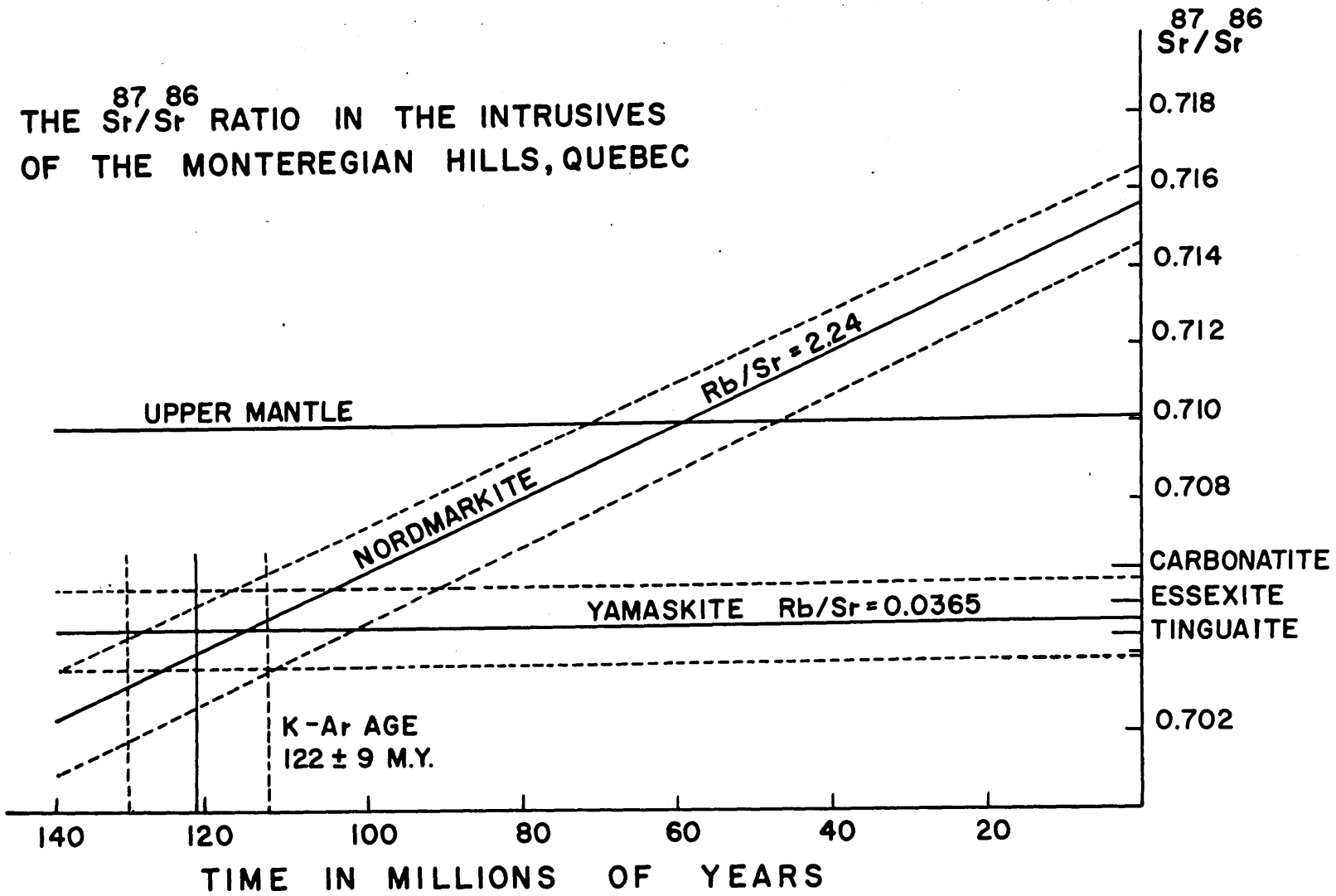
THE $^{87}Sr/^{86}Sr$ RATIO IN THE INTRUSIVES OF THE MONTEREGIAN HILLS, QUEBEC
$^{87}Sr/^{86}Sr$
0.718
0.716
0.714
0.712
0.710
0.708
0.702
Rb/Sr = 2.24
UPPER MANTLE
NORDMARKITE
CARBONATITE
ESSEXITE
TINGUAITE
YAMASKITE Rb/Sr = 0.0365
K-Ar AGE
122 ± 9 M.Y.
140
120
100
80
60
40
20
TIME IN MILLIONS OF YEARS

FIGURE A-3

other rock types. The only way in which the nordmarkite could develop a Sr^{87}/Sr^{86} ratio of 0.7156 in 115 million years is to have had an initial ratio of 0.7047. Had the nordmarkite magma been contaminated at the time of its intrusion with old crustal material having a Sr^{87}/Sr^{86} ratio much greater than 0.7047. It could not give an intersection with the yamaskite at a time which is known to be the age of these rocks from other evidence.

The Sr^{87}/Sr^{86} ratio of the parent magma was = 0.7047 $\pm$ 0.001. This is surprisingly low when compared to the average Sr^{87}/Sr^{86} ratio for oceanic and continental basalts which is $0.7078^{+0.002}_{-0.003}$ (Table A-3). The low abundance of the Sr^{87}/Sr^{86} ratio indicates that the source material from which the magma was formed had a very low Rb/Sr ratio, even lower than the source material for average basalts. The Rb/Sr ratio of the source material is estimated by assuming an age of the earth of 4.5 billion years and an initial Sr^{87}/Sr^{86} ratio of 0.7004 $\pm$ 0.002 (Gast, 1960a.). The Rb/Sr ratio calculated in this way is 0.022 $\pm$ 0.011. This value is so low that only an ultrabasic rock could qualify as a source for the primary Monteregian hill magma. If the content of

alkalis decreases downward in the upper mantle, this value would suggest that the source region for the magma was at considerable depth in the upper mantle.

The isotopic composition of strontium in calcite concentrated from Nb ore from a carbonatite at Oka, Quebec, was determined for comparison with the strontium in the igneous rocks of the Monteregian hills. The average of two independent determinations gave $Sr^{87}/Sr^{86} = 0.7062 \pm 0.0005$. The Sr^{87}/Sr^{86} ratio of the carbonatite is therefore not measurably different from that in the basic igneous rocks. The results are not inconsistent with the conclusion that the calcite of the carbonatite at Oka is of sub-crustal origin and is related to the igneous rocks.

This conclusion is strengthened by comparison with a Sr^{87}/Sr^{86} ratio of 0.709 ± 0.002 reported by Gast (1960a) for Grenville limestone. An impure Grenville limestone containing a small amount of mica would be expected to have an even higher ratio. Gast also gave a value of 0.713 ± 0.003 for an Ordovician limestone from Perry County, Texas.

Conclusions.

The results of isotopic analyses of strontium in 25 basalts from oceanic and continental localities indicate that the source regions of basalt magma in the upper mantle are homogeneous within narrow limits with respect to the Sr^{87}/Sr^{86} ratio. The average value of this ratio and its limits of variation in the basalts analyzed in this survey is $0.7078^{+0.002}_{-0.003}$.

The relatively narrow distribution of the Sr^{87}/Sr^{86} ratios in basalts is consistent with the conclusion that the source regions were initially homogeneous with respect to the abundance of Sr^{87}. The differences in the Sr^{87}/Sr^{86} ratios observed in Recent and Tertiary basalts from different geographic localities are believed to have developed in response to lateral and/or vertical variations of the Rb/Sr ratio in the upper mantle since the time the mantle solidified. Assuming that the initial Sr^{87}/Sr^{86} ratio was 0.7004 ± 0.002 and $t = 4.5 \times 10^9$ years, the Rb/Sr ratio of the source regions of basalt magma is calculated to be $0.039^{+0.012}_{-0.017}$. This value is in the range of the Rb/Sr ratios observed in eclogite, olivine basalts and certain ultrabasic igneous rocks.

The Rb/Sr ratio of the sialic portion of the continental crust is estimated to be 0.25 from the best geochemical evidence presently available. This value is significantly higher than that indicated for the source regions of basalt magma. It is therefore expected that the average Sr^{87}/Sr^{86} ratio of the sialic crust is measurably higher than that of the sub-crustal sources of basalt magma. Reasonable estimates of the age of the sialic crust and its initial Sr^{87}/Sr^{86} ratio suggest a probable present average value of 0.725 ± 0.005 for this ratio.

Based on this evidence the hypothesis is advanced that the Sr^{87}/Sr^{86} ratios of intrusive and volcanic igneous rocks in the sialic crust at the time of their crystallization, can be used to distinguish re-melted and granitized sialic material from differentiation products of basaltic magma of sub-crustal origin. The applicability of this test depends on the actual value of the initial ratio of an igneous rock of possible sialic derivation and on the degree of certainty with which it can be distinguished from the Sr^{87}/Sr^{86} ratio of the sub-crustal source regions of basalt.

The strontium development lines of co-magmatic igneous rocks which are fractionation products of a

common parent magma converge to a point when plotted backwards in time. The coordinates of this point are the time of differentiation and the Sr^{87}/Sr^{86} ratio of the parent magma at that time. It is suggested that the relationships between suites of diverse differentiation products can be determined by testing for possible convergence of their whole-rock strontium development lines. This method may also be used to determine the relationships of pegmatites, carbonatites and lamprophyres with associated intrusive igneous rocks.

The isotopic compositions of strontium in several intrusive igneous rocks from the Monteregian hills, Quebec, indicate that they are the differentiation products of a common parent magma which probably originated at considerable depth below the base of the crust. The abundance of Sr^{87} in a sample of calcite from the carbonatite at Oka, Quebec, is not inconsistent with the conclusion that it is directly related to the igneous rocks in the Monteregian hills.

Acknowledgments.

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Part II

Chapter 1

VARIATIONS OF THE SR^{87}/SR^{86} RATIO IN ROCKS AND THEIR GEOLOGIC SIGNIFICANCE.

Introduction.

The element strontium has four stable isotopes, namely: Sr^{88}, Sr^{87}, Sr^{86}, and Sr^{84}. One of these, Sr^{87}, is the daughter product of the radioactive decay of Rb^{87} and its abundance has therefore increased throughout geologic time. This increase in the abundance of Sr^{87} is conveniently expressed in terms of the Sr^{87}/Sr^{86} ratio.

As will be shown later, the ratio Sr^{87}/Sr^{86} at any point in the earth increases in time as a function of the Rb/Sr ratio at that point. This is true not only for mineral grains and rock specimens but also for large divisions of the earth such as the continental crust and the mantle. Both these large-scale geological environments have developed, throughout geologic time, characteristic Sr^{87}/Sr^{86} ratios in accordance with their Rb/Sr ratios.

A survey of the geochemical literature (Chapter 2) suggests that the Rb/Sr ratio of the continental crust is approximately 0.25. On the other hand, the isotopic

composition of strontium in basalts of sub-crustal origin demands a Rb/Sr ratio of about 0.04 for the upper mantle (Chapter 6). Because of this difference in the Rb/Sr ratios it is expected that the crust and the mantle have developed significantly different average Sr^{87}/Sr^{86} ratios.

The actual value of this ratio in the crust is not known with certainty at the present time. If the average age of the continents is 2 billion years, their Rb/Sr ratio is 0.25, and the initial Sr^{87}/Sr^{86} ratio is 0.7004 $\pm$ .002, the present value of the Sr^{87}/Sr^{86} ratio should be 0.725. This topic is discussed in more detail in Chapter 3. On the other hand, the average Sr^{87}/Sr^{86} ratio of 25 oceanic and continental basaltic rocks of sub-crustal origin is 0.7078 (Chapter 6). Mass spectrometric measurement precision of the Sr^{87}/Sr^{86} ratio can be as low as $\pm$ 0.001 for a single determination (Chapter 5) so that the difference between crustal strontium and mantle-strontium is clearly measurable.

This difference between mantle-strontium and crustal strontium has important geological implications: A body of magma formed by partial melting of the upper mantle and injected into the crust contains strontium which was developed in the low-Rb mantle environment. All products of magmatic differentiation of sub-crustal magma will

likewise contain mantle-strontium. Because of the difference of the Sr^{87}/Sr^{86} ratio in the crust, mantle-strontium can be recognized and identified as such. The Sr^{87}/Sr^{86} ratio of igneous rocks at the time of their crystallization is therefore a possible criterion for crustal or sub-crustal origin.

The purpose of this study is to ascertain the exact value and the range of variation of the Sr^{87}/Sr^{86} ratio in the sub-crustal magmatic source regions. This was done by analyzing the strontium in 25 basaltic rocks of sub-crustal origin from a large number of oceanic and continental localities. In addition concentrations of rubidium and strontium were determined for a representative number of basalts in order to compare the Rb/Sr ratios of the rocks to those calculated for their source regions. Such comparisons are one way in which information about the processes of magma formation can be obtained.

In addition several related topics were investigated: The age of an eclogite, the origin and differentiation of magma in the Monteregian hills and an attempt to study the variation of the Sr^{87}/Sr^{86} ratio of the upper mantle in the course of geologic time by determining the

initial Sr^{87}/Sr^{86} ratios in several Precambrian basic intrusives.

The value of the half life of Rb^{87} used throughout this thesis is $T = 47 \pm 1 \times 10^9$ years (Flynn and Glendenin, 1959).

Derivation of the Strontium Development Equation.

Russel and Allan (1955) derived completely general equations for the variations in the abundances of lead isotopes. These equations were adapted to the Rb^{87} decay scheme by Gast (1960, p.1291). In the following the strontium development equation is simplified into a more approximate but more easily useable form.

The disintegration of Rb^{87} to Sr^{87} is subject to the law of natural radioactive decay:

$$P = P_o e^{-\lambda t} \qquad (1)$$

where

P = number of parent atoms at time t
P_o = number of parent atoms at time $t = 0$
λ = decay constant
t = time.

The number of radiogenic daughter atoms *D is given by

$$^{*}D = P_o - P = P(e^{\lambda t} - 1). \quad (2)$$

Substituting appropriate chemical symbols for the numbers of daughter and parent atoms:

$$^{*}Sr^{87} = Rb^{87}(e^{\lambda t} - 1) \quad (3)$$

The total number of atoms of isotope Sr^{87} in a given sample of matter is

$$Sr^{87} = Sr^{87}_o + {}^{*}Sr^{87} \quad (4)$$

where Sr^{87}_o is the number of atoms of Sr^{87} at t = 0. Therefore the total number of atoms of Sr^{87} in any given system at any time is

$$Sr^{87} = Sr^{87}_o + Rb^{87}(e^{\lambda t} - 1) \quad (5)$$

While the number of Sr^{87} atoms increases as a function of time and the number of Rb^{87} atoms in the system, the number of Sr^{86} atoms remain unchanged. It is therefore permissible to divide both sides of equation (5) by Sr^{86}.

$$Sr^{87}/Sr^{86} = (Sr^{87}/Sr^{86})_o + Rb^{87}/Sr^{86}(e^{\lambda t} - 1) \quad (6)$$

Equation (6) is entirely rigorous. The first approximation is introduced by expanding $e^{\lambda t}$ in a power series and neglecting all but the first two terms.

Since $e^{\lambda t} = 1 + \lambda t + \frac{(\lambda t)^2}{2!} \quad \frac{(\lambda t)^3}{3!} \quad \ldots$

the term $(e^{\lambda t}-1) \sim \lambda t$ when $\lambda t \gg \frac{(\lambda t)^2}{2!}$

This approximation causes a maximum error of 3.4% when $t = 4.5$ billion years. If the third term is included, the error is reduced to 0.07%.

Therefore,

$$\frac{Sr^{87}}{Sr^{86}} \cong \frac{Sr^{87}}{Sr^{86}}_{o} + \frac{Rb^{87}}{Sr^{86}} \lambda t \qquad (7)$$

It is convenient to transform the atomic ratio $\frac{Rb^{87}}{Sr^{86}}$ into a weight ratio:

$$\frac{Rb^{87}}{Sr^{86}}_{atomic} = \left(\frac{Rb}{Sr}\right)_{weight} \times \frac{At.\ wt.\ Sr \times A^{Rb^{87}}}{At.wt.Rb \times A^{Sr^{86}}} \qquad (8)$$

where

$A^{Rb^{87}}$ = isotopic abundance of Rb^{87} at the present time, expressed as a fraction of the total number of rubidium atoms.

$A^{Sr^{86}}$ = isotopic abundance of Sr^{86} in the sample of strontium for which the Sr^{87}/Sr^{86} ratio was determined.

Substituting (8) into (7)

$$\frac{Sr^{87}}{Sr^{86}} \simeq \frac{Sr^{87}}{Sr^{86}_{o}} + \left(\frac{Rb}{Sr}_{wt}\right) \times \frac{At.Wt.Sr.A^{Rb^{87}}}{At.Wt.Rb.A^{Sr^{86}}} \lambda t \quad (9)$$

If $k = \frac{At.Wt.Sr \times A^{Rb^{87}}}{At.Wt.Rb \times A^{Sr^{86}}}$

$$\frac{Sr^{87}}{Sr^{86}_{t}} \simeq \frac{Sr^{87}}{Sr^{86}_{o}} + \left(\frac{Rb}{Sr}_{wt}\right) \times k\lambda t \quad (10)$$

The numerical value of the factor k is calculated from the atomic weights of rubidium and strontium and the abundances of Rb^{87} and Sr^{86} at the present time. Since the atomic weight of strontium and the abundance of Sr^{86} depend on the amount of radiogenic Sr^{87} present, the factor k is not strictly a constant but should be evaluated for each sample. The value of k increases by 1.35% when the isotopic composition of strontium varies between the limits $Sr^{87}/Sr^{86} = 0.712$ to 0.850.

For "normal" strontium $k = \frac{87.710 \times 0.2785}{85.557 \times 0.0986} = 2.8962.$

The strontium encountered here does not differ greatly from "normal" strontium and the value for k = 2.8962 will be used in all calculations unless otherwise stated.

The final form of the strontium development equation

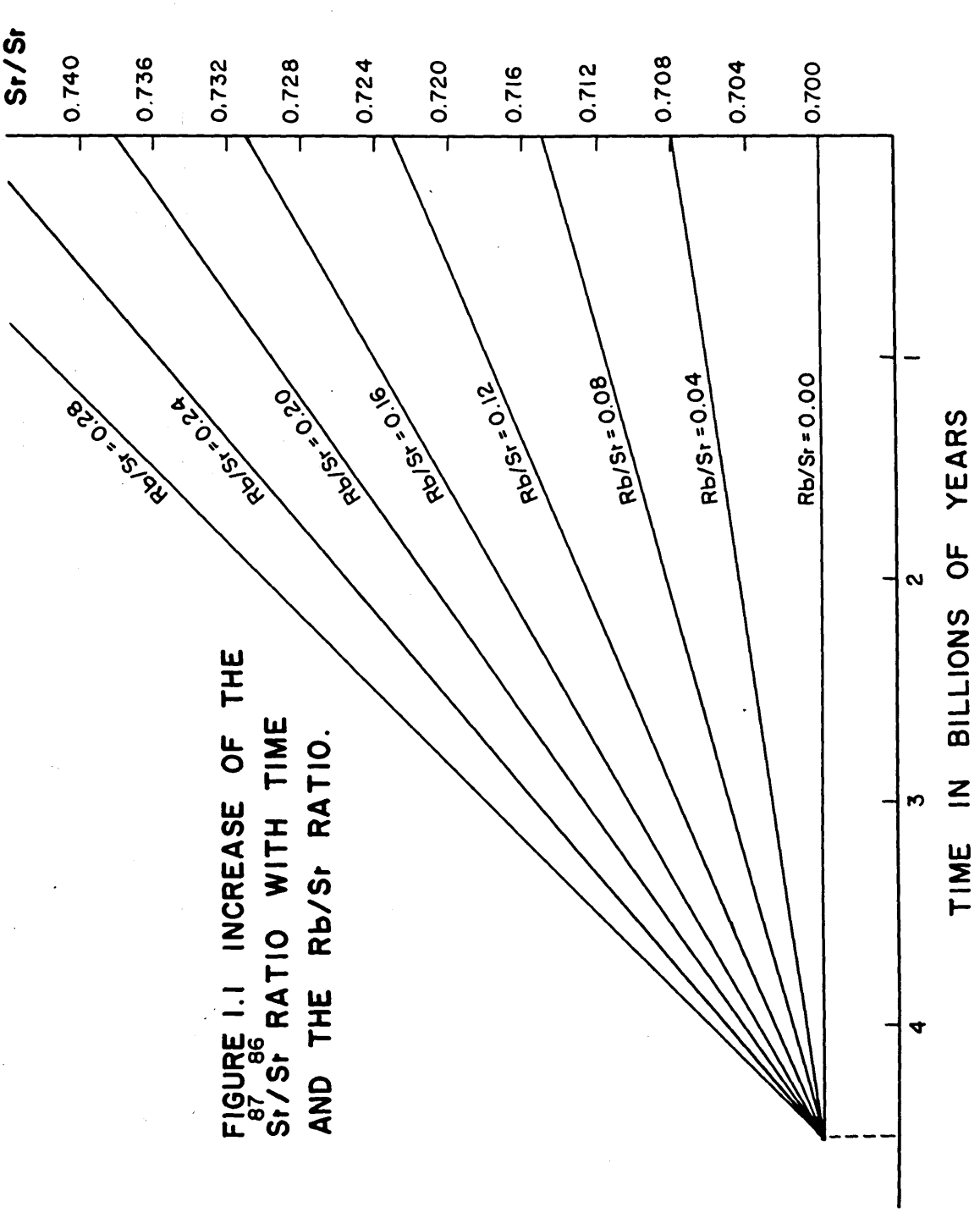


FIGURE 1.1 INCREASE OF THE $^{87}Sr/^{86}Sr$ RATIO WITH TIME AND THE Rb/Sr RATIO.

is:

$$\frac{Sr^{87}}{Sr^{86}_t} \simeq \frac{Sr^{87}}{Sr^{86}_o} + 2.896 \times \left(\frac{Rb}{Sr}_{wt}\right) \lambda \, t \qquad (11)$$

Equation (11) describes a family of straight lines which have a common origin at $t = 0$ when $Sr^{87}/Sr^{86} = (Sr^{87}/Sr^{86})_o$. The slope of the lines is given by $2.896(\frac{Rb}{Sr})\lambda$ and is therefore a function of the Rb/Sr ratio. A system of such straight lines is shown in Figure 1.1. The value of the initial Sr^{87}/Sr^{86} ratio is arbitrary on such a plot but has a definite fixed value for strontium in our solar system.

The Primordial Sr^{87}/Sr^{86} Ratio.

The value of the initial Sr^{87}/Sr^{86} ratio at the time of the differentiation of the earth has been determined from analyses of meteorites. Direct measurements of this ratio cannot be made because crustal rocks formed at that time have apparently not been preserved.

Before the isotopic composition of strontium in any meteorite can be identified as the primordial composition of terrestrial strontium it must be shown that:

1. Different types of meteorites were produced initially from homogeneous parent material and that they have existed as closed chemical systems since that time.

2. That terrestrial strontium originated from the same parent material and initially had the same abundance of Sr^{87} as the meteorites.

Patterson and his associates demonstrated that the abundances of lead isotopes in different types of meteorites and in the crust of the earth satisfy both conditions (Patterson, Goldberg and Inghram (1953), Patterson (1953), Patterson, Brown, Tilton and Inghram (1953), Patterson (1955), Patterson, Tilton and Inghram (1955), Patterson (1956)). The above authors showed that the abundances of lead isotopes in different stony meteorites and in young crustal rocks form an array converging at t = 4.5 billion years to the primordial abundances preserved in the troilite phase of the iron meteorite Henbury. The uranium and thorium contents of this meteorite are so low that the abundances of the lead isotopes have remained virtually unchanged.

By analogy with lead the assumption is justified that terrestrial strontium initially had the same isotopic composition as meteorite strontium. The value of the primordial Sr^{87}/Sr^{86} ratio can be found directly by

analyzing strontium in Rb-poor stony meteorites which have preserved their initial Sr^{87}/Sr^{86} ratio, or it can be determined from the point of convergence of the development lines of strontium in several different stony meteorites. The first approach has been preferred by several investigators who have reported Sr^{87}/Sr^{86} values for achondritic meteorites whose Rb/Sr ratios are less than 0.01 (Table 1.1).

Table 1.1 The Primordial Sr^{87}/Sr^{86} Ratio

Investigator	$(Sr87/Sr86)_o$	Achondrite
Herzog and Pinson, 1956, p. 560.	0.703	Pasamonte
	0.691	
Schumacher, 1956, p. 211.	0.687	Pasamonte
Gast, 1960, p.1290.	0.7011	Pasamonte
	0.7005	"
	0.6995	"
Average Pasamonte	0.7004, $\bar{\sigma}$ = ± 0.0005	
" "	0.7015 ± 0.002	Sioux County
" "	0.7027 ± 0.002	Nuevo Laredo

Herzog and Pinson (1956) preferred a Sr^{87}/Sr^{86} ratio of 0.703 for Pasamonte. This value is definitely higher than that quoted by Schumacher (1956). Gast (1960) re-

determined the Sr^{87}/Sr^{86} ratio for Pasamonte by three independent analyses performed on two mass spectrometers. His average value is 0.7004 ± 0.0005. This result therefore agrees with that of Herzog and Pinson (1956) within the limits of error stated by them. Schumacher's analysis is now considered to be in error.

Gast's values for the Sr^{87}/Sr^{86} ratios in Sioux County and Nuevo Laredo are 0.7015 and 0.7027, respectively. The error of $\pm$ 0.002 assigned to these analyses was not further explained by Gast and is assumed to be a limit of uncertainty.

It is unfortunate that no attempt has as yet been made to determine the initial Sr^{87}/Sr^{86} ratio from the point of convergence of the strontium development lines of several stony meteorites. This would give an independent check of the value obtained by direct analysis of Rb-poor achondrites. Forest City and Homestead are the only chondrites for which Sr^{87}/Sr^{86} ratios as well as Rb/Sr ratios have been determined. The analytical data for these two meteorites are shown in Table 1.2. Initial Sr^{87}/Sr^{86} ratios were calculated assuming that the age of the earth is 4.5×10^9 years and using a decay constant for Rb^{87} of

$47 \pm 1 \times 10^9$ years (Flynn and Glendenin, 1959).

Table 1.2 Initial Sr^{87}/Sr^{86} Ratio in Chondritic Meteorites.

Meteorite	Sr^{87}/Sr^{86}	Rb/Sr	$(Sr^{87}/Sr^{86})_o$
Forest City	0.755±0.003*	0.30±0.035**	0.698±0.007
Homestead	0.753±0.003***	0.32±0.028	0.692±0.006

* Gast, 1960.
** Table 2.1, Chaptez 2
*** Herzog and Pinson, 1956.

It is evident from the data in Table 1.2 that published values of the Sr^{87}/Sr^{86} and the Rb/Sr ratios in stony meteorites do not have sufficient precision to calculate reliable values of the initial Sr^{87}/Sr^{86} ratio. The best estimate of this ratio must therefore come from direct analyses of Rb-poor stony meteorites such as Pasamonte, Nuevo Laredo and Sioux County.

Gast's value of 0.7004±0.002 for Pasamonte is here accepted as the best estimate of the initial terrestrial Sr^{87}/Sr^{86} ratio not only because it is the most precise measurement but also because it has the lowest value of the Sr^{87}/Sr^{86} ratio of the three achondrites. The Rb/Sr ratio of Pasamonte is ~ 0.005 (Schumacher, 1956) and its Sr^{87}/Sr^{86} ratio has therefore remained virtually unchanged with time.

On the other hand, the Rb/Sr ratios of Nuevo Laredo and Sioux County are not known. It is therefore possible that the slightly higher Sr^{87}/Sr^{86} ratios in these two meteorites are caused by small increases of the Sr^{87}/Sr^{86} ratio with time. Nevertheless, a limit of uncertainty of $\pm$ 0.002 will be accepted with the measured Sr^{87}/Sr^{86} ratio of Pasamonte in order to include, at least partly, the other two achondrites. An initial Sr^{87}/Sr^{86} ratio of 0.7004 $\pm$ 0.002 will be used in all calculations throughout this thesis.

Geological Applications.

As early as 1932 Holmes proposed that the differences in the abundance of Ca^{41} could be used to distinguish between granites formed by refusion of granitic parent material and granites which are differentiation products of basaltic magma. This suggestion was based on the assumption, now disproved, that K^{41} decays by β^- emission to Ca^{41}. In the course of the thirty years since this remarkable scheme was proposed radioactive elements have become widely used for age determination purposes. The abundances of daughter isotopes, however, have not been applied

extensively to derive the geological information visualized by Holmes. It is the purpose of this thesis to reformulate Holmes's idea in terms of the abundances of the radiogenic isotope Sr^{87}.

The objectives in the study of Sr^{87}/Sr^{86} ratios in geological materials are conveniently listed as follows:

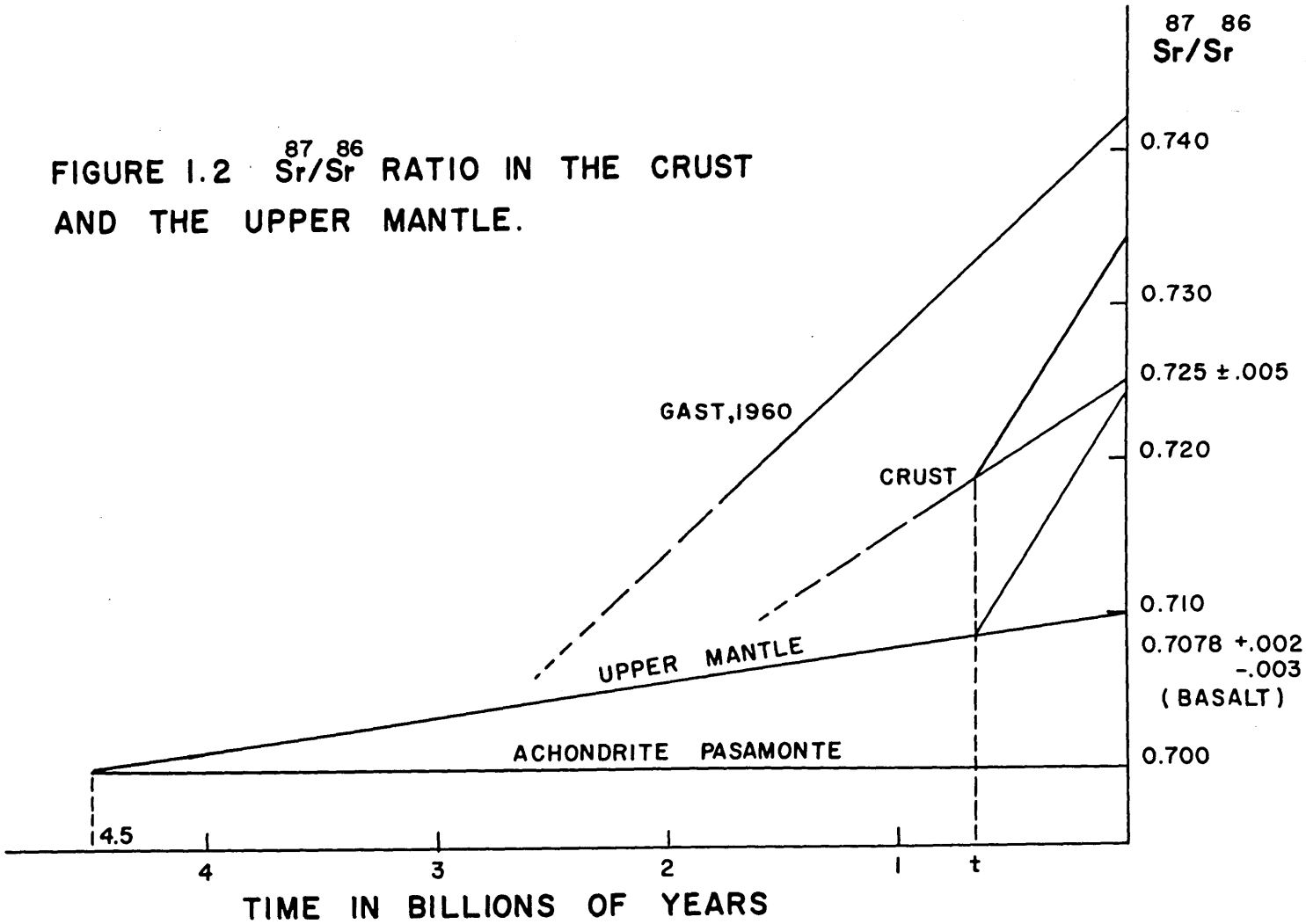
1. To distinguish igneous rocks of crustal origin from those of sub-crustal origin.
2. To relate diverse products of magmatic differentiation to a common parent.
3. To obtain information about the chemical composition of the magmatic source regions in the upper mantle.

In the following pages these three topics will be discussed in some detail.

The Origin of Granitic Igneous Rocks.

The average Sr^{87}/Sr^{86} ratio of the upper mantle at the present time is $0.7078 + 0.002 - 0.003$ (Chapter 6). On the other hand, there is evidence (Chapter 3) that this ratio in the continental crust is approximately $0.725 \pm .005$. Achondritic meteorites indicate that the Sr^{87}/Sr^{86} ratio 4.5 billion years ago was 0.7004 ± 0.002. These facts are combined in Figure 1.2 in order to illustrate the changes in the Sr^{87}/Sr^{86} ratio in the crust and

FIGURE 1.2 $^{87}Sr/^{86}Sr$ RATIO IN THE CRUST AND THE UPPER MANTLE.



in the upper mantle throughout geologic time.

When a volume of granitic magma is produced as a product of magmatic differentiation of basalt magma of sub-crustal origin, its initial Sr^{87}/Sr^{86} ratio at time t will be 0.709, or less. On the other hand, if granitic magma is produced by fusion or granitization of average crustal rocks, its Sr^{87}/Sr^{86} ratio at time t will be approximately 0.719. Both magmas and their crystallization products will then begin to accumulate radiogenic Sr^{87} in accordance with their Rb/Sr ratios. The "sub-crustal" granite would now have a Sr^{87}/Sr^{86} ratio of 0.724 whereas the "crustal" granite would have a ratio of 0.734. The initial Sr^{87}/Sr^{86} ratio at any point in geologic time t of any igneous rock now residing in the crust is therefore a potential criterion for a crustal or sub-crustal origin of this rock.

The value of the initial Sr^{87}/Sr^{86} ratio of an igneous rock which is the product of granitization of geosynclinal sediments depends on the nature of these sediments and does not necessarily lie on the development line of average crustal strontium as indicated in Figure 1.2. If the geosynclinal sediments consist predominantly of volcanic rocks or the weathering products of basic igneous rocks

of sub-crustal origin, the products of granitization will have initial Sr^{87}/Sr^{86} ratios lower than the crustal average at that time. On the other hand, the initial ratio could be higher than the average, if the sediments consisted largely of weathering products of old granitic rocks.

The actual value of the initical Sr^{87}/Sr^{86} ratio of such an igneous rock may be used to estimate the proportion of sub-crustal material in the original sedimentary assemblage, particularly if the Sr^{87}/Sr^{86} of the continental rocks at that time can be determined.

The development line for strontium in the mantle is drawn to the upper limit of variation of the Sr^{87}/Sr^{86} ratio in basalts as observed in this survey. Assuming that Figure 1.2 correctly indicates the time-variation of the Sr^{87}/Sr^{86} ratio in the upper mantle, a sub-crustal origin is indicated for any igneous rock whose initial Sr^{87}/Sr^{86} ratio at any time in geologic history falls below this line.

In order to determine the initial ratio of an igneous rock it is necessary to know its age, its Rb/Sr ratio and its present Sr^{87}/Sr^{86} ratio. If the age is not known,

the initial ratio can be determined by obtaining a point of intersection of the development lines from two or preferrably three whole rock specimens of differing Rb/Sr ratios. Finally, if the rock has not been metamorphozed after its crystallization, the initial ratio can also be found from the point of convergence of the development lines for the minerals composing the rock.

The ability to distinguish igneous rocks of crustal and sub-crustal origin will contribute materially to the solution of many geologic problems. Specifically the method offers a new approach to the problem of the origin of granite and will bring us closer to the answer of Bowen's classic question: "How much granite is magmatic and how much metamorphic?" (1948, p. 80). The distinction between products of granitization and igneous rocks added to the crust from the mantle in orogenic belts will also throw new light on processes of mountain formation, growth of the continents and many other geotectonic problems. The method can also be applied to the study of ore deposits: the origin of the porphyry copper deposits, the possible association of certain types of ore deposits with igneous intrusives of crustal or sub-crustal origin, and the possible volcanic, sub-crustal origin of conformable, sedimentary

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Cu-Pb-Zn deposits as suggested by Russel and Stanton, (1959) and Oftedahl (1958).

The Differentiation of Basalt Magma.

When a body of basalt magma undergoes crystal fractionation, the resulting products will differ among each other with respect to their Rb/Sr ratios. However, all fractions will initially have the same Sr^{87}/Sr^{86} ratio as their magmatic source material in the upper mantle. Thereafter each fraction will develop its own Sr^{87}/Sr^{86} ratio in accordance with its particular Rb/Sr ratio.

The increase with time of the Sr^{87}/Sr^{86} ratio in several igneous rocks which could be differentiation products of basalt magma is illustrated in Figure 1.3. The slopes of the development lines for the different types of plutonic igneous rocks or their volcanic equivalents were calculated using estimates of their Rb/Sr ratios presented in Chapter 2, Table 2.2.

This method can be used to test for common parentage of a series of volcanic or plutonic rocks of different compositions. Co-magmatic igneous rocks form an "array' because the strontium development lines of all fractions

of the primary magma converge to a point. This point has as its coordinates the time when differentiation occurred and the Sr^{87}/Sr^{86} ratio of the primary magma at that time. If certain igneous rocks with unusual chemical compositions are formed by assimilation of crustal material into part of the parent magma, their development lines will not converge to a point with the other fractions. Moreover, if a given association of igneous rocks is the result of differentiation of more than one parent magma, this fact may also be discovered. Two magma bodies formed by partial melting of source material having different Rb/Sr ratios, will show a corresponding difference in their Sr^{87}/Sr^{86} ratios. In general the strontium development lines of associated volcanic or plutonic rocks, treated as possible "arrays", can be used to study the differentiation of primary magmas under different physical conditions.

The method can also be applied to determine the relationships of lamprophyres, pegmatites and carbonatites to the igneous rocks with which they are associated. For instance, those pegmatities which are crystallization products of residual magma will fit into the array formed by other co-magmatic fractions of the parent magma. On

the other hand, pegmatites formed as the result of solid diffusion of ions (Ramberg, 1956) will not fit into any array. Their Sr^{87}/Sr^{86} ratios will instead resemble that of the country rock.

Carbonatites have been interpreted as xenoliths of limestone (Shand, 1947), as crystallization products of carbonatic liquid of magmatic origin (Pecora, 1956) and as products of hydrothermal solutions (Bowen, 1945). All three theories may be applicable to certain carbonatites. By determining initial Sr^{87}/Sr^{86} ratios of the carbonatite, the associated igneous rocks and possible limestone occurrences, a choice between the various hypothesis may be made. If a carbonatite can be shown to form an "array" with the associated igneous rocks in an area where the Sr^{87}/Sr^{86} ratio of the limestone is measurably different, a co-magmatic relationship between the carbonatite and the igneous rocks is demonstrated. This interpretation is consistent with the results obtained in Chapter 8 for the intrusives of the Monteregian hills and the carbonatite at Oka, Quebec.

The Composition of the Upper Mantle.

The abundance of radiogenic isotopes in rocks of known sub-crustal origin can be used to calculate ratios of the parent to daughter element in the upper mantle. For instance, according to the average Sr^{87}/Sr^{86} ratio in 25 basaltic rocks the average Rb/Sr ratio of the source material in the upper mantle is 0.039 and ranges from 0.022 to 0.051 (Chapter 6).

Similar information could be obtained for the K/Ca ratio as well as the U/Pb and Th/Pb ratios of the upper mantle from measurements of the abundances of the appropriate radiogenic isotopes.

The possibility of using the abundance of Ca^{40} in Recent basalts to calculate K/Ca ratios for the upper mantle merits particular attention. In order to carry out such a calculation the primordial abundance of Ca^{40} must be known. Backus (1952) attempted to do this by analyzing the calcium in the achondritic meteorite Pasamonte. Although he did report a slightly lower abundance than is found in calcium reagents, his measurement was of poor quality and is not conclusive.

From measurements of the abundances of Sr^{87} and Ca^{40}

in basalts it is at least theoretically possible to calculate Rb/Sr and K/Ca ratios for the upper mantle. On the other hand, it has been demonstrated that K/Rb and Ca/Sr ratios are relatively constant for each rock type. Since the upper mantle can be composed of only peridotite, eclogite or dunite for various geophysical and geochemical reasons, it should be possible to make reasonable estimates of the K/Rb and Ca/Sr ratios for the upper mantle. With these assumptions concentrations of Ca, Sr, K and Rb could be calculated.

Evidence is presented in Chapter 6 that the lavas extruded by volcanoes in Hawaii may be drawn from two sources differing slightly, but perhaps significantly, in their respective Sr^{87}/Sr^{86} ratios. Such difference in the abundance of Sr^{87} could be explained as evidence of vertical variations in the rubidium concentrations of the mantle.

Future work may show that some of these suggestions are unfounded or impractical. They are recorded here to stimulate a discussion of the many possible interpretations of the variations of the abundance of radiogenic isotopes in rocks.

Chapter 2

THE CONCENTRATIONS OF RUBIDIUM AND STRONTIUM IN IGNEOUS AND SEDIMENTARY ROCKS AND IN THE CRUST OF THE EARTH.

Introduction.

An extensive survey of the geochemical literature was undertaken in order to obtain the best possible values for the concentrations of rubidium and strontium in igneous and sedimentary rocks. Some 250 references were consulted in this search. A selection of the available analyses was made according to the following criteria:

1. Only analyses having precision errors of ± 15% or better were chosen.
2. All analyses which give no indication of precision errors or calibration of the method were discarded.
3. Average values for the concentrations of rubidium and strontium were calculated in terms of parts per million by weight. The analyses were weighted in the average according to the number of different samples represented.

These criteria eliminated most of the earlier analyses and the values which were finally chosen are from analyses published mostly since about 1950. Occasionally, as in the case of deep sea sediments and ultrabasic rocks, analyses with precision errors greater than ± 15% had to be included for lack of better data.

The compilation was undertaken because a knowledge of the concentrations of rubidium and strontium in igneous and sedimentary rocks is essential to a reliable evaluation of the abundance of Sr^{87} in the crust. The averages here calculated will be combined in certain proportions according to the crustal model of Poldervaart in order to estimate the Rb/Sr ratio of the continental crust. (See page II8)

The Sr^{87}/Sr^{86} ratio of igneous rocks of sub-crustal origin can be used with certain assumptions to calculate the Rb/Sr ratio of the magmatic source material. Comparison of this calculated value to average Rb/Sr ratios of various types of igneous rocks serves to identify the nature of the sub-crustal source material.

The Concentrations of Rubidium and Strontium in Igneous and Sedimentary Rocks.

In the following pages, Table 2.1, the superior rubidium and strontium analyses for igneous rocks are tabulated. The table includes the author, year of publication, the analytical method, the number of samples represented, the concentrations of rubidium and strontium in parts per million by weight (ppm) as well as remarks about the nature of the material analyzed. Weighted averages are calculated for each rock type. A summary of the results appears in Table 2.2 on page I06.

The presentation of the data on sedimentary rocks is

exactly analogous. A summary and general conclusions are found on page 131 , Table 2.13.

Table 2.1 Superior Analyses of Rubidium and Strontium in Igneous Rocks and Meteorites

Author and Reference	Method of Analysis	No. of Samples	Rb ppm	Sr ppm	Remarks
Granite					
Ahrens et al, 1952	O.Sp.	29	198	150	New England granite correction applied.
Turekian, 1955b, p532	O.Sp.	50		200	Calibration by I.D. on G-1 and W-1
Turekian and Kulp, 1956, p	O.Sp	85		100	Granite Ca 0.1 - 1.0%
Taylor et al, 1956	O.Sp.	4	534		granite, St. Austell, Cornwall
"	"	6	219		Granophyre Slieve Gullion
"	"	6	209		Porph. felsite Slieve Gullion
"	"	2	332		Granite West Mourne Mountain
Horstman, 1957	F.Ph	66	170		granite
Sazhina, 1958	O.Sp.	90	257		granite
Gast, 1960	I.D.	27	133	348	Composite of Finnish granite and granite gneisses.
"	I.D.	50	125	283	Precambrian granitic and gneissic rocks from Western U.S.A.

Table 2.1 continued

Author and Reference	Method of Analysis	No. of Samples	Rb ppm	Sr ppm	Remarks
Demin and Khitarov 1958, p. 124	F.Ph	4	138		Course 2 mica and microcline, granite
"	"	4	164		leucocratic granite Caucasus
"	"	2	187		Alaskite dike Caucasus
Katchenkovetal. 1958, p.226	O.Sp.	4		457	Granite, Eastern Russian Platform
weighted average for granite			196 (290)	197 (245)	
Granodiorite					
Taylor et al, 1956	O.Sp.	7	126		granodiorite Slieve Gullion Armagh
Turekian and Kulp, 1956	O.Sp.	85		440	Ca 1.0 - 5.0%
Demin and Khitarov 1958, p.724	F.Ph.	2	108		Porphyroid granodiorite
weighted average for granodiorite			122 (9)	440 (85)	

Table 2.1 continued

Author and Reference	Method of Analysis	No. of Samples	Rb ppm	Sr ppm	Remarks
Syenite					
Taylor et al, 1956	O.Sp.	1	105		Syenite
" p.225		8	147		Trachyte
Horstman, 1957	F.Ph	3	110		Syenite
Wager and Mitchell, 1953 p. 218	O.Sp.	1	150	250	Trachyte
Faure and Hurley (in press)	I.D.	1	140	62.4	Nordmarkite
Weighted average for syenite			136 (14)	156 (2)	
Andesites and Diorites					
Taylor et al, 1956, p. 225	O.Sp.	7	72		Andesite, New Zealand
Turekian and Kulp, 1956	F.Ph	9	88		Tonalite from the Malaya Laba massif, Caucasus
Horstman, 1957, p.11	F.Ph.	5	110 ± 15		diorite
Weighted average for andesites and diorites			88 (21)	500 (13)	

Table 2.1 continued

Author and Reference	Method of Analysis	No. of Samples	Rb ppm	Sr ppm	Remarks
Basaltic Rocks					
Ahrens et al., 1952	O.Sp.	8	41		Gabbro. Correction applied
Fairbairn et al., 1953, p. 43	O.Sp.		49 (40)	183 (57)	Ontario diabase Correction applied.
Turekian, 1955b, p.532.	O.Sp.	50		500	Basalt
Turekian & Kulp, 1956, p.267	O.Sp.	244		467	Basalt
Taylor et al., 1956, p.225-226.	O.Sp.	13 1	34 9		Basalt Gabbro
Horstman, 1957.	F.Ph.	15	30 ± 18		Gabbro
Cabell and Smales, 1957, p.403.	N.Act.	1	21.9		Skaergaard, fayalite ferrogabbro
Katchenkov et al., 1958, p. 227.	O.Sp.	8		430	Gabbro - norite East.Russ.platform
Gast, 1960, p. 1290.	I.D.	83	26	460	Composite basalt I
"	"	83	30	469	" " II
"	"	83	32	454	" " III
Faure, 1961, Ph.D. Thesis at M.I.T.	I.D.	2	35	273	Tholeeitic basalt
	"	1	7.0	346	Duluth Gabbro
	"	1	8.0	262	Norite, Bushveld Complex
Weighted average for basaltic rocks			32 (331)	440 (612)	

Table 2.1 continued

Author and Reference	Method of Analysis	No. of Samples	Rb ppm	Sr ppm	Remarks
Olivine Basalt and Eclogite.					
Gast, 1960, p.1290.	I.D.	1	0.98	102	Olivine basalt Mid-Atlantic Ridge
"	"	1	6.45	312	Olivine basalt Hawaii
Faure, 1961, Ph.D. Thesis, M.I.T.	I.D.	9	21.5	492	Olivine basalts from oceanic islands.
Weighted average for olivine basalt			18 (11)	440 (11)	
Eclogite					
Faure, 1961, Ph.D.Thesis, M.I.T.	I.D.	1	6.9	149	Eclogite xenolith from kimberlite pipe, Robert Victor Mine, S. Africa.
Ultrabasic Rocks					
Ahrens et al., 1952. All values corrected by factor: 0.45.	O.Sp.	13	0.9		Ultrabasic rocks.
	"	1	495		Mica augite peridotite. Murfreesboro, Arkansas
	"		171		Kimberlite, S. Africa
Pinson et al., 1953, p.254 All values corrected by factor of 0.61.	O.Sp.	4		0.9	dunite, correction applied
	"	2		0.6	Serpentine
		2		1.2	Websterite and Pyroxenite
	"	1		12	Lherzolite
	"	1		170	Kimberlite, S.Africa

Table 2.1 continued

Author and Reference	Method of Analysis	No. of Samples	Rb ppm	Sr ppm	Remarks
Pinson et al., cont.	O.Sp.	1		80	Mica augite peridotite Murfreesboro, Arkansas
"	"	1		177	Anorthosite Split Rock, Minn.
Horstman, 1957.	F.Ph.	5	10 ± 10		Ultramafics
Faure, 1961, Ph.D. Thesis, M.I.T.	I.D.	1	0.6	379	Anorthosite Bushveld Complex
	"	1	0.5	49	Pyroxenite Bushveld Complex

No synthesis is attempted for ultrabasic rocks in general.

Anorthosite	0.6	280
Kimberlite, S. Africa	171	170
Mica augite peridotite	495	80
Pyroxenite	0.5	49

omit

omit

Chondritic Meteorites.

Meteorite	Method of Analysis	Rb ppm	Sr ppm	Analyst.
Forest	I.D.	3.5	9.8	Herzog et al., 1956, p.558.
City	I.D.	3.91	11.9	Schumacher, 1956, p. 546.
"	N.Act.	3.04		Webster et al., 1957, p.544.
"	I.D.	2.90	10.2	" "
"	N.Act.	3.04		Cabell and Smales, 1957, p. 404.
"	I.D.	2.75		Gast, 1960, p.2.
Average Forest City		3.19 (6)	10.6 (3)	

Table 2.1 continued

Meteorite	Method of Analysis	Rb ppm	Sr ppm	Analyst.
Chondritic Meteorites continued.				
Homestead	I.D.	3.6	10.6	Herzog and Pinson, 1956, p. 558.
"	N.Act.	3.15		Cabell and Smales, 1957, p. 404.
Average Homestead		3.37 (2)	10.6 (1)	
Modoc, Scott Co., Kansas.	N.Act.	2.97		Cabell and Smales, 1957, p. 404.
	I.D.	3.45		Gast, 1960, p. 2.
Average Modoc		3.21 (2)		
Ness Co., Kansas	N.Act.	2.90		Cabell and Smales, 1957, p. 404.
Faha, Co. Limerick	N.Act.	2.28		" "
Long Island, Phillips Co., Kansas.	N.Act.	2.11		" "
Beardsley	I.D.	4.90 ± .06		Gast, 1960, p. 2.
Nininger 1349	I.D.	4.83 ± .06		"
Richardton	I.D.	2.96 ± .035		"
Holbrook	I.D.	2.22 ± .04		"
AMHM 1162	I.D.	2.3		"

Table 2.1 continued

Meteorite	Method of Analysis	Rb ppm	Sr ppm	Analyst.
Chondritic Meteorites continued.				
ANHM	I.D.	2.9		Quoted from the litera-
"	"	3.5		ture by Gast, 1960,
"	"	3.9		p. 2.
Average ANHM		3.8 (3)		
Weighted average for chondritic meteorites		3.17 (12)	10.6 (2)	
Achondritic Meteorites				
Pasamonte				
grey phase	I.D.	0.65	89.5	Schumacher, 1956, p. 546.
white phase	I.D.	0.50	94.7	" "
white phase	I.D.	0.21(2)		Gast, 1960, p. 2
Average Pasamonte				
White phase	I.D.	0.31	94.7	
grey phase	I.D.	0.65	89.5	
both combined		0.48	92.1	(Rb/Sr = 0.005)
Nuevo Laredo	I.D.	0.37(2)		Gast, 1960, p. 2.
Sioux Co.	I.D.	0.18		"
Nininger 298	I.D.	0.29		"
Moore County	I.D.	0.16		"
Johnstown	I.D.	0.105	2.07	Webster et al., 1957,
"	N.Act.	0.04		p. 544.
Average Johnstown		0.72	2.07	

Table 2.1 continued

Meteorite	Method of Analysis	Rb ppm	Sr ppm	Analyst
Achondritic Meteorites continued				
*Bluff, Fayette Co., Texas.	N.Act.	1.01		Cabell and Smales, 1957, P. 404.
Weighted average for achondritic meteorites		0.37 (6)	92.1** (1)	

*Omitted from average.
**Gast, 1960, p. 1290, on the basis of previously unpublished data gives value of 74ppm.

I.D. - Isotope Dilution
O.Sp. - Optical Spectroscopy
F.Ph. - Flame Photometry
N.Act.- Neutron Activation

Table 2.2 Summary of Rubidium and Strontium Concentrations in Igneous Rocks.

Rock Type	Rb ppm	Sr ppm	Rb/Sr
Granite	196 (290)	197 (245)	1.00
Granodiorite	122 (9)	440 (85)	0.28
Syenite	136 (14)	156 (2)	0.87
Diorite & Andesite	88 (21)	500 (13)	0.18
Gabbro & Basalt	32 (331)	440 (612)	0.07
Olivine Basalt	18 (11)	440 (11)	0.04
Eclogite	6.9 (1)	149 (1)	0.05
Anorthosite	0.6 (1)	280 (2)	0.002
Kimberlite, S. Africa	171 (1)	170 (1)	1.00
Mica-augite peridotite	495 (1)	80 (1)	6.20
Pyroxenite	0.5 (1)	49 (1)	0.01
Dunite		0.9 (4)	
Chondrites	3.17 (12)	10.6 (2)	0.30
Achondrites	0.37 (6)	92.1 (1)	0.004

Figure in brackets indicates the number of specimens represented in the average.

Summary.

The data for syenites and various types of ultrabasic rocks are not as precise and representative as those for granite and basalt. A plot of the concentrations of Rb, Sr, K, and Ca in certain types of igneous rocks appears in Figure 2.1. Syenites were omitted because of the poor quality of the data. The concentrations of K and Ca were taken from Turekian and Wedepohl (1961) with the exception of the values for diorite and andesite which are from Poldervaart (1955, p. 134). The pattern is quite normal and resembles many of the variation diagrams published by Nockolds and Allen (1953, p. 105). This is a qualitative confirmation that the average rubidium and strontium concentrations here calculated are of the correct order of magnitude and bear the proper relationship to the major constituents.

The concentrations of Rb and K increase uniformly in the more acid rock types. Ca decreases steadily from a high in the basaltic rocks. Strontium, however, increases at first and assumes a maximum value in andesites and diorites. Nockolds and Allen (1953) reported similar patterns for rocks from East Central Sierra Nevada (Fig. 13d,

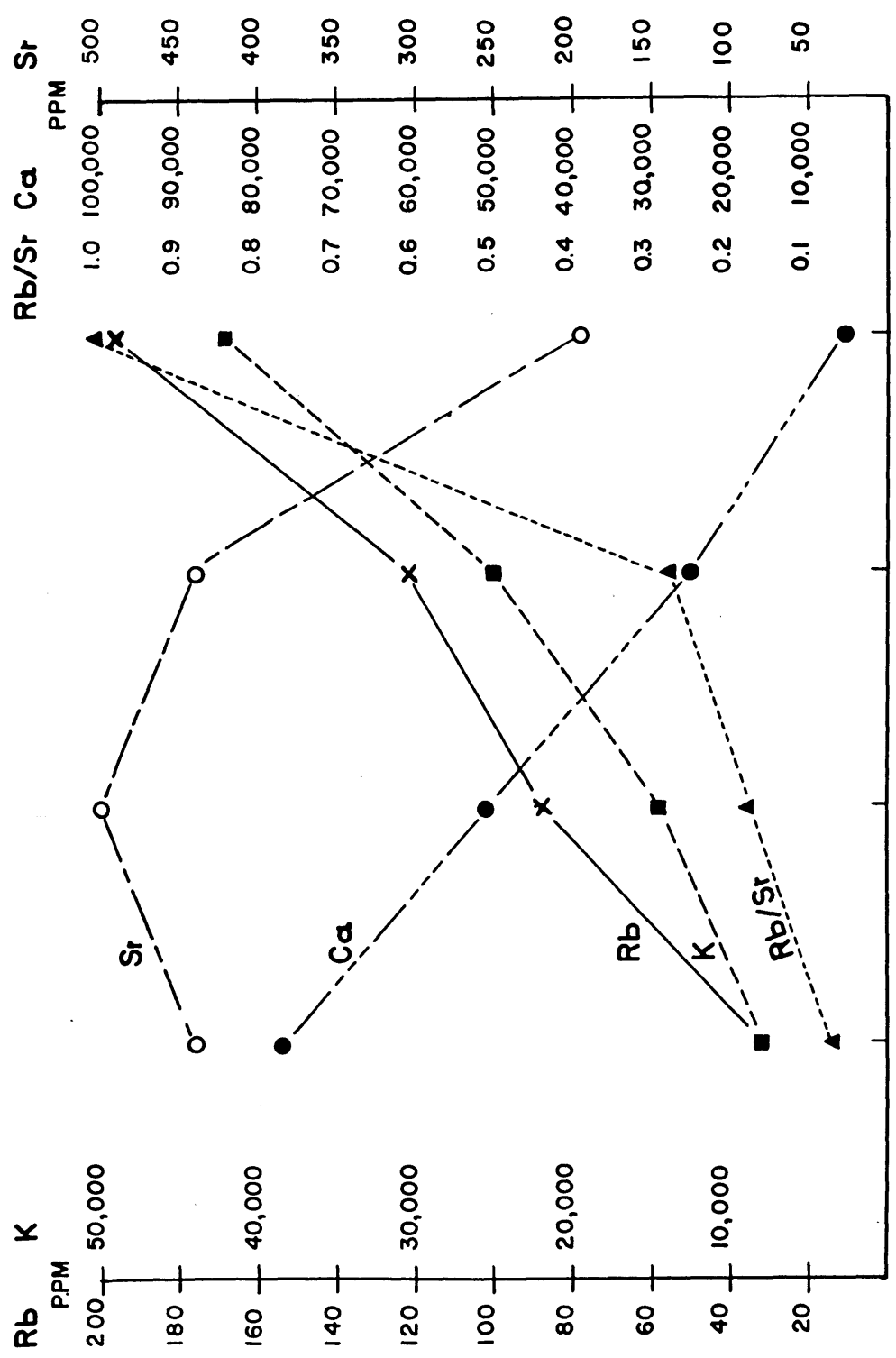


FIGURE 2.1 CONCENTRATIONS OF Rb, Sr, K AND Ca IN IGNEOUS ROCKS.

p.134), the Scottish Caledonian (Fig.13c,p.135), the Scottish Tertiary alkali basalts (1954,Fig.28a,p.272), the Hawaiian alkali basalt-trachyte series (1954,Fig.28b,p.272), and the Polynesian alkali basalt-trachyte series (1954,Fig.28c,p.273). On the other hand, a steady decrease of calcium as well as strontium as a function of $(\frac{1}{3}\ Si\ K)-(Ca\ Mg)$ was observed in rocks from the Southern California Batholith (1953,Fig.13a, p.133) and the lava series at Lassen Peak (1953,Fig.13b, p.133). The maximum in the strontium concentration is also lacking in the differentiation products of tholeeitic basalt magma (Nockolds and Allen, 1956).

The last mentioned authors give the following explanation for the two types of behavior: Strontium can be accomodated in the feldspar structure as a replacement of calcium in plagioclase and potassium in potash feldspar. Strontium cannot, however, replace calcium in ferromagnesian minerals (Nockolds and Mitchell, 1948). If plagioclase crystallizes early, the residual liquid is steadily depleted in strontium and the later acid fractions will contain progressively lower concentrations of strontium. In the case that ferromagnesian minerals crystallize first, strontium is concentrated in the residual liquid and thus attains a

maximum value before it is removed by incorporation into the feldspars.

The Rb/Sr ratio increases smoothly from basalts to granodiorites but rises sharply in granites. This is the result of the extreme differentiation of rubidium and strontium in the more acid rocks. While strontium is depleted, rubidium becomes concentrated in the residual magmatic liquids. Thus acid volcanics (obsidians) may have Rb/Sr ratios as high as 35? (Professor W. H. Pinson, oral communication).

Table 2.3 Superior Analyses of Rubidium and Strontium in Sedimentary Rocks

Author and Reference	Method of Analysis	No. of Samples	Rb ppm	Sr ppm	Remarks
Shale					
Heide and Christ, 1953, p.327	O.Sp.	3	227		Shale
Turekian and Kulp, 1956, p.287.	O.Sp.	35		245	Non-calc. shale
	"	69		300	Average shale
Horstman, 1957.	F.Ph	26	140±50		Shale
Weighted average for shale			149 (29)	300 (69)	

Table 2.3 continued

Author and Reference	Method of Analysis	No. of Samples	Rb ppm	Sr ppm	Remarks
Limestone					
Heide and Christ, 1953.	O.Sp.	5		608	Muschelkalk
Turekian and Kulp, 1956, p.290.	O.Sp.	155		610	Pure limestone
Horstman, 1957.	F.Ph.	7	< 5		Limestone
Weighted average for limestone			< 5 (7)	610 (160)	
Sandstone					
Horstman, 1957.	F.Ph.	4	60 ± 61		Sandstone
Turekian and Kulp, 1956, p. 284.	O.Sp.			< 20	Estimated from Sr constant of quartz.
Weighted average for sandstone			60 (4)	< 20	
Deep Sea Sediments					
Clarke, 1924.	Ch.An.	51		470	Red clay composite.
Hevesy et al., 1934, p.313.	X.Fluor.	1		760	Red clay Challenger st.353
	"	1		254	" " 253
Horstman, 1957.	F.Ph.	4	160		Composite red clay.
	"	4	60		" "

Table 2.3 continued

Author and Reference	Method of Analysis	No. of Samples	Rb ppm	Sr ppm	Remarks
Deep Sea Sediments continued					
Turekian and Kulp, 1956, p. 289.	O.Sp.	10		2075	Pleistocene sediment from Atlantic Core A 180-74
Goldberg et al., 1958, p. 170.	O.Sp.	35		710	Pacific Pelagic sediments
Weighted average for deep sea clay			110 (8)	720 (98)	
Horstman, 1957.	F.Ph.	6	10		Globigerina ooze.
Goldberg et al., 1958.	O.Sp.	3		800	Pacific foram. & globigerina ooze.
Weighted average for globigerina ooze			10 (6)	800 (3)	
Ocean Water					
Heide et al., 1953, p. 327.	O.Sp.	1		13*	Sea water
Smales and Salmon, 1955.	N.Act.	1	0.117±.01		
Smales and Webster, 1957, p. 139.	I.D.	4	0.118±.001		North Atlantic 49°02'N, 15°19'W, depth 400 m.

Table 2.3 continued

Author and Reference	Method of Analysis	No. of Samples	Rb ppm	Sr ppm	Remarks
Ocean Water continued					
Pinson et al., 1957, p. 1781.	I.D.	1	.115 .019	7.2 .6	Surface water 66°18'W, 39°01'N
Weighted average for sea water			.117 (3)	7.2 (1)	

°omitted from the average.

I.D.	-	Isotope Dilution
O.Sp.	-	Optical Spectroscopy
N.Act.	-	Neutron Activation
F.Ph.	-	Flame Photometry
X.Fluor.	-	X-ray Fluorescence
Ch.An.	-	Chemical Analysis

Summary and Conclusions.

The results of the compilation for sedimentary rocks are summarized in Table 2.4.

Compilations of analyses of trace elements from the literature such as this one have been undertaken by other investigators. The most recent of these are by Vinogradov (1956) and by Turekian and Wedepohl (1961). Table 2.5 is a comparison of the results obtained here to those reported in the other two surveys.

Table 2.4 Summary of Rubidium and Strontium Concentrations in Sedimentary Rocks.

Rock Type	Rb ppm	Sr ppm	Rb/Sr
Shale	149 (29)	300 (69)	0.50
Limestone	< 5 (7)	610(160)	< 0.008
Sandstone	60 (4)	< 20	~ 3
Deep sea clay	110 (8)	720(98)	0.15
Globigerina ooze	10 (6)	800 (3)	0.012
Sea water	0.117 (3)	7.2 (1)	0.016

Turekian and Wedepohl (1961) derived most of their data for igneous and sedimentary rocks from Horstman (1957), Turekian and Kulp (1956), Gast (1960), and Goldberg and Arrhenius (1958). Their values agree with those obtained in this study with only a few exceptions. The concentration of strontium in ultrabasic rocks, for instance, is certainly greater than 1 ppm. A value of 6 ppm would give a Rb/Sr ratio of 0.03 which is about right for magmatic source material in the upper mantle.

Vinogradov's compilation includes results from many different sources without any selection of the more reliable analyses. His values are therefore less trust-worthy than those of Turekian and Wedepohl or this author.

Table 2.5 Concentrations of Rubidium and Strontium in Igneous and Sedimentary Rocks.

	This author			Turekian et al., 1961			Vinogradov, 1956		
Rock Type	Rb ppm	Sr ppm	Rb/Sr	Rb ppm	Sr ppm	Rb/Sr	Rb ppm	Sr ppm	Rb/Sr
Granite	196	197	1.00	170	100	1.7	400	300	1.2
Grano-diorite	122	440	0.28	110	440	0.25			
Syenite	136	156	0.87	110	200	0.55			
Diorite & Andesite	88	500	0.18				70	800	0.09
Basaltic rocks	32	440	0.07	30	465	0.065	45	440	0.10
Ultra-mafics				0.2	1	0.2	2	27	0.07
Chondrites	3.17	10.6	0.30				5.5	20	0.28
Shale	149	300	0.50	140	300	0.47			
Limestone	<5	610	<0.008	3	610	0.005			
Sandstone	60	<20	~ 3	60	20	3			
Deep sea clay	110	720	0.15	110	180	0.61			
Deep sea carbonate	10	800	0.012	10	2000	0.005			
Sea water	0.117	7.2	0.016						

The Concentrations of Rubidium and Strontium in the Crust of the Earth

Introduction.

In order to calculate the concentration of the elements in the crust of the earth estimates must be made of the proportions of the various types of igneous and sedimentary rocks in the crust. Knowing the concentrations of the elements in these rock types one can then arrive at a figure for the concentration of each element in the crust.

This is a problem of considerable complexity and geochemical interest. Contributions towards its solution have been made by many geochemists. Basically three different approaches have been tried:

1. Geochemical balance calculations.
2. Estimates based on the proportion and composition of rocks exposed at the surface.
3. Detailed analysis of the surface of the earth and definition of certain regions having characteristic rock assemblages.

Geochemical balance calculations are based on the assumption that the amount of any element released by the weathering of igneous rocks is equal to the amounts incorporated in sediments and dissolved in the oceans. Calculations of this nature have been made by Goldschmidt (1933), Correns (1948),

Kuenen (1941), Wickman (1954) and Goldberg and Arrhenius (1958. Each author suggested certain refinements of the basic premise. Kuenen (1941) first drew attention to the importance of deep sea sediments particularly to the geochemical balance of calcium. Wickman (1954) attempted to set limits of uncertainty to the results. Goldberg and Arrhenius (1958) incorporated their analytical results for deep sea sediments into the calculations. From the solution of several simultaneous linear equations amounts of igneous rocks weathered and sedimentary rocks formed can be obtained. The method has the following difficulties:

1. No allowance is made for erosion and recycling of sediments.
2. The elements now dissolved in the oceans are assumed to be derived entirely from weathering of igneous rocks.
3. No allowance is made for the addition of volcanic material.
4. The proportions of igneous rocks and sediments so calculated apply only to the rocks having the particular composition used in the calculation.

The second method is more arbitrary but has been employed frequently because of its simplicity. Many geochemists have made and used their own estimates. See, for example, Mead (1914), Clarke, (1924,p.29), Horstman (1957),

Turekian and Kulp (1956). Many of the later estimates go back to Clarke (1924) who proposed the following composition for a crust 10 miles in thickness: 95% igneous rocks made up of granite and basalt in the ratio of 2:1, 5% sedimentary rocks which are 80% shale, 15% sandstone and 5% limestone. An average igneous rock composed of granite and basalt in the ratio of 2:1 is equivalent to granodiorite. Some geochemists therefore take granodiorite as the most representative of the average composition of the continental crust. (Turekian and Kulp, 1956).

The third approach is the most satisfactory and is used here. The best crustal model is that proposed by Poldervaart (1955). In the following section this model will be described in some detail and the concentrations of rubidium and strontium in the crust will be calculated from it.

Poldervaart's Model of the Crust.

Introduction.

Poldervaart (1955) proposed that the surface of the earth can be subdivided into five regions each of which consists of igneous and sedimentary rocks of certain compositions and in certain proportions appropriate for the

particular environment. He assumed that metamorphic sediments can be included with the igneous rocks in such a model. The five regions of the earth are:

1. Deep oceanic
2. Continental shield
3. Young folded belt
4. Suboceanic
5. Volcanic island

For each of these regions Poldervaart estimated surface area, depth to the Moho, proportion of igneous to sedimentary rocks and their compositions. These estimates are based on published information in the geochemical literature and are well documented in Poldervaart's paper. The values adopted by him need no additional justification and are accepted for the present purpose.

Deep Oceanic Region.

This region includes the deep ocean basins which are 268×10^6 km^2 in area. The average depth of water is $4\frac{1}{2}$ km, followed by 0.6 km of unconsolidated (0.3 km solid) sediments and 5.75 km of a rock whose compressional wave velocity is 6.5 km/sec. The total depth to the Moho is 10.75 km on the average.

The total volume of the sediments (solid) is 80.4×10^6 km^3 with a mass of 217×10^{15} tons at a density of 2.7.

This mass of sediments consists of 104 x 10^{15} tons of calcareous sand and ooze, 82.5 x 10^{15} tons of red clay and 30.5 x 10^{15} tons of siliceous ooze.

The layer below the sediments is assumed to be an olivine basalt with a density of 3.0. Its volume is 1540 x 10^{6} km^3 with a mass of 4620 x 10^{15} tons. The total mass of the oceanic crust is 4837 x 10^{15} tons.

The calculations of the rubidium and strontium concentrations in the oceanic crust are summarized in Table 2.6 The concentrations used here and in all subsequent calculations are those derived from the survey of the literature.

Table 2.6 Concentrations of Rubidium and Strontium in the Oceanic Crust.

Rock Type	% Wt.	Rb ppm	Sr ppm	Rb x % 100	Sr x % 100
Olivine Basalt	96	18	440	17.2	421
Calc. ooze	2.15	10	800	0.2	17
Red clay	1.71	110	720	1.9	12
Sil. ooze	0.63	60	< 20	0.4	—
Totals	100.49			19.7	450

Best estimates: Rb $\bar{=}$ 20 ppm
Sr =450 ppm
Rb/Sr =0.045

Continental Shield Region.

The area of this region is estimated at 105 x $10^6 km^2$, its elevation above sea level is 0.75 km, the average thickness of sedimentary cover is 0.5 km (solid) and the depth to the Moho is 35 km below sea level.

The volume of the igneous rocks is 3700 x $10^6 km^3$. Their composition is expressed in terms of granodiorite, diorite and basalt in the proportions 7.67:1:3.67 or 2300 x $10^6 km^3$ granodiorite, 300 x $10^6 km^3$ diorite and 1100 x $10^6 km^3$ basalt. Assuming densities of 2.7, 2.85 and 3.0, respectively, the mass distribution is 6200 x 10^{15} tons granodiorite, 850 x 10^{15} tons diorite and 3300 x 10^{15} tons basalt. The total mass of the igneous rocks is 10,350 x 10^{15} tons.

The volume of the sediments is 52.5 x $10^6 km^3$ with a weight of 140 x 10^{15} tons. They are constituted of 41% (57.4x 10^{15} tons) shale, 43% (60.0 x 10^{15} tons) sandstone and 16% (22.4 x 10^{15} tons) limestone. The combined weight of igneous and sedimentary rocks is 10,490 x 10^{15} tons.

Table 2.7 Concentrations of Rubidium and Strontium in the Continental Shield.

Rock Type	% Wt.	Rb ppm	Sr ppm	Rb x % / 100	Sr x % / 100
Granodiorite	59.2	122	440	72	260
Diorite	8.1	88	500	7	40
Basalt	31.5	32	440	10	139
Shale	0.5	149	300	0.7	1.5
Sandstone	0.6	60	< 20	0.4	—
Limestone	0.2	< 5	610	—	1.2
Total	100.1			90.1	441.7

Best estimate: Rb = 90 ppm
Sr = 442 ppm
Rb/Sr = 0.20

Young Folded Belts.

The young folded belts are assumed to occupy an area of 42 x $10^6 km^2$. Their average elevation above sea level is 1.25 km with the Moho at a depth of 37 km below sea level. The prism of geosynclinal sediments is estimated to extend to a depth of 5 km (5.5 if porespaces are included) and is thought to include 40% of igneous rocks of granodioritic composition.

The volume of sediments is therefore 126 x $10^6 km^3$ and its mass is 340 x 10^{15} tons. The sediments consist of

176.5×10^{15} tons (52%) shale, 44.1×10^{15} tons (13%) sandstone, 74.7×10^{15} tons (22%) limestone, 17×10^{15} tons (5%) graywacke, 20.4×10^{15} tons (6%) andesite and 6.8×10^{15} tons (2%) rhyolite.

The total thickness of the igneous rocks below the sediments is 32.8 km giving a volume of $1370 \times 10^{6} km^{3}$. To this must be added $84 \times 10^{6} km^{3}$ of igneous rocks intruded into the sedimentary rocks. The total is therefore $1454 \times 10^{6} km^{3}$. The main mass of igneous rocks is composed of granodiorite, diorite and basalt in the proportions 8.47 : 1 : 2.85 or, in terms of volume, $9.33 \times 10^{6} km^{3}$, $111.3 \times 10^{6} km^{3}$ and $316 \times 10^{6} km^{3}$. The total volume of granodiorite is $1017 \times 10^{6} km^{3}$. Taking appropriate densities (see p. I2I) the mass distribution is as follows: 2750×10^{15} tons granodiorite, 317×10^{15} tons of diorite and 948×10^{15} tons of basalt. The total weight of the igneous rocks is 4015×10^{15} tons. The combined mass of igneous and sedimentary rocks is 4355×10^{15} tons.

Table 2.8 Concentrations of Rubidium and Strontium in the Young Folded Belt.

Rock Type	% Wt.	Rb ppm	Sr ppm	Rb x % 100	Sr x % 100
Granodiorite	63.1	122	440	77	277
Diorite	7.3	88	500	6.4	36.5
Basalt	21.8	32	440	7	95.7
Shale	4.5	149	300	6.7	13.5
Sandstone	1.0	60	< 20	0.6	0.2
Limestone	1.7	< 5	610	—	10.4
Graywacke	0.4	88	500	0.4	2.0
Andesite	0.5	88	500	0.4	2.5
Rhyolite	0.2	196	197	0.4	0.4
Total	100.1			98.9	438.2

Best estimate: Rb = 99 ppm
Sr = 438 ppm
Rb/Sr = 0.23

Suboceanic Region

This is the region of the continental platforms and slopes occupying an area of 93 x $10^6 km^2$. The average depth of water is 1.75 km, the sediments are 4 km (5 km including pore spaces) thick followed by 11 km of igneous rocks. The Moho is about 18 km below sea level.

The sediments consist of two types: hemipelagic sediments which are 252 x $10^6 km^3$ in volume and shelf sediments

which occupy 120 x 10^6km^3. The composition of the latter is approximately that of the young folded belts. The mass of the shelf sediments is 324 x 10^{15} tons and they consist accordingly of 168.5 x 10^{15} tons of shale, 42 x 10^{15} tons of sandstone, 71 x 10^{15} tons of limestone, 16.2 x 10^{15} tons of graywacke, 19.4 x 10^{15} tons of andesite and 6.5 x 10^{15} tons of rhyolite.

The hemipelagic sediments amount to 680 x 10^{15} tons and consist of 519 x 10^{15} tons of terrigenous mud, 129.5 x 10^{15} tons of coral mud and 32.4 x 10^{15} tons of volcanic mud. In the calculations shale is substituted for terrigenous mud, globigerina ooze for coral mud and andesite for the volcanics.

The igneous rocks occupy a volume of 1025 x 10^6km^3 and are composed of 372 x 10^6km^3 of diorite, 186 x 10^6km^3 of tholeeitic basalt and 465 x 10^6km^3 of olivine basalt. The masses of these types of igneous rock are 1060 x 10^{15} tons of diorite, 530 x 10^{15} tons of tholeeitic basalt and 1325 x 10^{15} tons of olivine basalt. The total mass of the igneous rocks is 2915 x 10^{15} tons. The weight of all the rocks in the suboceanic region is 3919 x 10^{15} tons.

Table 2.9 Concentrations of Rubidium and Strontium in the Suboceanic Region

Rock Type	% Wt.	Rb ppm	Sr ppm	Rb x % 100	Sr x % 100
Diorite	27.1	88	500	23.8	135.5
Thol. Basalt	13.5	32	440	4.3	59.3
Ol. Basalt	33.8	18	440	6.1	149
Shale	4.3	149	300	6.4	12.9
Sandstone	1.1	60	< 20	0.7	0.2
Limestone	1.8	< 5	610	—	11.0
Graywacke	0.4	88	500	0.4	2.0
Andesite	0.5	88	500	0.4	2.5
Rhyolite	0.2	196	197	0.4	0.4
Terrig. mud	13.2	149	300	19.7	39.6
Coral mud	3.3	10	800	0.3	26.4
Volcanic mud	0.8	88	500	0.7	4.0
Totals	100.0			63.2	442.8

Best estimate: Rb = 63 ppm
Sr = 443 ppm
Rb/Sr = 0.14

Volcanic Islands.

This region occupies the remaining 2 x $10^6 km^2$, rises 0.5 km above sea level and consists of 4 km of andesite, 4.5 km of tholeeitic basalt and 6 km of olivine basalt.

The Moho is 14 km below sea level.

The volumes of the different rock types are: 8 x $10^6 km^3$ of andesite, 9 x $10^6 km^3$ of tholeeite and 12 x $10^6 km^3$ of olivine basalt. The total volume is 29 x $10^6 km^3$. The distribution of masses is as follows: andesite 22.8 x 10^{15} tons, tholeeite 27 x 10^{15} tons, olivine 36 x 10^{15} tons, totalling 85.8 x 10^{15} tons.

Table 2.10 Concentrations of Rubidium and Strontium in Oceanic Islands

Rock Type	% Wt.	Rb ppm	Sr ppm	Rb x % / 100	Sr x % / 100
Andesite	26.6	88	500	23.4	133
Tholeeite	31.5	32	440	10.1	138.5
Olivine Basalt	42.0	18	440	7.6	185
Total	100.1			41.1	456.5

Best estimate: Rb = 41 ppm
Sr = 457 ppm
Rb/Sr = 0.09

The Crust of the Earth.

The weight of all the rocks in the crust of the earth above the Moho is 23,687 x 10^{15} tons. The sedimentary rocks amount to 1701 x 10^{15} tons (7.17%) whereas the igneous rocks account for 21,986 x 10^{15} tons or 92.8% of the total.

Table 2.11 Concentrations of Rubidium and Strontium in the Total Crust

Region	% Wt.	Rb ppm	Sr ppm	Rb x % / 100	Sr x % / 100
Deep Oceans	20.4	20	450	4.8	91.6
Cont. Shield	44.3	90	442	39.9	196
Young fold belts	18.4	99	438	18.2	80.5
Sub Oceanic	16.5	63	443	10.4	70.9
Volc. Islands	0.4	41	457	0.2	1.8
Total	100.0			73.5	440.8

Best estimate: Rb = 74 ppm
Sr = 441 ppm
Rb/Sr = 0.17

In addition to the Rb/Sr ratio for the entire crust values of this ratio were also calculated for certain restricted environments. The value of 0.17 obtained for the whole crust includes the basalts and calcareous oozes of the deep sea region which in fact is not accessible and is not involved in geological processes. Therefore it is more realistic to exclude the deep sea environment and to accept the value of the Rb/Sr ratio for the continental crust as most representative. The results of these additional calculations are tabulated in Table 2.12.

Table 2.12 Concentrations of Rubidium and Strontium in Various Parts of the Crust

Geological Environment	Rb ppm	Sr ppm	Rb/Sr
Total Crust above Moho	74	441	0.17
Continental Crust only*	87	442	0.20
Sediments in young fold belts	100	351	0.29
Sediments in sub oceanic regions	114	388	0.29
Sediments on continental shields	88	229	0.39
Deep sea sediments	55	660	0.08
Igneous rocks in continental shields	90	443	0.20

* Excluding deep oceanic and volcanic islands region.

The Rb/Sr ratio of the continental crust is 0.20, that of the sediments in young folded mountains is 0.29 as is that of the sediments on the continental margins and slopes. The value of the Rb/Sr ratio for the entire continental crust is lowered by inclusion of basaltic rocks assumed to exist at the base of the crust. Because we are primarily concerned with the upper parts of the continental crust, a more realistic estimate would place the value of the "effective" Rb/Sr ratio of the crust between 0.20 and

0.29 at about 0.25.

Estimates of the concentrations of rubidium and strontium have been made in recent years by Turekian and Kulp (1956), Horstman (1957) and Gast (1960) on the basis of new analytical results. Previous estimates of crustal abundances of the elements were compiled by Fleischer (1953). Almost all of the latter overestimated the abundance of rubidium while underestimating that of strontium. As a result the crustal Rb/Sr ratios are high by as much as an order of magnitude. Goldschmidt (1937), for example, suggested a value of 2.07. Rankama and Sahama (1950) still reported 1.03. Even Vinogradov (1956) arrived at Rb/Sr - 0.8. These high estimates led to the suggestion by Wickman (1948) that Sr^{87}/Sr^{86} ratios in limestone could be used for age determination purposes.

Summary and Conclusions.

Average concentrations of rubidium and strontium in various types of igneous and sedimentary rocks were compiled from the most reliable analyses presently available in the literature. The results obtained here agree with those just published by Turekian and Wedepohl (1961) but are more complete and thus judged to be more representative.

A brief summary of the results is given in Table 2.13.

Table 2.13 Concentrations of Rubidium and Strontium in Igneous and Sedimentary Rocks

Rock Type	Rb ppm	Sr ppm	Rb/Sr
Granite	196	197	1.0
Granodiorite	122	440	0.28
Diorite and Andesite	88	500	0.18
Gabbro and Basalt	32	440	0.07
Olivine Basalt	18	440	0.04
Eclogite	6.9	149	0.05
Chondrites	3.17	10.6	0.30
Shale	149	300	0.50
Sandstone	60	< 20	~ 3
Limestone	< 5	610	< 0.008

These values were used to calculate average concentrations of rubidium and strontium in various parts of the earth's crust according to Poldervaart's model. A recapitulation of the results and a comparison to estimates by earlier investigators appears in Table 2.14.

Table 2.14 The Concentrations of Rubidium and Strontium in the Crust

Reference	Rb ppm	Sr ppm	Rb/Sr	Remarks
This author	74	441	0.17	Entire crust above Moho
"	87	442	0.20	Continental Crust
"	100	351	0.29	Geosynclinal sediment
"	114	388	0.29	Shelf sediments
Turekian & Kulp, 1956.		450	= 0.27	Basalt & granodiorite.
Horstman, 1957.	120			Average igneous rock
Gast, 1960.	74	450	0.16	Basalt:granodiorite = 1:1

The preferred value for the Rb/Sr ratio of the upper part of the continental crust is 0.25.

Chapter 3

THE ISOTOPIC COMPOSITION OF STRONTIUM IN THE CRUST OF THE EARTH

Introduction:

The best geochemical evidence available at the present time leads to the conclusion that the rocks of the continental crust have a Rb/Sr ratio of approximately 0.25. On the other hand, the isotopic composition of strontium in basalts of sub-crustal origin demands a Rb/Sr ratio of the magmatic source regions in the upper mantle of about 0.040. Because the ratio Sr^{87}/Sr^{86} is a function of the age and the Rb/Sr ratio of the environment, it is expected that average crustal strontium has a significantly higher Sr^{87}/Sr^{86} ratio than mantle-strontium. The actual value of this ratio depends on the average age of the crust and its Rb/Sr ratio. The range of values is large because the crust is composed of a great variety of rock types of different ages whose Rb/Sr ratios vary through several orders of magnitude (Chapter 2, Table 2.2). In spite of this inhomogeneity meaningful average values can be obtained by analyzing the strontium in those geological environments which are composed of or con-

tain weathering products of a variety of rock types. Two such environments are ocean water and sediments in geosynclinal basins. Other such environments are metamorphic sedimentary rocks and para-gneisses, glacial till and river water. Because geosynclinal sediments are generally subjected to metamorphic processes during orogenies and may become "granitized" as a result, the isotopic composition of the strontium in this particular environment is most meaningful.

In the following sections available analyses of the isotopic composition of strontium in chemical reagents, sea water and a variety of rocks will be reviewed in order to arrive at the best estimate for the value of the Sr^{87}/Sr^{86} ratio in the crust.

The Isotopic Composition of Strontium in Chemical Reagents and in Ocean Water.

The definitive determination of the isotopic composition of strontium was made by Nier (1938) using matallic strontium of 99.9% purity marketed by Eimer and Amend. His measurements of the abundances of the non-radiogenic isotopes have remained unchallenged since that time. Nier's value for the ratio Sr^{87}/Sr^{86} was 0.712.

Aldrich et al. (1953) and Herzog et al. (1953) each repeated Nier's measurements on a strontium carbonate

reagent from Eimer and Amend, lot 492327, and obtained almost identical results. A summary of the data appears in Table 3.1. The geological environment from which the strontium in the Eimer and Amend reagents was derived has never been established with certainty. The company is no longer in business.

Table 3.1 Isotopic Composition of Strontium in Chemical Reagents

Author	87/86	86/88	84/88	Remarks
Nier, 1938, p. 277.	0.712 ±.007	0.1194 ±.0012	0.0068 ±.00014	Sr metal 99.9% pure Eimer and Amend.
Aldrich et al. 1953, p. 458.	0.711 ±.0004	0.1195 ±.0003	0.0067 ±0.0005	$SrCO_3$, Eimer & Amend average of six analyses.
Herzog et al. 1953, p. 462.	0.712	0.1196	0.0070	$SrCO_3$, Eimer & Amend lot 492327
Schumacher, 1956, p. 219.	Sr^{87}/Sr = 0.0703 ± 0.0002			$SrCO_3$, Gen.Chem., C.P., lot 10
This work.	0.712 ±0.0003	0.1195 ±0.0002	0.0066 ±0.0001	$SrCO_3$, Eimer & Amend, lot 492327, average of eight analyses in nine months.

Errors are the standard deviations of the mean.

It is evident from Table 3.1 that the precision of the determinations has improved steadily but that Nier's original values are confirmed by all investigators. The most precise analyses are those reported here.

Surprisingly (or perhaps naturally), several analyses of the isotopic composition of strontium in ocean water seem to indicate that it too has a ratio of Sr^{87}/Sr^{86} = 0.712 (Table 3.2). It is reasonable to regard sea water strontium as an adequate sample of crustal strontium and to conclude that the Sr^{87}/Sr^{86} ratio in the entire continental crust has a value of 0.712. This value has been widely used in age determination by the Rb-Sr method. However, it gives meaningful age values only when the material is strongly enriched in Sr^{87} so that the exact value of the initial abundance of Sr^{87} is not important.

Table 3.2 Isotopic Composition of Sea Water Strontium

Author	87/86	86/88	84/88	Remarks
Aldrich and Herzog, 1952*	0.712	0.1196	0.0070	sea water
Herzog et al., 1954*	0.711	0.1201	0.0067	sea water
Ewald et al., 1956.	0.718 ±0.003	0.1195 ±0.0004		sea water
Pinson et al., 1957, p. 1782.	0.712 ±0.002	0.1189 ±0.0003	0.0067 ±0.0001	Oceanic surface water, 66°18'W, 39°01 N
Gast, 1960.	0.712 ±0.002			

*Referred to by Pinson et al., 1957, p. 1782.

It can easily be demonstrated that a value of 0.712 for the average crustal Sr^{87}/Sr^{86} ratio is incompatible with an average Rb/Sr ratio of 0.25. If the average age of the crust is 2 billion years and its Sr^{87}/Sr^{86} ratio at that time was 0.704, the value of this ratio today would be 0.725. If the average Sr^{87}/Sr^{86} ratio today is 0.712 and the average Rb/Sr ratio for the crust is 0.25, the age of the crust would have to be about 600 million years. This is clearly not so. Calculations of this nature indicate very strongly that the crustal Sr^{87}/Sr^{86} ratio must be greater than 0.712. If this is the case, then the problem arises that the isotopic composition of sea water strontium is not in equilibrium with crustal strontium.

Whether this apparent discrepancy is real or not cannot be decided at this time because of the lack of representative data. If it is real, it could be taken as evidence that much of the strontium in solution in the oceans is of sub-crustal, volcanic origin. Because rubidium is enriched in the micas which are not affected by chemical weathering to any great extent, it is possible that ordinary weathering processes on the continents never

release rubidium or its daughter product into solution. If this is true, much of the radiogenic Sr^{87} existing in continental rocks may never enter the oceans but is immediately trapped in sedimentary basins. The Rb/Sr ratio of sea water itself is too low to develop any radiogenic Sr^{87} of its own. (See Chapter 2.)

An alternative explanation is to postulate that the Sr^{87}/Sr^{86} ratio in sea water is variable depending on the nature and age of the rocks in the nearest land-mass or in the source of the ocean water. In this case a more representative value of the Sr^{87}/Sr^{86} ratio for the entire ocean may well be higher than 0.712 and the discrepancy may disappear.

A critical inspection of the data presented in Table 3.2 shows that the isotopic composition of sea water may not be as uniform as it seems. When the Sr^{87}/Sr^{86} ratios are normalized to $Sr^{86}/Sr^{88} = 0.1194$, the corrected values range from 0.7097 (Pinson et al., 1957) to 0.7145 (Herzog et al., 1954). The Sr^{87}/Sr^{86} ratio (0.718) reported by Ewald et al., 1956, is suspect because their results for other materials are unreasonable. There is therefore some evidence in support of the hypothesis that geographic variations in the isotopic composition of sea water-strontium

exist. An attempt to demonstrate such variations is planned for the future.

Estimate of the Sr^{87}/Sr^{86} Ratio in the Crust.

Only a few determinations of the isotopic compositions of strontium in rocks have been reported in the literature. Gast (1960) analyzed ten granitic rocks ranging in age from 200 to greater than 2650 million years and found Sr^{87}/Sr^{86} ratios ranging from 0.720 to 1.003, averaging 0.830. The mean of the Rb/Sr ratios for these rocks is 1.64 and their average age is at least 1750 million years. On the other hand four limestones analyzed by Gast (1960) show a variation from 0.704 to 0.713. Ewald et al. (1956) reported Sr^{87}/Sr^{86} ratios for strontianites, celestites and limestones which range from a low of 0.692 ± 0.002 for a Cambrian limestone to a high of 0.710 ± 0.002 for an Upper Cretaceous strontianite. The low value is almost certainly in error.

It is clear that existing data are not adequate to define the composition of crustal strontium but serve merely to demonstrate the extreme variations which exist. The best estimate must therefore be made by assuming a reasonable age for the continents and calculating the

resulting Sr^{87}/Sr^{86} ratio from the known Rb/Sr ratio.

An upper limit to the abundance of Sr^{87} can be set by assuming that the crust is 4.5 billion years old and has had a Rb/Sr ratio of 0.25 throughout this time. Taking the initial Sr^{87}/Sr^{86} ratio as 0.7004 (Achondrite:Pasamonte, Gast, 1960), the present Sr^{87}/Sr^{86} ratio should be 0.748. It is highly probable that the continental masses are younger than 4.5 billion year and the average Sr^{87}/Sr^{86} ratio should therefore be less than 0.748.

A lower limit is obtained with the assumption that the age of the continents is only 1 billion years and that the initial ratio was 0.706. This value is a reasonable estimate of the Sr^{87}/Sr^{86} ratio of the upper mantle 1 billion years ago which has a Rb/Sr ratio of 0.04 and a present value for the Sr^{87}/Sr^{86} ratio of 0.708. With these assumptions the present Sr^{87}/Sr^{86} ratio in the crust is 0.717.

The possible range for the <u>average</u> Sr^{87}/Sr^{86} ratio in the continental masses is therefore from 0.717 to 0.748. Gast (1960) used an initial ratio of 0.714, a Rb/Sr ratio of 0.33 and an average age of 2 billion years to propose that the present Sr^{87}/Sr^{86} ratio of the silicic crust is 0.742.

Perhaps the most meaningful estimate can be made by calculating the average Sr^{87}/Sr^{86} ratio of a geosynclinal assemblage of sedimentary and volcanic rocks. The composition of such a geosynclinal assemblage is approximated by the proportions of sediments and volcanics in Poldervaart's sedimentary rocks of young folded belts (See Chapter 2). The calculations leading to the final estimate in such an environment are summarized in Table 3.3.

Table 3.3 The Sr^{87}/Sr^{86} Ratio in a Hypothetical Geosynclinal Assemblage.

Rock Type	Wt.%	Sr.ppm	Wt.% x Sr / 100	Sr%	Sr^{87}/Sr^{86}	87/86 x Sr% / 100
Shale	52	300	156	44.3	0.733*	0.324
Sandstone	13	< 20	3	0.9	0.733	0.007
Limestone	22	610	134	38.1	0.712	0.271
Graywacke	5	500	25	7.1	0.708	0.050
Andesite	6	500	30	8.5	0.708	0.060
Rhyolite	2	197	4	1.1	0.708	0.008
Totals			352	100.0		0.720

* Pure shale and sandstone derived from weathering of granodiorite 2 billion years in age, Rb/Sr = 0.29, $(Sr^{87}/Sr^{86})_o$ = 0.708.

The Sr^{87}/Sr^{86} ratio of such an assemblage is therefore approximately 0.720. This is considered to be a reasonable

estimate of the initial Sr^{87}/Sr^{86} ratio of a paragneiss or granite formed by extreme metamorphism and granitization of geosynclinal sediments.

Experimental Evidence.

The isotopic compositions of strontium in two composites of Paleozoic shale from the east and west coasts of North America were determined as a check on the previous estimates. The composites were prepared by Mr. Julian Feiss and were made available by Professor W. H. Dennen. All pertinent analytical data are compiled in Table 3.4.

The average value of the corrected Sr^{87}/Sr^{86} ratio for the two shale composites is 0.7215 ± 0.001. This is remarkably close agreement with the predicted value of 0.720. It should be borne in mind that these are not samples of pure shale but contain calcium carbonate and volcanic material. They therefore resemble the average geosynclinal sediment more than the pure shale. The other two analyses are included here for the sake of completeness. The sandy clay analyzed by Pinson and Schnetzler is close to the shale composites.

Table 3.4 Isotopic Composition of Strontium in Crustal Rocks

M.I.T. Sample No.	Material	87/86	(87/86) corr	86/88	84/88	No. of scans	Qual.	Remarks
R4184	Shale composite	.7204	.7204	.1194	.0064	44	Fair	East Coast
R4185	"	.7232	.7226	.1192	.0066	90	Fair	West Coast
	Average shale	.7218	.7215	.1193	.0065			
R4132	Gneiss	.8116	.8115	.1193	.0066	60	Fair	Labrador
R4109	Sandy clay*	.718	.719	.1199		49		Jackson formation, Texas.

* Pinson and Schnetzler, 1960, p. 197.

Summary and Conclusions.

Repeated measurements by several investigators seem to indicate that the Sr^{87}/Sr^{86} ratios of strontium carbonate reagent (Eimer and Amend) and sea water-strontium are identical at 0.712. It has become customary in age determination work using the Rb-Sr method to assume a crustal average Sr^{87}/Sr^{86} ratio of 0.712 on the grounds that the strontium in the oceans is an adequate sample of strontium in the crust.

The Rb/Sr ratio of the crust and its probable age make a higher value more likely. Extreme assumptions lead to a predicted range for the average Sr^{87}/Sr^{86} ratio of 0.717 to 0.748. Making realistic assumptions of the composition and types of strontium present a value of 0.720 is obtained for a geosynclinal assemblage. Measurements of the Sr^{87}/Sr^{86} ratio of two composites of Paleozoic shales from the east and west coasts of North America average 0.7215 thus confirming the earlier estimate.

The best information now available points to an average crustal Sr^{87}/Sr^{86} ratio of about 0.725 ± 0.005. An extensive study is planned to confirm this estimate.

Chapter 4.

RUBIDIUM AND STRONTIUM ANALYSES.

Introduction.

All determinations of the concentrations of rubidium and strontium were made by the method of isotope dilution (Webster, 1960, p.203). The method involves the addition of a known amount of "spike" to a known weight of the sample and the subsequent measurement of the resulting isotope ratios on a mass spectrometer. The "spike" is a solution of the element to be analyzed whose isotopic composition has been greatly altered by enrichment of one of the isotopes of this element.

Experimental Procedures.

The procedures used in the preparation of rock samples for analysis are identical to those given by Hart (1960, p.182). Briefly, a known weight of the dried and powdered rock sample is spiked and then digested in 10:1 mixture of hydrofluoric acid and sulfuric acid in a large Pt crucible on a boiling water bath. After the rock is digested the hydro-

fluoric acid is driven off by evaporation and the residue is dissolved in about 25 ml of 2N vycor-distilled hydrochloric acid. Rubidium and strontium are separated from each other and most of the other elements by passing the solution through a cation exchange column (Dowex 50, 300 mesh, 12% cross-linked resin). The progress of the Rb ions in the column is monitored by a Pt-wire flame test. Strontium is detected by use of a radioactive Sr^{85} tracer which is added to the solution before it is put on the column. The strontium and rubidium fractions are evaporated to dryness, dissolved in a small amount of demineralized water and stored in clean 1 oz. polyethylene bottles until they can be run on the mass spectrometer. Strontium samples are placed on the filament as strontium oxalate which is converted to the oxide by heating the filament briefly to red heat. Rubidium samples are converted to nitrates before being put on the filament. As a rule from 42 to 54 scans were recorded in each analysis.

The measurement of the desired isotope ratio has a standard eviation error of the mean of less than

0.2%. Systematic errors caused by contamination of the sample during the chemical processing were reduced by using vycor-distilled hydrochloric acid and demineralized water. The amount of contamination was determined by making a total of four blank analyses throughout the course of the investigation. The results are discussed in more detail on page 160. Blank corrections for rubidium (0.0674 μgrs) and strontium (0.249 μgrs) were applied to all analyses.

One of the advantages of the isotope dilution technique is that after the spike and the normal elements are thoroughly mixed quantitative recovery is unnecessary. Provided the isotopes have equilibrated, any part of the solution will give the desired result. Moreover, the isotopic ratios can be measured with a precision of 0.1% precision standard deviation of the mean, or better. Assuming that the spikes are properly calibrated and contamination is carefully controlled, the absolute accuracy of isotope dilution analyses can be high.

Preparation of Sr^{85} Radioactive Tracer.

Radioactive Sr^{85} is prepared by irradiating solid RbCl with 15 Mev deuterons in the M.I.T. cyclotron. The Sr^{85} is formed by the nuclear reaction Rb^{85}(d, 2n) Sr^{85}. It decays by K electron capture to Rb^{85} with a half life of 65 days and emits a delayed γ ray of 0.51 Mev. The irradiation time is 1 to 2 hours depending on the amount of Sr^{85} desired. After irradiation the sample is stored in a lead container for two or three days to allow short-lived activity to decay.

Besides the desired Sr^{85}, a number of other isotopes are produced by nuclear reactions affecting the rubidium and the chlorine as well as the impurities present such as potassium and sodium. The following types of nuclear reactions can occur: (d, p), (d, n), (d, 2n), (d, 2p) and (d,α). The products of these reactions either decay rapidly, are noble gases or can be separated from Sr^{85} by cation exchange techniques.

After the cooling period the sample is dissolved in about 20 ml of 2N vycor-distilled hydrochloric acid, filtered, and put on a clean cation exchange column. It is advisable to keep the column inside a fume hood and to use lead bricks to protect the operator. The sample is eluted in the normal fashion using 2N

hydrochloric acid. The rubidium fraction is collected and stored in a lead container because it contains 18.6 day Rb^{86} produced by Rb^{85}(d, p) Rb^{86}. The fraction containing Sr^{85} is easily located by its activity. It is evaporated to dryness, redissolved and passed through the column a second time. The final concentrated strontium fraction is diluted with 2N HCl to fill a 500 ml polyethylene bottle which is kept in a metal container. Only 2 or 3 milliliters of this solution are added per sample to give an activity of $\sim$ 15 cts/min which is easily detected by a Geiger counter.

The purity of the tracer solution with respect to rubidium and strontium was checked by adding the tracer to the spike mixture used to determine blanks. Since these contamination experiments, described in detail on page I60 , indicated very low levels of contamination, sufficient purity of the tracer was demonstrated. The small number of Sr^{85} atoms added is not detectable by the mass spectrometer.

Calibration of the "Spike" Solutions.

Introduction.

The preparation of the "spike" and the "shelf" solutions used in the calibration of the "spikes" is a

joint venture by several members of the Project staff of the Geochronology Laboratory at M.I.T. under the supervision of Professor W. H. Pinson. Much detailed information was given by Pinson (1960, p.237). For this reason these topics will be considered only briefly here. The actual analytical data concerned with the spike calibration experiments are treated in more detail to preserve them for the record.

The "spikes" used in this investigation are enriched in Rb^{87} and Sr^{86}, respectively. A few analyses were made using a Sr^{84} spike. They were originally obtained in the form of salts from the Oak Ridge National Laboratory. The salts were carefully weighed and dissolved in a known volume of demineralized water. Temperature corrections were made as needed. Before these spike solutions can be used for analytical purposes the isotopic composition of the element and its concentration in the solution must be confirmed with the greatest accuracy and precision possible. Errors in the calibration of the spikes are systematic errors and detract from the accuracy of the analyses.

Rubidium and Strontium Shelf Solutions.

A "shelf" solution is a solution containing a known amount of an element of normal isotopic composition. The concentrations of rubidium and strontium in the Rb^{87} and Sr^{86} spikes, respectively were determined by isotope dilution using such "shelf" solutions.

The rubidium shelf solution was prepared by Professor W. H. Pinson by weighing purified RbCl and dissolving it in a known volume of demineralized water. A temperature correction and a correction for the presence of 0.52% K were applied. The calculated concentration of this solution is 140.9 μgrs Rb/ml. Two independent gravimetric determinations using rubidium perchlorate precipitation averaged 142.5 μgrs Rb/ml. This was considered to be satisfactory agreement and the calculated value of 140.9 μgr Rb/ml was used in the calibration experiments (Pinson, 1960, p.242).

The strontium shelf solution was originally prepared by R. F. Cormier on July 2, 1956 by weighing and dissolving strontium carbonate reagent (Eimer and Amend, lot 492327). The concentration of this solution is 280 μgr Sr/ml. A portion of it was diluted by Professor W. H. Pinson on June 24, 1960 to 14.03 μgrs Sr/ml. Cormier's solution was

also used as standard for strontium isotope ratio measurements (Chapter 5, Table 5.2).

Calibration of the Rb^{87} Spike.

The isotopic composition of the rubidium spike and concentration of rubidium in the solution were each determined by three independent measurements (Table 4.1).

Table 4.1 Analytical Data for Rb^{87} Spike Calibration.

Date	85/87	Qual.	Date	Shelf spike	85/87	Rb μgr/ml.
2/20/60	.01760	Fair		3:10	.4320	63.49
2/25/61	.01789	Good		1:1	1.0158	64.07
2/28/61	.01787	Good	2/26/61	1:1	1.0329	62.30
Average	.01779					63.30
$\bar{\sigma} = \pm .000094$						$\pm$ 0.52
$\bar{E} = \pm .526\%$						$\pm$ .82%

$$\bar{\sigma} = \sqrt[2]{\frac{\Sigma d^2}{n(n-1)}}, \quad \bar{E} = \frac{\bar{\sigma}}{M} \times 100, \quad M = \text{mean}$$

The abundances of Rb^{85} and Rb^{87} were calculated from the average measured 85/87 ratio as follows:

85/87 = 0.01779 $\pm$ 0.000094
87/87 = 1.00000 $\pm$ 0.0
Total = 1.01779 $\pm$ 0.000094, E $\pm$ 0.0092%

Fractional atomic abundance	$\bar{\sigma}$	$\bar{E}\%$
85 = 0.01747	± 0.000092	± 0.527
87 = 0.98252	± 0.00009	± 0.0092

The Oak Ridge analysis of this spike was 85 = 0.0177 and 87 = 0.0923. The results obtained at M.I.T. are therefore identical to the Oak Ridge analysis within experimental error.

The atomic weight (physical scale) of the spike-rubidium was calculated, disregarding the packing fraction for the two nuclides.

85 x 0.01747 ± 0.000092	= 1.4857 ± 0.00782
87 x 0.98252 ± 0.00099	= 85.4792 ± 0.00783
Total atomic weight	= 86.9649 ± 0.011 (0.13%)

If N and S are the total numbers of atoms of normal and spike-rubidium, respectively, then the resulting ratio Rb^{85}/Rb^{87} in a mixture of spike and normal rubidium is equal to

$$x = \frac{0.7215N + 0.0175S}{0.2785N + 0.9825S} , \qquad (1)$$

where the atomic abundances for the isotopes of normal rubidium are assumed to be $Rb^{85} = 0.7215$, $Rb^{87} = 0.2785$.

Equation (1) is solved for the ratio $\frac{N}{S}$ which is transformed into a weight ratio through multiplication by a

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

" = $\frac{85.557}{86.965}$ = 0.9838.

The weight ratio is then solved for N, the weight of normal rubidium in the sample, by substituting appropriate values for S, the weight of spike-rubidium added.

Preparation of Dilute Rubidium Spike.

In order to minimize errors it is desirable to spike samples in such a way that the resulting 85/87 ratio will be close to unity. Because basalts contain very low concentrations of rubidium, a more dilute spike was prepared and was used in almost all analyses reported here.

The dilute spike was prepared as follows: 10 ml of Rb^{87} spike containing 63.29 μgr Rb/ml were pipetted into a clean volumetric flask and diluted to 100 ml with demineralized water at 29° C. A temperature correction was made both to the 10 ml volume and the final solution. The corrections were taken from the Handbook of Chemistry and Physics (1951-1952, p. 1791).

Actual volume pipetted at 20° C = $\frac{10}{1.002275}$

= 9.9773 ml.

Amount of Rb delivered = 63.29 x 9.9773 = 631.46 μgrs

This amount was dissolved in $\frac{100}{1.002275}$ = 99.773 ml of water

Final concentration = $\frac{631.46 \mu grs.}{99.773 \text{ ml}}$ = 6.33 μgRb/ml.

The concentration of this spike solution was checked by an isotope dilution measurement using the normal rubidium shelf solution. The result obtained was 6.58 μgRb/ml which is in satisfactory agreement with the calculated value. Nevertheless, the calculated value was preferred.

A further check was made by analyzing the rubidium content of R1292 using both the dilute and the concentrated spike. The results are identical within experimental error (Table 4.6).

Calibration of Sr^{86} spike Solution.

The isotopic composition and the concentration of strontium in the Sr^{86} spike solution were determined by triplicate isotope ratio and isotope dilution runs, respectively. The analytical data are presented in Table 4.2.

Table 4.2 Analytical Data for Calibration of Sr^{86} Spike.

A. Isotopic Composition.

Date	87/88	86/88	84/88	Scans	Qual.
6/22/60	1.4176	12.4168		70	Fair
7/25/60	1.4002	12.4715	.0074	72	Good
2/27/61	1.4002	12.3765	.0077	90	Good
Average	1.4060	12.4216	.0076		
$\bar{\sigma}$	± .0058	± .0275	±.00009		
$\bar{E}$	± 0.413%	±0.221%	±1.18%		

B. Concentration of Strontium.

Date	Shelf:spike	86/88	Sr μgr/ml.
	2:2	1.5110	21.54
2/26/61	2:1	0.8537	21.44
2/26/61	2:1	0.8577	21.56
Average			21.51
$\bar{\sigma}$			± 0.037
$\bar{E}$			± 0.172%

$$\bar{\sigma} = \sqrt{\frac{\Sigma d^2}{n(n-1)}}, \quad \bar{E} = \frac{\bar{\sigma}}{M} \times 100, \quad M = \text{mean}$$

Shelf solution contained 14.03 μgrSr/ml.

The atomic weight (physical scale) was calculated disregarding the packing fractions for the different nuclides:

88/88 = 1.0000 ± 0.00
87/88 = 1.4060 ± 0.0058
86/88 = 12.4216 ± 0.0275
84/88 = 0.0076 ± 0.00009
Total 14.8352 ± 0.281, $\bar{E}$ = 0.189%

Atomic abundance	$\bar{\sigma}$	$\bar{E}$(%)
88 = 0.06741	± 0.00013	± 0.193
87 = 0.09477	± 0.00043	± 0.455
86 = 0.83731	± 0.00243	± 0.290
84 = 0.00051	± 0.000006	± 1.20

Atomic weight (physical scale)

88 x 0.06741 ± 0.00013 = 5.93208 ± 0.0114
87 x 0.09477 ± 0.00043 = 8.24499 ± 0.0374
86 x 0.83730 ± 0.00243 = 72.00780 ± 0.209
84 x 0.00051 ± 0.000006 = 0.04284 ± 0.000504
Total = 86.22771
= 86.228 ± 0.213 (0.247%)

The ratio of Sr^{86}/Sr^{88} of a mixture of N atoms of normal strontium and S atoms of spike strontium is equal to

$$y = \frac{0.0986N \quad 0.8373S}{0.8256N \quad 0.0674S} \qquad (2)$$

The weight factor which converts the atomic ratio of N/S to a weight ratio is

$$= \frac{\text{Atomic weight of normal Sr}}{\text{Atomic weight of spike Sr}} = \frac{87.7100}{86.2280}$$

$$= 1.0172$$

The assumption that the strontium in the unknown has a "normal" composition is usually not strictly true for geological materials. Normal strontium is assumed to have the following isotope ratios: $Sr^{87}/Sr^{86} = 0.712$, $Sr^{86}/Sr^{88} = 0.1194$ and $Sr^{84}/Sr^{88} = 0.0068$ (Nier, 1938). Many samples analyzed for the purpose of age determination by the Rb-Sr method are enriched in the Sr^{87} isotope.

For best results it is therefore desirable to substitute the proper isotopic abundances for the strontium in the sample into equation (2). This is particularly true for samples which are strongly enriched in radiogenic Sr^{87}. Almost all samples analyzed here differed only very slightly from "normal" strontium and all concentrations could therefore safely be calculated using the equation as given above.

Calibration of the Sr^{84} Spike.

Only a few analyses were made using this spike and

its calibration data are briefly stated here for the record in Table 4.3.

Table 4.3 Atomic Abundances of the Isotopes.

	Oak Ridge		M.I.T.
84	.543	.002	.5356
86	.137	.002	.1401
87	.038	.002	.0428
88	.282	.003	.2808

The M.I.T. values are averages of two independent determinations. An isotope dilution measurement gave Sr = 19.74μgr/ml. The calculated value is 19.8μgrSr/ml indicating very good agreement. The weight factor is 1.0253.

Precision of Rubidium and Strontium Analyses.

Introduction.

The reproducibility of isotope dilution analyses of rubidium and strontium was determined by making triplicate analyses of several samples containing different concentrations of the two elements. All systematic errors were removed as far as possible by careful spike calibrations and by making a blank correction to all determinations. A temperature correction to the volume of spike added was not made because it is insignificant.

Rubidium and Strontium Blanks.

The blanks were determined by mixing known amounts of Rb^{87} and Sr^{86} spike in a Pt crucible. The mixture was then subjected to the entire procedure ordinarily used to prepare rock samples for isotope dilution analysis. Comparable amounts of reagents were used throughout and the blanks were put through an ion exchange column which had been cleaned previously in the customary way. Finally the resulting isotopic compositions of the rubidium and the strontium were determined on the mass spectrometer.

The amount of contamination of each element was calculated by assuming it to have normal isotopic composition.

During the course of this investigation four such rubidium and strontium blanks were determined (Table 4.4).

Table 4.4 Normal Rubidium and Strontium Blank Determinations.

Date	Rb μgr.	Sr μgr.
8/60	0.173*	0.425
9/60	0.0826	2.75*
11/60	0.0560	0.138
2/61	0.0636	0.183

The starred values were omitted from the average because they are unusually high and above the general level of the others. The values used to make blank corrections are Rb = 0.0675 μgr, Sr = 0.249 μgr

The magnitude of the blank corrections to 0.5 gram samples containing various concentrations of rubidium and strontium are illustrated in Table 4.5.

Table 4.5 Magnitude of Rubidium and Strontium Blank Corrections.

Concentration of Rb & Sr in rock (ppm)	Blank correction Sr%	Rb%
1	-50	-13.5
10	- 5	- 1.35
100	- .5	- 0.135

Sample size = 0.5 grams.

Results of Triplicate Rubidium and Strontium Analyses.

Triplicate analyses of Rubidium and strontium were made on four samples. Each of these samples was analyzed by routine procedures used in the Geochronology Laboratory at M.I.T. Therefore the spread of the data at various concentration levels is a realistic indication of the reproducibility (Table 4.6).

Table 4.6 Summary of Triplicate Rb and Sr Analyses.

Sample No.		Rb ppm	Sr ppm
R1292		9.72*	394.9**
Olivine basalt		9.97	402.9
		9.59	397.1
Average		9.76	398.6
	$\bar{\sigma}$	± 0.11	± 2.0
	E	± 1.13%	± 0.50%
	σ	± 0.19	± 3.?
	E	± 1.98%	± 0.93%
R3111		3.42***	131.7***
Eclogite		7.00	148.3
		6.82	149.7
Average		6.90	149.0
	$\bar{\sigma}$	± 0.09	± 0.7
	$\bar{E}$	± 1.30%	± 0.47%
	σ	± 0.128	± 0.99
	E	± 1.86%	± 0.665%

* Using concentrated Rb^{87} spike (63.29 μgr./ml).

** Using Sr^{84} spike.

*** Spiking in doubt. Omitted from the average.

(continued)

Table 4.6 continued

Sample No.		Rb ppm	Sr ppm
P3111		12.7	272.7
Pyroxene concentr.		13.2	257.9
		13.0	254.9
Average		13.0	261.7
	$\bar{\sigma}$	± 0.147	± 5.6
	$\bar{E}$	± 1.13%	± 2.14%
	σ	± 0.255	± 9.6
	E	± 1.96%	± 3.67%
G3111		0.92	17.50
Garnet concentr.		1.41	21.80
		1.03	17.70
Average		1.12	19.00
	$\bar{\sigma}$	± 0.148	± 1.40
	$\bar{E}$	± 13.2%	± 7.37%
	σ	± 0.257	± 2.42
	E	± 22.9%	± 12.7%

$$\sigma = \sqrt[2]{\frac{\sum d^2}{n-1}}\,, \quad \bar{\sigma} = \sqrt[2]{\frac{\sum d^2}{n(n-1)}}\,, \quad E = \frac{\sigma}{M} \times 100$$

For the purpose of evaluating the precision error of an individual analysis the standard deviations for a single analysis (σ) is most applicable. In general the precision of rubidium analyses in material containing ~10 ppm Rb is of the order of ± 2%. As the concentration decreases to 1 ppm the error increases rapidly to

$\pm$25%. The precision error for strontium analyses in material containing 150 ppm Sr or more is of the order of $\pm$ 1%, but may be as high as $\pm$4%. At the 20 ppm level the precision approaches $\pm$ 15%. From the evidence presented here a conservative estimate of the probable precision error of a single analysis is $\pm$ 2% for both rubidium and strontium where Rb $>$ 10 ppm and Sr $>$ 150 ppm.

It is of interest to note that the rubidium and strontium concentrations of R1292 which were made using the concentrated Rb^{87} spike and the Sr^{84} spike, respectively, are in perfect agreement with the other values. This gives confidence in the calibration of the dilute Rb^{87} spike and the Sr^{86} spike which were used on almost all the other analyses.

Tilton's Rubidium Shelf Solution.

The accuracy of rubidium analyses is indicated by a comparison of the results obtained here for a RbCl solution prepared by G. R. Tilton to those of several other laboratories (Pinson, 1960, p.244). This solution was analyzed in triplicate by Professor W. H. Pinson using different proportions of spike and shelf solution. The results given here have been recalculated using the

latest calibration data for the Rb^{87} spike solution (March, 1961).

Table 4.7 Analytical Data for Tilton's Shelf Solution.

Spike:shelf	$(Rb^{85}/Rb^{87})_{measured}$		Rb μgr/ml.
1:1	0.6355		69.41
1:2	1.008		68.77
1:3	1.263	67.69	68.18
	1.254	68.66	

Average Concentration: 68.79 μgr/ml.
$\bar{\sigma} = \pm 0.36 (0.5\%)$
$\sigma = \pm 0.62 (0.9\%)$

The reproducibility in terms of the standard deviation for a single analysis is ± 1%. This is a minimum value because these analyses did not include the chemical processing used for analysis of rock samples.

The average of the M.I.T. analyses is identical within experimental error to the results obtained elsewhere. (Table 4.8).

Table 4.8 Interlaboratory Results for Tilton's Rubidium Shelf Solution

Laboratory	Rb μgr/ml.
M.I.T.	68.8 ± 0.4
Carnegie Institution	67.5
Gast, University of Minnesota	68.5

Chapter 5.

MEASUREMENT OF THE ISOTOPIC COMPOSITION OF STRONTIUM.

Introduction.

The chemical procedures and instrumental techniques used in this investigation are not new but were developed over a period of years by members of the Geochronology Laboratory at M.I.T. Various aspects of these procedures have been described in the Annual Progress Reports as well as in the geochemical literature (Hart, 1960, p.169; Pinson, 1960, p.237; Herzog et al., 1960, Herzog et al., 1958, Herzog and Pinson, 1956). In this chapter these analytical techniques are briefly summarized followed by a discussion of measurement precision and absolute accuracy.

Chemical Procedures.

For strontium isotope ratio determinations rock samples were ground to a grain size of less than 250 microns in a steel percussion mortar. Approximately 0.5 grams of the powder, which was well mixed by rolling

it on a sheet of paper, was placed in a Pt crucible and digested in about 25 mls of a 10:1 mixture of HF and H_2SO_4 on a boiling-water bath in a fume hood. Silica was volatilized as SiF_4 by a reaction with F^- ions and a solution of soluble sulfates was obtained (Vincent, 1960, p.41). The decomposition process required from 3 to 4 hours. The residue was dissolved in about 50 mls of demineralized water. The solution was stirred with a clean Teflon stirring rod, if necessary, to dissolve all of the residue. In order to remove all traces of HF the water solution was evaporated almost to dryness. Approximately 25 mls of 2N vycor-distilled HCl were then added, thus converting the salts to chlorides. The solution was cooled and filtered into a pyrex beaker for temporary storage.

Strontium was separated from the other elements by cation exchange techniques using Dowex 50, 300 mesh, 12% cross-linked resin and 2N vycor-distilled HCl as eluant. The exchange columns were cleaned between successive samples by duplicate washings with 6N vycor-distilled HCl followed by 2N HCl or demineralized water. Before the solution was put on the column it was filtered

a second time to remove precipitates which usually formed on standing (KCl, $BaCl_2$). A few milliliters of a solution containing radioactive Sr^{85} were added to give sufficient activity so that the location of the strontium on the ion exchange column could be detected with a Geiger Counter. The top of the resin was then levelled and the solution was placed on the column by means of a pipette. Care was taken not to disturb the surface of the resin to obtain the best possible separation of strontium from calcium, rubidium and potassium. The order in which the alkalis and alkaline earths are eluted from the column is Li, Na, K, Rb, Ca, Sr (Cormier, 1952, p.72). The fraction containing the strontium was collected in 25 ml portions in 3 to 4 pyrex beakers which were then evaporated to dryness. The beakers containing the greatest amount of activity were selected and the residues were dissolved in a few milliliters of demineralized water. This strontium concentrate was stored in a clean 1 oz. polyethylene bottle until it could be analyzed on the mass spectrometer.

When analyzing strontium in basalts it was usually

not possible to obtain a complete separation of calcium and strontium. The purity of the strontium concentrates was improved by rejecting all beakers which showed evidence of the presence of hydroscopic $CaCl_2$ by the moisture which quickly accumulated at the bottom of the beaker. Moderate amounts of calcium (as much as 50% of the total sample) do not directly interfere with the measurement of the isotope ratios of strontium on the mass spectrometer. The presence of calcium does, however, increase the bulk of the sample and by acting as an inert matrix it may affect the emission of strontium ions and the process of isotopic fractionation.

In preparation for the isotopic analysis the strontium solution was evaporated to dryness in a clean vycor dish. The residue was dissolved in a few drops of cold, demineralized water and strontium was precipitated as strontium oxalate by the addition of a small crystal of ammonium oxalate. The precipitate usually formed in 5 to 10 minutes. The supernatant liquid was removed by means of a medical syringe using a clean glass capillary tip. The precipitate was washed once or twice with ice-cold, demineralized water to remove

all soluble oxalates. Next, it was picked up in the capillary tube and deposited in the center of a clean tantalum filament in the source of the mass spectrometer. The liquid was evaporated by passing a small current (~0.5 amperes) through the filament until the sample formed a small white cake. The filament temperature was raised for an instance to red heat to expel occluded gases from the sample and to convert the oxalate to the oxide. The source was now re-assembled and placed in the tube of the mass spectrometer in preparation for the analysis.

Mass Spectrometric Techniques.

The instrument is a 60° sector, 6 inch radius, solid source, single collector mass spectrometer which was built at M.I.T. It employs a magnet sweep and the ion current is amplified by means of a vibrating reed electrometer (Model 30, Applied Physics Corporation, Pasadena, California). Samples were mounted on a tantalum ribbon (0.001 x 0.030" by Fansteel Metallurgical Corporation, North Chicago, Illinois) spot welded to posts in the source.

Operating pressures ranging from 3×10^{-6} to 5×10^{-7} mm Hg were obtained by means of a high capacity mercury diffusion pump using a large cold trap cooled with liquid nitrogen (H.S. Martin Co., Evanston, Illinois), coupled with a fore-pump (Duo-Seal Pumps, W.M. Welch Scientific Co., Chicago). The peaks were recorded on a Brown Electric Strip Chart Recorder (Brown Instrument Co., Philadelphia).

After the sample had been applied to the filament the source was returned to the mass spectrometer and bolted into place. To ensure a tight seal a new Aluminum gasket was used for each run. The tube of the mass spectrometer was then evacuated. Pressures were measured by means of an ion gauge (Type DPA 38 Consolidated Electrodynamics Co., Pasadena, California, formerly Dist. Prod. Corp.). When the pressure had fallen to about 2×10^{-5} mm Hg (usually in less than one hour) the filament current was turned on and the sample was conditioned for 2 to 3 hours at a temperature just below that at which strontium ion emission begins. Conditioning the sample in this way allows rubidium contamination to be burned off, gives a better operating vacuum and

improves the sensitivity of ion emission during the run. When the pressure had dropped to about 2×10^{-6} mm Hg the filament current was increased slowly, to prevent the sample from falling off the filament, until the emission of strontium ions began to increase spontaneously. When the peak heights were great enough to be in the range of the 100 (Sr^{87}, Sr^{86}, Sr^{84}) and 1000 millivolt (Sr^{88}) scales of the V.R.E., from 80 to 100 consecutive scans were recorded without further changes in the filament temperature.

In this investigation an instrumental precision for the Sr^{87}/Sr^{86} ratio of better than 0.1% was desired. Experience showed that such precision could be achieved by recording between 80 and 100 consecutive scans and by using the 100 and 1000 mv scales on the V.R.E. (These two scales are least sensitive to high frequency noise and small irregularities in the ion emission.)

The resolution of the instrument in the mass range 84 to 88 is adequate at pressures less than 5×10^{-6} mm Hg. At higher pressures collisions of ions with gas molecules causes broadening of the ion beam resulting in overlap of the peaks. The Sr^{88} peak in particular

interferes with the smaller Sr^{87} peak with the result that the measured values of the Sr^{87}/Sr^{86} ratios are too high. In this work pressures of less than 2×10^{-6} mm of Hg were preferred for a reliable measurement of the Sr^{87}/Sr^{86} ratio.

After strontium isotope ratio and isotope dilution runs the filament was cleaned by heating at maximum temperature until no trace of strontium or rubidium could be detected at a filament current higher than that employed during a run. In this way up to six or eight consecutive samples were run on the same filament without danger of contamination. It was found to be safe to interspace strontium isotope dilution and isotope ratio runs although this was avoided as much as possible in this project. After making a rubidium analysis the filament must be discarded because rubidium is difficult to clean off the filament.

After completion of the run the chart was analyzed as follows. Baselines were drawn with a sharp No. 4 pencil and peak heights were measured to the closest 0.01 inch using an engineering ruler. The peak heights were averaged in sets of six and isotopic

ratios were calculated for each set. The final average values for the entire run were calculated from the ratios obtained for all the sets. The number of scans included in each set should be even in order to remove the effect of increasing or decreasing peak heights from the isotope ratios. An instrumental precision error in the form of the standard deviation of the mean was calculated for the average Sr^{87}/Sr^{86} ratio of each run. This error was used to judge the quality of the measurement. It will be discussed in more detail in the next section.

Discussion of Errors.

Introduction.

In the following discussion a distinction is made between measurement precision or reproducibility and the absolute accuracy. The former is the sum of random errors arising from several sources. The magnitudes of these random errors in a mass spectrometer cannot be predicted with certainty. In this study the reproducibility of the Sr^{87}/Sr^{86} ratio was determined from a number of analyses of the same sample and was expressed

as the standard deviation for a single analysis calculated from these results. The standard deviation, $\sigma = \sqrt{\frac{\Sigma d^2}{n-1}}$, of a number of measurements whose average is M implies that an additional measurement of the same quantity has a 68% probability of falling inside the band $M \pm \sigma$.

The absolute accuracy is the algebraic sum of all systematic errors affecting a series of measurements. Again such errors arise from many sources and are difficult to evaluate in the lengthy and complex procedure used to determine isotope ratios. Because the true value of the quantity to be measured is usually not known, it is customary to analyze inter-laboratory standards to ensure that at least a certain degree of consistency is maintained. The standard used here is a $SrCO_3$ by Eimer and Amend which has previously been analyzed by Aldrich et al. (1953) and Herzog et al. (1953).

The Reproducibility.

The precision error or reproducibility of a measurement of the Sr^{87}/Sr^{86} ratio is the sum of

several random errors. Several of these errors, which are listed below, may be systematic for a single measurement but are random for a series of repeated measurements. They therefore affect the reproducibility and are included in this discussion with the truly random errors. These are:

1. Contamination of the sample with variable amounts of "normal" or "spike" strontium during chemical processing or mass spectrometric analysis.

2. Variable effects of fractionation of isotopes during evaporation from the filament, ionization, acceleration, deflection by the magnetic analyzer and collection of ions.

3. Fluctuations in the rate of emission of ions from the filament caused by inadequate temperature control of the hot filament, changes in the resistance of the filament, excessive bulk or near-exhaustion of the sample and other reasons.

4. High frequency electronic noise as well as instrumental drift due to temperature changes, interference from the operation of other electronic equipment, etc.

5. Lack of sufficient resolution of peaks due to broadening of the ion beam as a result of collisions of ions with gas atoms in the mass spectrometer tube. The resolution is also affected when the ions are not mono-energetic because of improper alignment of the filament, the sample and the slit of the accelerating plate.

6. Instability of the magnetic field and of the accelerating voltage. Low frequency noise in the strength of the magnetic field results in corresponding instability of peak heights. Variations in the accelerating voltage affect the spacing of peaks but may also affect the peak height if such changes occur just before the recorder reaches the top of a peak.

7. Uncertainties in drawing baselines and measuring peak heights with a ruler.

Of these sources of errors contamination of the sample, isotopic fractionation and poor resolution may be systematic for a single run but differ from one analysis to the next thus affecting the reproducibility.

An isotopic fractionation correction was applied to all measured Sr^{87}/Sr^{86} ratios on the assumption that the Sr^{86}/Sr^{88} ratio is constant and equal to 0.1194 (Nier, 1938). Any deviation from this value was ascribed to the effects of isotopic fractionation. Only one-half of the correction needed to readjust the Sr^{86}/Sr^{88} ratio was applied to the Sr^{87}/Sr^{86} ratio because the difference in the masses 86 and 87 is only one-half that between 86 and 88. For example, given that

$$Sr^{86}/Sr^{88} = 0.1187$$

$$Sr^{87}/Sr^{86} = 0.712$$

then,

$$(Sr^{87}/Sr^{86})_{corr} = \frac{0.712}{\frac{0.1194}{0.11905}} = 0.7099$$

Even though the exact nature of this isotopic fractionation in the mass spectrometer is not understood,

"normalization" of the Sr^{87}/Sr^{86} ratios is justified by the resulting improvement in the precision of the data and by the fact that the mean of several analyses is not greatly changed. This is well illustrated by analyses of a basalt from Kilauea, Hawaii (Table 5.1) and the $SrCO_3$ standard (Table 5.2).

Table 5.1 Isotopic Composition of Strontium in Basalt from Kilauea, Hawaii (R1292)

No.	Date	87/86	$E_{\frac{87}{86}}$	$(87/86)_{corr}$	86/88	84/88	No. of scans	Qual.
1)	6/1/60	.7062	.091	.7068	.1196	.0070	138	Fair
2)	8/31/60	.7102	.067	.7072	.1184	.0063	84	Good
3)	9/3/60	.7090	.054	.7069	.1187	.0066	84	Good
4)	1/25/61	.7040	.13	.7058	.1200	--	104	Fair
5)	2/8/61	.7091	.073	.7061	.1184	.0065	90	Good
Average		.7077		.7066	.1190	.0066		
$\bar{\sigma}$		± 0.00114		± 0.00026	± 0.00033	± 0.00015		
$\bar{E}$		± 0.16%		± 0.037%	± 0.28%	± 2.23%		
σ		± 0.00254		± 0.00059	± 0.00074	± 0.00029		
E		± 0.36%		± 0.083%	± 0.62%	± 4.45%		

The results in Table 5.1 show that the reproducibility of the Sr^{87}/Sr^{86} ratio, expressed as the standard deviation for a single analysis, is improved by about a factor of four by the fractionation correction. In this set of measurements a reproducibility of ± 0.0006 (0.08%) has been achieved for the corrected Sr^{87}/Sr^{86} ratio.

The column headed $E_{87/86}$ gives the instrumental precision error of the Sr^{87}/Sr^{86} for each run. This error is not identical with the reproducibility of the measurement but indicates only the extent of variation of truly random errors affecting the particular mass spectrometric measurement.

The quality of a run was determined partly on the basis of this instrument precision error of the Sr^{87}/Sr^{86} ratio and partly from other criteria such as the number of scans recorded, the stability of ion emission, the pressure during the run and evidence of excessive fractionation. As a rule measurements having an instrument error of 0.08% or better are of "Good" quality. Those with errors between 0.08% and 0.2% are judged to be "Good", "Fair", or "Poor" on the basis of the other criteria mentioned above. Runs having an error greater than 0.2% were considered to be "Poor" and were generally discarded or repeated.

The reproducibility of the Sr^{86}/Sr^{88} ratio in Table 5.1 is $\pm$0.62% whereas that of the uncorrected Sr^{87}/Sr^{86} ratio is $\pm$0.36%. This supports the earlier assumption that the Sr^{87}/Sr^{86} ratio is subject to only one-half of the

isotopic fractionation effect recorded in the Sr^{86}/Sr^{88} ratio. The reproducibility of the Sr^{84}/Sr^{88} ratio as indicated in Table 5.1 is ±4.45%.

Accuracy.

The absolute accuracy of isotope ratio measurements is difficult to assess. The best that can be done is to demonstrate consistency of the measurements with others made elsewhere. For this purpose the strontium of a $SrCO_3$ reagent (Eimer and Amend, lot 492327, Cormier's shelf solution) was analyzed at intervals throughout the course of the investigation. The results are given in Table 5.2.

Table 5.2 Strontium Carbonate Reagent, Eimer and Amend lot 492327

No.	Date	87/86	$(87/86)_{corr}$	86/88	84/88	Qual.
1	5/3/60	.7098	.7116	.1200	.0068	Good
2	5/15/60	.7114	.7117	.1195	.0066	Good
3	6/30/60	.7133	.7130	.1193	.0064	Good
4	7/20/60	.7133	.7127	.1192	.0062	Good
5	8/21/60	.7136	.7127	.1191	.0069	Good
6	10/17/60	.7128	.7116	.1190	.0069	Good
7	12/1/60	.7111	.7102	.1191	.0067	Fair
8	2/13/61	.7083	.7077	.1192	.0064	Good
9	2/27/61	.7093	.7123	.1200	----	Good
Average		0.7114	0.7115	0.1194	0.0066	
$\bar{\sigma}$		± 0.00064	± 0.00055	± 0.00016	± 0.00008	
$\bar{E}$		± 0.090%	± 0.077%	± 0.134%	± 1.23%	
σ		± 0.0018	± 0.0016	± 0.00045	± 0.00023	
E		± 0.25%	± 0.22%	± 0.38%	± 3.48%	

The corrected Sr^{87}/Sr^{86} ratios have a markedly smaller spread than the uncorrected ratios. The only exceptions are runs #7 and #8. The values of the corrected Sr^{87}/Sr^{86} ratios of these two runs differ from the mean by 0.8 σ and 2.4 σ. The probabilities that these or lower values will occur in a normal population whose mean is 0.7115 and whose standard deviation σ = 0.0016 are 21.2% and 0.8%, respectively (Dixon and Massey, 1957, Table A4). Run #8 is outside the customary 5% confidence limit and is therefore rejected.

With the omission of run #8 the isotope ratios assume the following average values.

		$\bar{\sigma}$	σ
Sr^{87}/Sr^{86}	= 0.7119	± 0.0006	, ± 0.0016
$(Sr^{87}/Sr^{86})_{corr}$	= 0.7120	± 0.0003	, ± 0.0009
Sr^{86}/Sr^{88}	= 0.1195	± 0.0002	, ± 0.0005
Sr^{85}/Sr^{88}	= 0.0066	± 0.0001	, ± 0.0003

It is apparent that the average Sr^{87}/Sr^{86} ratio is identical to the corrected value of this ratio. The reproducibility of the latter is ± 0.0009 or 0.12%.

The results of this series of measurements compare favourably with those previously reported by other investigators for similar strontium compounds. A summary of this work is given in Table 5.3 (Also Chapter 3, Table 3.1).

Table 5.3 Isotopic Composition of Strontium in Chemical Reagents.

Author	87/86	86/88	84/88	Remarks
Nier, 1938, p.277.	0.712 ± 0.007	0.1194 ± 0.0012	0.0068 ± 0.00014	Sr metal 99.9% pure, Eimer and Amend.
Aldrich et al., 1953, p.458.	0.711 ± 0.0004	0.1195 ± 0.0003	0.0067 ± 0.0005	$SrCO_3$, Eimer & Amend, Average of 6 analyses.
Herzog et al., 1953, p.462.	0.712	0.1196	0.0070	$SrCO_3$, Eimer & Amend, lot 492327.
Schumacher, 1956, p.210.	Sr^{87}/Sr = 0.0703 ± 0.0002			$SrCO_3$, Gen. Chem., C.P., lot 10.
This work.	0.712 ± 0.0003	0.1195 ± 0.0002	0.0066 ± 0.0001	$SrCO_3$, Eimer & Amend, lot 492327, aver. of 8 analyses in nine months.

Errors are the standard deviations of the mean.

The agreement between the results of all of the eight analyses of the $SrCO_3$ with those previously reported by other investigators gives confidence in the quality of other isotope ratio measurements. Such agreement is not necessarily an indication of accuracy but merely demonstrates consistency. A single measurement cannot be accepted with confidence unless it is part of a set of similar measurements with which it can be compared. It is well to remember that one out of the nine analyses of the $SrCO_3$ had to be rejected even though the run seemed to be of good quality.

Conclusions.

The reproducibility of measurements of the Sr^{87}/Sr^{86} ratio is improved by as much as a factor of four by making a fractionation correction based on the assumption that the Sr^{86}/Sr^{88} ratio is a constant equal to 0.1194.

The reproducibility demonstrated by repeated analyses of an oceanic basalt (R1292) and a $SrCO_3$ standard is $\pm$ 0.0006 (0.08%) and $\pm$ 0.0009 (0.12%), respectively. Based on these results the reproducibility of a single analysis of good quality is assumed to be $\pm$ 0.001 or 0.14%.

The instrument precision error for the measurement of Sr^{87}/Sr^{86} ratios is a useful criterion for judging the quality of a run. Because it is smaller than the reproducibility it is unrealistic to claim a precision error of 0.001 (0.14%) for the corrected Sr^{87}/Sr^{86} ratio when the instrument error alone has a value of 0.14%.

The isotope ratios obtained for the $SrCO_3$ standard are in good agreement with results reported by Nier (1938), Aldrich et al. (1953), and Herzog et al. (1953) and give confidence in the accuracy of the isotopic analyses of strontium in rocks reported in this thesis.

Chapter 6

THE ISOTOPIC COMPOSITION OF STRONTIUM IN OCEANIC AND CONTINENTAL BASALTS.

Introduction.

Before the ratio of Sr^{87}/Sr^{86} in igneous rocks can be used as a criterion for a crustal or subcrustal origin, the range of variation of this ratio in rocks of known subcrustal origin must be determined. For this purpose a survey was made of the isotopic composition of strontium in a number of oceanic and continental basalts from many widely scattered geographic localities. The geographic distribution of the sample localities tests the lateral and/or vertical homogeneity of the subcrustal source regions of basalt magma with respect to the abundance of Sr^{87}.

All conclusions and calculations in this chapter are based on corrected values of the Sr^{87}/Sr^{86} ratio. The nature of the correction and the reasons for making it are described in Chapter 5, page *177*. The conclusions regarding the apparent homogeneity of the upper mantle are not affected by the use of the corrected Sr^{87}/Sr^{86} ratios.

Measurements of the Sr^{86}/Sr^{88} ratio varied by as much as 1.4% between successive analyses of the same sample (R1292, Chapter 5, Table 5.1, p.I78). This variation is the result of isotope fractionation in the mass spectrometer. Because of it a reliable determination of the Sr^{86}/Sr^{88} ratio of a sample should be based on several independent measurements spaced over an extended period of time. Evidence that the effects of isotope fractionation in the mass spectrometer are random is presented in Chapter 9 along with a discussion of the numerical value of the Sr^{86}/Sr^{88} ratio in terrestrial material and tektites.

The precision of the Sr^{84}/Sr^{88} ratios is very low ($\pm$5%). Frequently only 12 to 18 Sr^{84} peaks were scanned. A more detailed account is given in Chapter 9.

The concentrations of rubidium and strontium in a representative number of basalts were determined by the method of isotope dilution (Chapter 4). This was done in order to compare the Rb/Sr ratios of basalts to the calculated values of the Rb/Sr ratios in their source regions.

The Rb/Sr ratios of the magmatic source material were calculated from the Sr^{87}/Sr^{86} ratio of Recent basalts by

assuming that the initial Sr^{87}/Sr^{86} ratio was 0.7004 ±0.002 (Gast, 1960) and that the age of the earth is 4.5 billion years (Chapter 1). If basalt or andesite magma forms by partial melting of rocks in the upper mantle, then the difference between the Rb/Sr ratios in basalts and the calculated values of the source rock is evidence of magmatic differentiation or of fractional melting of the source rocks to produce the magma. Another purpose of these analyses was to outline the range of variation of the concentrations of rubidium and strontium in oceanic basalts for geochemical interest.

Real variations of the Sr^{87}/Sr^{86} ratios in basalts from the same or from different localities are an indication that magma was derived from several sources having different Rb/Sr ratios. A comparison of these ratios, calculated with the assumptions outlined above, to those found in different types of ultrabasic and basic rocks may serve to give an indication of the nature of the source material.

Analytical Results.

All experimental data pertaining to the basalts

are compiled in Table 6.1. A description of the specimens as well as information about their localities is given in Chapter 10.

Oceanic Basalts.

The localities from which specimens were chosen for analysis are Hawaii, Samoa, Ascension Island, the Mid-Atlantic Ridge and the Azores. In the following sections the results will be discussed for each of these localities.

Hawaiian Islands.

The Hawaiian Islands are a group of shield volcanoes formed by flows of primary tholeeitic lava. The olivine basalts and their alkali-rich derivatives either formed as a result of fractional crystallization of tholeeitic basalt magma or represent a different magma series originating from other source regions in the mantle. The depth of these source regions, judging on the basis of earthquake foci, is estimated to be between 48 and 56 km, which is well below the base of the crust (Turner and Verhogen, 1960, p. 219).

The isotopic compositions of strontium and the Rb/Sr ratios of five basalts from the Hawaiian Islands were determined. The Sr^{87}/Sr^{86} ratio for one of these,

Table 6.1 Oceanic Basalts

Sample Number	Locality	Date	87/86	$(87/86)_{corr}$	86/88	84/88	No. of scans	Qual.	Rb ppm	Sr ppm	Rb/Sr
Hawaii Island											
R1292*	Kilauea		.7077	.7066	.1190	.0066		Exc.	9.76	398.6	.0245
			± .001	± .0003	± .0003	± .0001					
R1282	Kilauea	7/14/60	.7094	.7073	.1187	.0065	48	Fair	9.13	380.6**	.0240
R2001	Kilauea	9/8/60	.7084	.7063	.1187	.0064	90	Good	9.78	379.3	.0258
R1993	Mauna Kea	7/18/60	.7097	.7073	.1186	.0062	108	Good	46.7	1249	.0375
Average Hawaii Basalt			.7088	.7069	.1188	.0064					
		$\bar{\sigma}$	± .0005	± .0003	± .0001	± .0001					
		σ	± .0009	± .0005	± .0002	± .0002					
Maui Island											
R2002		10/24/60	.7046	.7037	.1191	.0064	84	Good			
"		1/7/61	.7072	.7057	.1189	.0064	90	Good			
Average for R2002			.7059	$.70_{47}$	.1190	.0064					
Average for five basalts from Hawaiian Islands			.7082	.7064	.1188	.0064			18.8	601.9	.031
		$\bar{\sigma}$	± .0007	± .0005	± .00008	± .00007					
		σ	± .0015	± .0011	± .0002	± .0002					

* Average of five analyses, See Chapter 5, Table 5.1, p.

** Sr^{84} spike.

Table 6.1 continued

Sample Number	Locality	Date	87/86	$(87/86)_{corr}$	86/88	84/88	No. of scans	Qual.	Rb ppm	Sr ppm	Rb/Sr
Samoan Islands											
R2029	Tutuila	2/8/61	.7098	.7077	.1187	.0066	90	Good	41.6	567.6*	.0733
R1995	Ofu	9/4/60	.7093	.7078	.1189	.0066	78	Good	14.10	222.5	.0634
R2030	Ofu	7/11/60	.7096	.7075	.1187	.0060	78	Fair	20.9	469.3	.0445
Average for three Samoan basalts			.7096	.7077	.1188	.0064			25.5	419.8	.061
		$\bar{\sigma}$ ±	.00015	± .00009	± .00002	± .0002			± 8.3	± 105	± .025
		σ ±	.0003	± .0002	± .0001	± .0004					
Ascension Island											
R2031		5/25/60	.7073	.7070	.1193	.0065	96	Good	31.9	643.0	.0496
Mid-Atlantic Ridge											
R4125	31°18'.8N	8/30/60	.7059	.7068	.1197	.0066	48	Fair	9.75	118.3**	.0824
"	40°54'.3W	1/10/61	.7097	.7055	.1180	.0065	84	Good			
Average for R4125			.7078	.7062	.1188	.0066					
Azore Islands											
R4156	Horta Fayal	9/2/60	.7106	.7088	.1188	.0066	78	Good			
Average of eleven oceanic basalts			.7087	.7072	.1188	.0065			21.5	492.0	.044
		$\bar{\sigma}$ ±	.0006	± .0003	± .0002	± .00006			± 5.0	± 108.5	± .014
		σ ±	.002	± .0011	± .0006	± .0002					

* and ** Sr^{84} spike.

a basalt from Kilauea (R1292), was measured five times. The average Sr^{87}/Sr^{86} ratio for this rocks is 0.7066, $\bar{\sigma} = \pm .00026$, $\sigma = \pm .00059$ (Chapter 5, Table 5.1, p. I78).

The Sr^{87}/Sr^{86} ratios of the other basalts from Hawaii Island (R1282, R2001, and R1993) fall inside the band $0.7066 \pm 0.0012(2\sigma)$. They therefore do not differ significantly from R1292 at the 95% confidence limit although the possibility that they belong to a slightly different population is not excluded. All four basalts average $Sr^{87}/Sr^{86} = 0.7069 \pm 0.00025(\bar{\sigma})$.

The Sr^{87}/Sr^{86} ratio for a basalt from Maui Island (R2002) is 0.7047 ± 0.001 calculated from duplicate analyses. This basalt therefore seems to differ considerably from the other four. It is customary to reject the hypothesis that two means are identical when the difference between them exceeds its own error at the 95% confidence limit (Evans, 1955, p. 746). In this case the difference $D = 0.0022$ and its error, $\bar{\sigma}_D$, calculated from the standard deviations of the two means, is $\pm .00106$. Since $D > 2\bar{\sigma}_D$, the evidence is sufficient to conclude that the two means are significantly different. We therefore have evidence of at least two source regions from which Hawaiian magmas have been derived.

The calculated Rb/Sr ratios for the two source regions are: For the Island of Hawaii $(Rb/Sr)_{source} = 0.034 \pm .011$, Maui Island $(Rb/Sr)_{source} = 0.022 \pm 0.012$. The errors are limits of uncertainty and do not necessarily reflect on the precision of these values.

A comparison to the Rb/Sr ratios of igneous rocks (Chapter 2, Table 2.2) shows that the magmatic source material resembles most closely the basic and ultrabasic igneous rocks. Moreover, it is evident that neither chondrites nor the achondrites listed in Table 2.2 are a suitable source material for the Hawaiian basalts. The Rb/Sr ratio of the chondrites is too high whereas that of the achondrites is too low. It is unfortunate that the data on the concentrations of rubidium and strontium in ultrabasic igneous rocks are so fragmentary. A systematic survey of these rocks is desirable if the calculated values of the Rb/Sr ratio are to be used to identify the nature of the magmatic source material.

The mean Rb/Sr ratio for the three basalts from Kilauea is 0.0248 ± 0.0005. The rubidium and strontium concentrations are remarkably uniform and average 9.56 ± 0.21 ppm and 386 $\pm$ 6.2 ppm, respectively. R1993, a basalt from Mauna Kea,

contains 46.7 ppm rubidium and 1249 ppm strontium but has a Rb/Sr ratio of 0.0374. The average values for all four basalts are: Rb = 18.8 ± 9.3 ppm, Sr = 601.9 ± 209 ppm and Rb/Sr = 0.031 ± 0.019.

The Rb/Sr ratio of the basalts from the Island of Hawaii is identical, within experimental error, to the Rb/Sr ratio of their source region calculated from the average Sr^{87}/Sr^{86} with the assumptions outlined on page .

Samoan Islands.

The rocks of the Samoan islands belong to the typical alkali-rich olivine basalt association of the Pacific petrographic province. Two of the three rocks analyzed are olivine basalts, the third (R1995) is an olivine gabbro from a volcanic neck on Ofu Island. The corrected Sr^{87}/Sr^{86} ratios form a homogeneous set of values averaging 0.7077 ± 0.00009.

The Samoan rocks differ significantly from the basalt on Maui Island in their Sr^{87}/Sr^{86} ratios. The difference between them and the rocks from the island of Hawaii, however, may not be significant.

The average concentrations of rubidium and strontium and the Rb/Sr ratio of the three Samoan rocks are Rb = 25.5 ± 8.3 ppm, Sr = 419.8 ± 105 ppm, Rb/Sr = 0.061 ± 0.025. The large standard deviations of the means indicate a fairly wide range of values which for rubidium is from 14.1 to 41.6 ppm and for strontium from 222.5 to 567.6 ppm.

The calculated value of the Rb/Sr ratio of the source region is 0.038 ± 0.011. This value is less than the present Rb/Sr ratio of the basalts and indicates enrichment of the basalt magma in rubidium (or depletion of strontium) relative to the source material.

Ascension Island, Mid-Atlantic Ridge, and the Azores.

The Sr^{87}/Sr^{86} ratios of the specimens from Ascension Island and the Mid-Atlantic are 0.7070 and 0.7062 0.00065 ($\bar{\sigma}$), respectively. The value for the boulder from the Mid-Atlantic Ridge is based on duplicate analyses. The Sr^{87}/Sr^{86} ratio of the olivine basalt from the Azores is 0.7088. This is higher than observed in any of the other oceanic basalts.

Concentrations of rubidium and strontium were obtained

for the basalts from Ascension Island and the Mid-Atlantic Ridge. The results for the former are Rb = 31.9 ppm, Sr = 643.0 ppm, Rb/Sr = 0.0496 and for the latter Rb = 9.75 ppm, Sr = 118.3 ppm, Rb/Sr = 0.0824.

The calculated Rb/Sr ratios of the source material of the basalts are as follows: Ascension Island Rb/Sr = 0.035, Mid-Atlantic Ridge Rb/Sr = 0.030, and the Azores Rb/Sr = 0.044. The value for the Azores is the highest of all oceanic basalts.

Summary.

All averages discussed in the previous section are summarized in Table 6.2.

Table 6.2 Summary of Data on Oceanic Basalts.

Locality	No. of samples	$(87/86)_{corr}$	Rb ppm	Sr ppm	Rb/Sr	(Rb/Sr) source
Hawaii	4	0.7069(8) ± 0.00025	18.8 ± 9.3	601.9 ± 209	0.031 ± 0.019	0.034 ± 0.011
Maui	1	0.7047(2) ± 0.001				0.022 ± 0.012
Samoa	3	0.7077(3) ± 0.00009	25.5 ± 8.3	419.8 ± 105	0.061 ± 0.025	0.038 ± 0.011
Ascension	1	0.7070(1)	31.9	643.0	0.050	0.035
Mid-Atlantic Ridge	1	0.7062(2) ± 0.00065	9.75	118.3	0.082	0.030
Azores	1	0.7088				0.044
Averages	11	0.7072 ± 0.00033	21.5 ± 5.0	492.0 ± 108.5	0.044 ± 0.014	0.036 ± 0.011

Note: (1) All errors are standard deviations of the mean or are calculated from them.

(2) The average Rb/Sr ratios were calculated from the average concentrations of Rb and Sr.

(3) Number in brackets indicates number of analyses.

Continental Basalts.

Sr^{87}/Sr^{86} ratios were determined for 16 volcanic rocks from eight continental localities. This part of the investigation is an important phase of the test of the lateral homogeneity of the upper mantle. The isotopic composition of strontium entering the crust from the mantle is of particular significance for any interpretation of the origin of crustal igneous rocks. Specimens of volcanic rocks from the following localities were chosen: Japan; Deccan Plateau, India; Columbia River area, Oregon; Diabase from New Jersey; Iceland; Mt. Vesuvius, Italy; Yellowstone Park; and Squaw Creek, Montana.

The experimental data are compiled in Table 6.3.

Japan.

Three rocks from two Japanese localities were analyzed. Two of these are andesites from Sakurajima, the third is a dacite from Bandai San. All three rocks were erupted in historic time.

The average corrected Sr^{87}/Sr^{86} ratio is 0.7081, $\bar{\sigma} = \pm 0.00013$, $\sigma = \pm 0.00023$. Japan is generally considered to lie outside the Pacific petrographic province

Table 6.3 Continental Volcanic Rocks of Sub-crustal Origin

Sample Number	Locality	Date	87/86	$(87/86)_{corr}$	86/88	84/88	No. of scans	Qual.	Rb ppm	Sr ppm	Rb/Sr
Japan											
R4161	Sakura-jima	9/13/60	.7124	.7084	.1181	.0061	60	Fair			
R4221	"	1/7/61	.7086	.7080	.1192	.0066	84	Good			
R4244	Bandai San	1/16/61	.7098	.7080	.1188	.0069	90	Good			
Average for three Japanese rocks			.7103	.7081	.1187	.0065					
		$\bar{\sigma}$ ±	.0011	±.0001	±.0003	±.0002					
		σ ±	.0019	±.0002	±.0006	±.0004					
Deccan Plateau, India											
R1864	Kogna Riv.	8/22/60	.7106	.7085	.1187		40	Fair	16.10	234.9	.0685
R1865	" "	9/20/60	.7121	.7091	.1184	.0063	78	Good			
R1868	" "	9/14/60	.7096	.7090	.1192	.0069	54	Fair			
Average Deccan Basalt			.7108	.7089	.1188	.0066			16.10	234.9	.0685
		$\bar{\sigma}$ ±	.0007	±.0002	±.0002	±.0003					
		σ ±	.0013	±.0003	±.0003	±.0004					

Table 6.3 continued

Sample Number	Locality	Date	87/86	$(87/86)_{corr}$	86/88	84/88	No. of scans	Qual.	Rb ppm	Sr ppm	Rb/Sr
Columbia River Plateau, Oregon											
R1428	Wahkeenah	9/15/60	.7087	.7066	.1187	.0064	30	Poor			
"	Trail, Ore.	1/10/61	.7060	.7069	.1195	.0067	84	Fair			
"	"	2/7/61	.7093	.7066	.1185		84	Good			
Average for R1428			.7080	.7067	.1189	.0066					
		$\bar{\sigma}$	± .0010	±.0001	±.0003	±.0002					
		σ	± .0018	±.0002	±.0005	±.0002					
R1435*	"	8/26/60	.7092	.7113	.1201	.0067	90	Poor	54.8	310.6	0.176
R1443*	"	9/16/60	.7125	.7113	.1190	.0064	60	Poor			
Best estimate for Columbia River basalt			.7080	.7067	.1189	.0066			54.8	310.6	0.176
		$\bar{\sigma}$	± .0010	±.0001	±.0003	±.0002					
		σ	± .0018	±.0002	±.0005	±.0002					
Triassic Diabase, New Jersey and Connecticut											
R4209	Palisades Park, N.Y.	12/12/60	.7106	.7079	.1185	.0065	90	Good			
R4210	"	12/1/60	.7100	.7070	.1184	.0066	102	Good			
R4211	Mt.Carmel	12/3/60	.7123	.7087	.1182		32	Poor			
"	"	12/21/60	.7127	.7100	.1185		48	Fair			
Average R4211			.7125	.7094	.1184						
Average diabase			.7110	.7081	.1184	.0066					
		$\bar{\sigma}$	± .0008	± .0007	± .00004	±.0001					
		σ	± .0013	± .0012	± .00007	±.0001					

* Judged to be of Poor quality because of vacuum difficulties.

Table 6.3 continued

Sample Number	Locality	Date	87/86	(87/86) corr	86/88	84/88	No. of scans	Qual.	Rb ppm	Sr ppm	Rb/Sr
Iceland											
R4195		9/10/60	.7128	.7101	.1185	.0064	78	Good			
Italy											
R4243	Mt.Vesuvius	1/14/60	.7088	.7082	.1192	.0065	84	Good			
United States											
R1574	Yellowstone Park	1/23/61	.7108	.7084	.1186	.0064	90	Good			
R4245	Squaw Creek, Montana	2/6/61	.7123	.7096	.1185	.0066	90	Good			
Average for all continental volcanic rocks			.7106	.7085	.1187	.0065					
		$\bar{\sigma}$	±.0004	±.0003	±.00009	±.00007					
		σ	±.0016	±.0010	±.0003	±.0002					

and to fall inside the andesite line. It is therefore of interest to compare the average Sr^{87}/Sr^{86} ratio of the Japanese rocks to those for Hawaii and Samoa. The test for the difference of two means reveals that the Japanese rocks differ significantly from those of Hawaii and Samoa, withing experimental error.

The calculated Rb/Sr ratio of the source region is 0.040 ± 0.011 which is not too different from the value of this ratio in olivine basalts.

The concentrations of rubidium and strontium in the andesites and the dacite were not determined.

Deccan Plateau, India.

The tholeeitic basalts of the Deccan Plateau in western India today occupy an area of 200,000 square miles and reach a maximum thickness of 6000 feet near Bombay. This immense quantity of basalt was extruded in Cretaceous - Eocene time. The rocks resemble closely in chemical composition and volume similar occurrences in the Columbia - Snake River area of Washington, Oregon and Idaho, the Keweenawan lavas of Lake Superior, the Stromberg lavas of South Africa, the Triassic diabases

of New Jersey, and the Parana' basalts of South America (Turner and Verhoogen, 1960, p. 205).

The isotopic composition of strontium of three basalt specimens from the Deccan Plateau were determined. The average corrected Sr^{87}/Sr^{86} ratio is 0.7089, $\bar{\sigma} = \pm 0.00019$, $\sigma = \pm 0.00032$. The Rb/Sr ratio of one of the three basalts (R1864) is 0.069. If the age of the basalts is taken to be 100 million years, the Sr^{87}/Sr^{86} ratio has increased by 0.0003 since the time of solidification. The initial ratio would therefore be 0.7086. The average Sr^{87}/Sr^{86} ratio for the Deccan basalts is very slightly higher than that of the Japanese volcanics. The calculated Rb/Sr ratio of the source region is 0.043 ± 0.011.

Columbia River Plateau, Oregon.

Three specimens of basalt were selected for analysis. Unfortunately the results obtained on two of these (R1435, R1443) are of inferior quality because of instrumental difficulties (poor vacuum). The third speciment (R1428) was analyzed in triplicate and the average of these, $Sr^{87}/Sr^{86} = 0.7067 \pm 0.0001$, is considered to be the best

estimate of the true value. Specimens R1435 and R1443 average 0.7113.

The concentrations of rubidium and strontium of R1435 are Rb = 54.8 ppm, Sr = 310.6 ppm, and Rb/Sr = 0.176. Since the age of the basalts is Miocene (25 million years) an age correction of 0.0002 is applied to the average Sr^{87}/Sr^{86} ratio. The best estimate of the initial Sr^{87}/Sr^{86} ratio is therefore 0.7065 ± 0.0001. The calculated Rb/Sr ratio of the source region is 0.032 ± 0.011.

Triassic Diabases of New Jersey and Connecticut.

Two specimens of diabase from the Palisade sill (R4209, R4210) average $Sr^{87}/Sr^{86} = 0.7075 \pm 0.00045$. A third specimen of diabase from Mt. Carmel, Connecticut, was analyzed in duplicate. The average Sr^{87}/Sr^{86} ratio = 0.7094 0.00065. The test for the difference between two means shows that D = 0.0019, $\overline{\sigma}_D = \pm$ 0.00079, Since $D > 2\,\overline{\sigma}_D$, the difference is significant, However, because the age of these diabases is approximately 200 million years, the difference may be due to differences in the amounts of radiogenic Sr^{87} accumulated since solidification of the magma. Since analyses for rubidium

and strontium are not available, the average Sr^{87}/Sr^{86} ratio for all three rocks is calculated and an age correction is applied to the average on the assumption that Rb/Sr = 0.1 and the age is 200 million years. The best estimate is therefore Sr^{87}/Sr^{86} = 0.7081 - 0.0009 = 0.7072, $\bar{\sigma} = \pm$ 0.0007, $\sigma = \pm$ 0.0012. The calculated Rb/Sr ratio of the source region is 0.036 ± 0.011.

Miscellaneous Localities.

Single isotope ratio analyses were performed on basalts from four continental localities. The Sr^{87}/Sr^{86} ratios of these are: Iceland: 0.7101, Mt. Vesuvius, Italy: 0.7082, Yellowstone Park: 0.7084, Squaw Creek, Montana: 0.7096.

The olivine basalt from Iceland is post-Pleistocene in age and has the highest abundance of Sr^{87} of any basalt encountered in the survey. Its sub-crustal source region has a calculated Rb/Sr ratio = 0.051 ± 0.012.

The Sr^{87}/Sr^{86} ratios of the other rocks are well within the range of what may be considered average sub-crustal strontium. The basalt from Squaw Creek is of Tertiary age. Assuming an age of 50 million years

and a Rb/Sr ratio = 0.1, its Sr^{87}/Sr^{86} ratio is reduced by 0.0002 to 0.7094. The Rb/Sr ratios calculated for the source regions are as follows: Mt. Vesuvius 0.041, Yellowstone Park 0.042, Squaw Creek, Montana, 0.047.

Summary.

The results discussed in the previous section are summarized in Table 6.4.

Table 6.4 Summary of Data for Continental Basalts at the Time of Their Extrusion.

Locality	No. of Sples.	$(87/86)_{corr}$	Rb ppm	Sr ppm	Rb/Sr	$(Rb/Sr)_{source}$
Japan	3	.7081 ± 0.00013				0.040 ± 0.011
Deccan Plat., India	3	.7086* 0.00019	16.1	234.9	0.069	0.043 ± 0.011
Columbia Riv., Oregon	1	0.7065*(3) 0.0001	54.8	310.6	0.176	0.032 ± 0.011
Triassic Diabase, New Jersey	3	0.7072*				0.036 ± 0.011
Iceland	1	0.7101				0.051 ± 0.012
Mt. Vesuvius Italy	1	0.7082				0.041 ± 0.012
Yellowstone Park	1	0.7084				0.042 ± 0.012
Squaw Creek Montana	1	0.7094*				0.047 ± 0.012
Average	14	0.7083 ± 0.0004	35.5 ±19.4	272.8 ± 38	0.13 ± 0.07	0.041 ± 0.011

* Small age correction applied.

Conclusions.

The average Sr^{87}/Sr^{86} ratio for 25 basalts and other volcanic rocks of sub-crustal origin from oceanic and continental localities is = 0.7078, $\bar{\sigma} = \pm$ 0.0002, $\sigma = \pm$ 0.0012. The values range from a low of 0.7047 for a basalt from Maui Island to 0.7101 for an olivine basalt from Iceland.

The average Sr^{87}/Sr^{86} for eleven basalts from oceanic localities is 0.7072 ± 0.0003. Fourteen volcanic rocks from continental localities average 0.7083 ± 0.0004.

The difference between oceanic and continental basalts is probably not significant. Although there is a tendency for continental basalts to have slightly higher Sr^{87}/Sr^{86} ratios than oceanic basalts, exceptions are common.

The magmatic source regions in the upper mantle are therefore homogeneous within narrow limits. The limits of homogeneity expressed in terms of the Sr^{87}/Sr^{86} ratio are $0.7078^{+0.002}_{-0.003}$.

The Rb/Sr ratio for the magmatic source regions, calculated from the average Sr^{87}/Sr^{86} ratio, is 0.039 ranging from 0.022 to 0.051. The upper mantle is therefore

homogeneous with respect to its Rb/Sr ratio within the limits $Rb/Sr = 0.039^{+0.012}_{-0.017}$.

The sub-oceanic source regions have a calculated Rb/Sr ratio of 0.036 whereas the sub-continental sources average 0.041.

Small but real differences in the Sr^{87}/Sr^{86} ratio between basalts from different localities seem to exist. Such differences are evidence that magma was derived from more than one source and that small variations in the Rb/Sr ratio of the upper mantle exist.

Small differences in the Sr^{87}/Sr^{86} ratio are difficult to determine reliably because of isotopic fractionation in the mass spectrometer. This can be overcome partly by applying a fractionation correction based on a constant value for the Sr^{86}/Sr^{88} ratio and by making several independent analyses spaced over a period of time.

The concentrations of rubidium and strontium in the oceanic basalts average 21.50 ± 5.0 ppm and 492 ± 108.5 ppm, respectively. Rubidium concentrations range from 9.13 to 46.7 ppm whereas strontium concentrations vary between 118.3 and 1249 ppm. The Rb/Sr ratio, calculated from the average concentrations, is 0.044 ± 0.014.

Concentrations of rubidium and strontium for tholeeitic basalts were determined for only two rocks. The average values are Rb = 35.5 ± 19.4 ppm, Sr = 272.8 ± 38. ppm. The corresponding average Rb/Sr ratio is 0.13 ± 0.07. Tholeeitic basalts therefore seem to have a higher Rb/Sr ratio than oceanic basalts.

A comparison of the Rb/Sr ratios of the basalts with those calculated for their source regions may give some indication of the processes of magma formation. Generally the Rb/Sr ratios of the rocks are higher than those of their source material. This is evidence that Rb is enriched (or Sr is depleted) in the liquid fraction. The only exception to this occurs in the basalts from the island of Hawaii where the Rb/Sr ratio of the basalt is identical to that of their source. This may be interpreted as evidence of essentially complete melting of the source rock. If this is true, the lavas of Kilauea may be identical to their sub-crustal source material with respect to the concentrations of major elements as well.

A comparison of the Rb/Sr ratios of the magmatic source regions with those of certain types of igneous

rocks may give some indication of the nature of the upper mantle. According to Chapter 2, Table 2.2 olivine basalts and the eclogite have identical Rb/Sr ratios at about 0.045. Very similar values are indicated for the source regions in the following localities: Japan (0.040), Deccan Plateau (0.043), Mt. Vesuvius (0.041), Yellowstone Park (0.042), Squaw Creek (0.047) and the Azores (0.044).

This similarity does not necessarily prove that the above mentioned volcanic rocks were formed by partial melting of a basaltic or eclogitic mantle. Other ultrabasic rock types such as peridotites, pyroxenites, etc. may have suitable Rb/Sr ratios as well. Because of such possible interpretations, a comprehensive survey of the concentrations of rubidium and strontium in ultrabasic igneous rocks is highly desirable.

Neither chondritic nor achondritic meteorites listed in Table 2.2 are a suitable source material for Recent basalts. The Rb/Sr ratio of chondritic meteorites is too high whereas that of the achondritic meteorites is too low.

Chapter 7

THE Sr^{87}/Sr^{86} RATIO IN PRECAMBRIAN BASIC INTRUSIVES.

Introduction.

The isotopic composition of strontium of the source material of basalt magma can be determined by analyzing Recent basalts. The value of the Sr^{87}/Sr^{86} ratio 4.5 billion years ago is known from measurements of the achondrite Pasamonte (Chapter 1). With this information a development line for the Sr^{87}/Sr^{86} ratio in the sub-crustal source regions throughout geologic time can be drawn (Figure 7.4).

An attempt has been made to determine the slope of this development line independent of any meteorite data by obtaining initial Sr^{87}/Sr^{86} ratios for basic igneous intrusives of sub-crustal origin whose ages are known. The samples chosen for this study are from the Bushveld Complex in South Africa, and the Duluth Gabbro in Minnesota.

The Bushveld Igneous Complex, S. Africa.

Introduction.

The basic rocks of the Bushveld Complex are the products of fractional crystallization and differentiation of a large volume of basaltic magma. They are overlain and intruded by the so-called "Red Granite" or Bushveld Granite. The relationship of the granite to the basic rocks is not clear. Turner and Verhoogen (1960, p.298) suggest that all igneous rocks of the Complex belong to the same cycle of igneous activity.

Concentrations of rubidium and strontium as well as Sr^{87}/Sr^{86} ratios were determined for three basic and ultrabasic igneous rocks in an attempt to measure the initial Sr^{87}/Sr^{86} ratio at the time of emplacement.

The Age of the Bushveld Complex.

Schreiner (1958) reported an average age of 1920 million years by the Rb-Sr method for four whole granites and three feldspars separated from them. His data have been recalculated and are presented in Figure 7.1 in diagrammatic form. Three of the whole rocks (B21, B10, and B6) form an "array" and converge

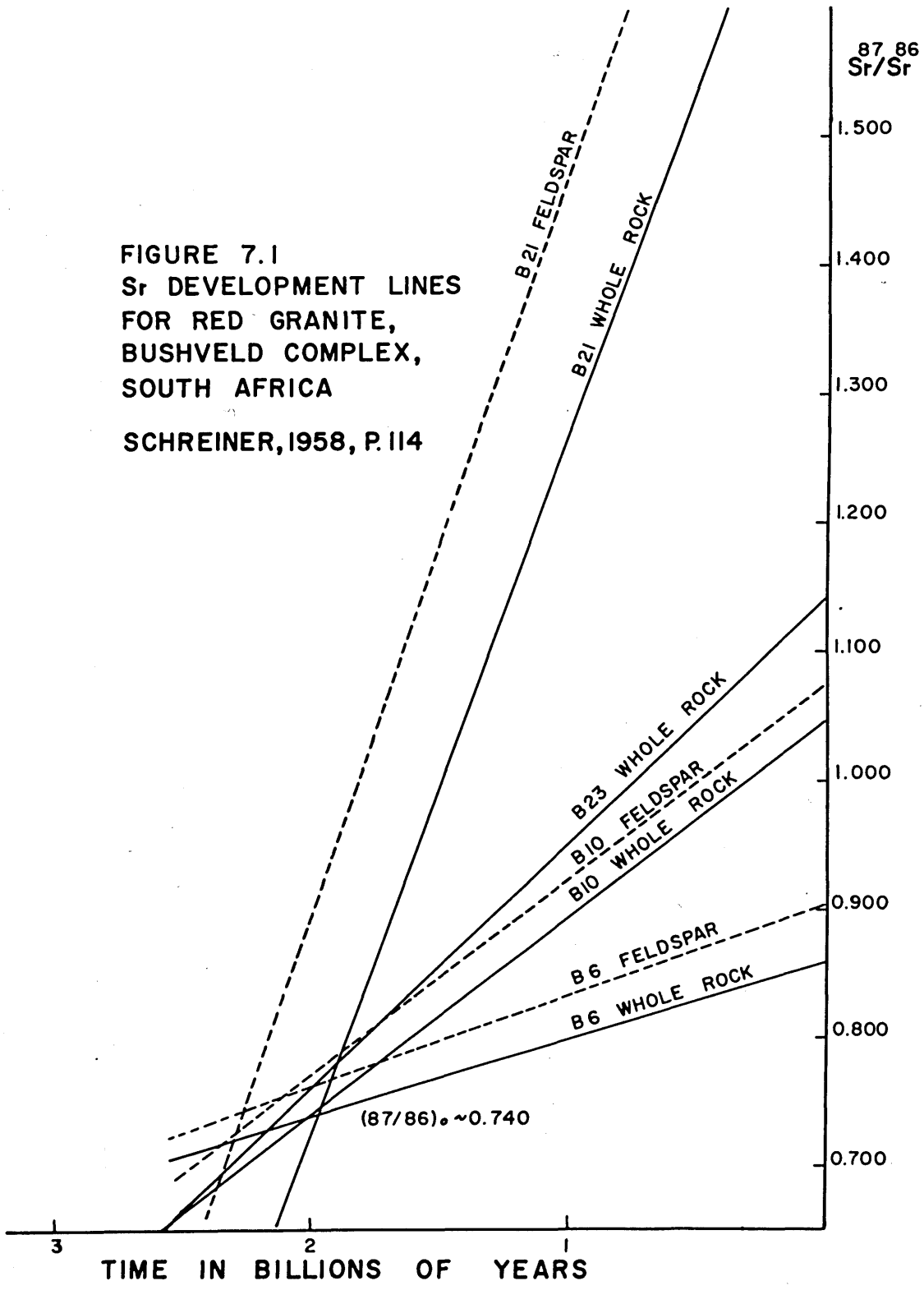


FIGURE 7.1
Sr DEVELOPMENT LINES FOR RED GRANITE, BUSHVELD COMPLEX, SOUTH AFRICA

SCHREINER, 1958, P. 114

at t = 1975 million years, Sr^{87}/Sr^{86} = 0.740. The granite B23 probably does not differ significantly from the other three whole rocks. The feldspars (B21, B10 and B6) seem to form a slightly different array converging at about t = 2225 and Sr^{87}/Sr^{86} = .740. The reason for this difference is not clear and it may not be significant. According to Schreiner's data the initial Sr^{87}/Sr^{86} ratio of the Bushveld Granite is $\sim$ 0.740. which definitely excludes a sub-crustal origin for this rock. Moreover, the granite and the underlying basic rocks cannot be co-magmatic.

Nicolaysen et al. (1958) reported a Rb-Sr age of 1915 $\pm$ 50* million years for biotite from a coarse-grained mica-pyroxene gabbro at the Rustenburg Platinum Mine. The same authors also obtained U-Pb and Th-Pb ages on crystals of monazite and zircon from the Bushveld granite. They concluded that an age of 1950 $\pm$ 150 million years for both the granite and the basic rocks was consistent with their results.

Experimental Results.

The analytical data are shown in Table 7.1 and are presented graphically in Figure 7.2. Only single isotope ratio determinations were made for each rock and an error

*recalculated to $\lambda = 1.47 \times 10^{-11}$ yrs.$^{-1}$

of±0.001 is assigned to the corrected Sr^{87}/Sr^{86} ratios. The errors shown for the rubidium and strontium analyses are considered to be realistic estimates of the reproducibility at the particular concentration levels (Chapter 4, Table 4.6). Descriptions of the rock specimens and information about the sample localities are given in Chapter 10.

Discussion.

The pattern of the Sr^{87}/Sr^{86} ratios is consistent with the Rb/Sr ratios in the three rocks. The development lines converge toward a point at about 4.5 billion years and a Sr^{87}/Sr^{86} ratio of 0.707. However, the large error envelopes make these values meaningless. In fact intersections are observed from zero up to about 14.3 billion years. An intersection at about 2 billion years is therefore not excluded by the data.

Intersections of the development lines for the strontium in the three rocks with t = 1915 ± 50 million years give $(Sr^{87}/Sr^{86})_o$ = 0.710 ± 0.001, 0.708 ± 0.001 and 0.707 ± 0.001, respectively. Since the Sr^{87}/Sr^{86} ratio of the anorthosite is almost constant in time, its initial ratio of 0.707 ± 0.001 is considered to be

Table 7.1 Bushveld Complex.

Sample Number	Rock Type		87/86	$(87/86)_{corr}$	86/88	84/88	No. of scans	Qual.	Rb ppm	Sr ppm	Rb/Sr
R4193	Anortho-site	11/6/60	.7083	.7071 ± .001	.1190	.0066	102	Good	0.63 ± 25%	379.3 ± 2%	.0017 ± .0004
R4194	Norite	11/16/60	.7107	.7122 ± .001	.1199	.0065	90	Good	7.77 ± 3%	262.3 ± 2%	.0296 ± .0011
R4195	Pyrox-enite	11/21/60	.7073	.7091 ± .001	.1200	.0069	126	Good	.55 ± 25%	49.13 ± 5%	.0112 ± .0030

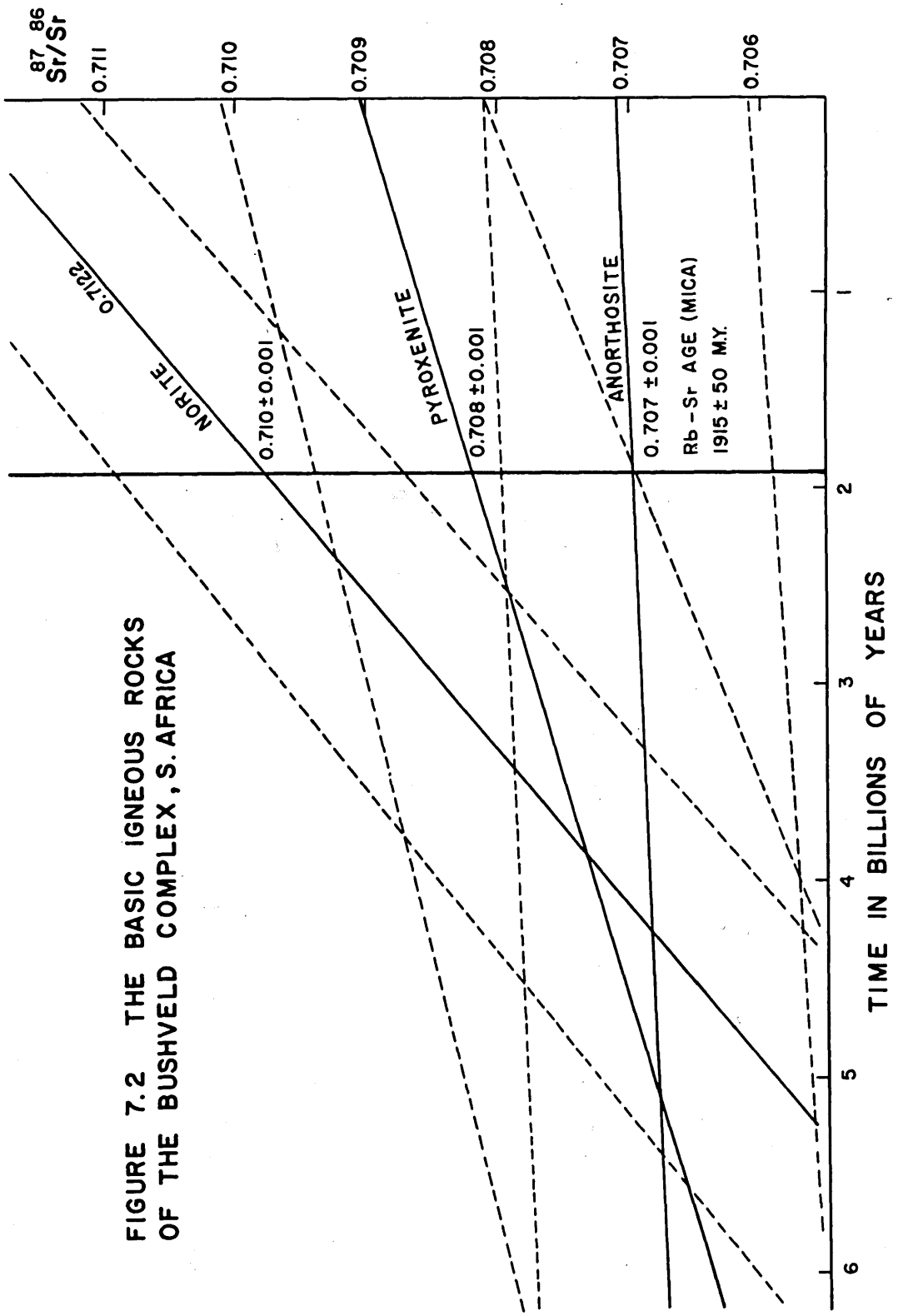


FIGURE 7.2 THE BASIC IGNEOUS ROCKS OF THE BUSHVELD COMPLEX, S. AFRICA

the best estimate of this quantity for the basic rocks of the Bushveld Complex.

Figure 7.2 illustrates the difficulty of obtaining precise age values and initial Sr^{87}/Sr^{86} ratios for rocks having such low Rb/Sr ratios. The precision of the measurements can be improved and the results made more meaningful by making all determinations in triplicate.

Conclusions.

The age of the basic igneous rocks of the Bushveld Complex is 1915 ± 50 million years (Nicolaysen et al., 1958). An attempt to determine their Sr^{87}/Sr^{86} ratio at that time met with indifferent success because of the low precision of the measurements. The best value for the initial Sr^{87}/Sr^{86} ratio is 0.707 ± 0.001.

The Duluth Gabbro.

Introduction.

The Duluth Gabbro Complex is an immense sill-like mass extending 150 miles north east from Duluth, Minnesota. It was formed by repeated intrusion and crystallization of feldspathic gabbro, layered gabbro, grano-

diorite and granophyre. Lack of chilled margins indicates that the separate intrusions took place in relatively rapid succession. The various rock types can be explained in terms of differentiation of a common parent magma of basaltic composition (Taylor, 1956, p.42). An excellent summary of the geology of the Duluth Gabbro Complex was given by Goldich et al. (1961).

The age of the Duluth Gabbro as reported by Goldich et al. (1961) is about 1100 million years. This is an average value of several independent determinations by the K-Ar method on several samples from different localities.

A single specimen of gabbro was analyzed for its rubidium and strontium content and its Sr^{87}/Sr^{86} ratio. The stratigraphic position of the specimen in the Duluth Complex is not known.

Experimental Results.

The analytical data are shown in Table 7.2 and Figure 7.3. Errors assigned to the corrected Sr^{87}/Sr^{86} ratio and the concentrations of rubidium and strontium are considered to be realistic estimates of the reproducibility.

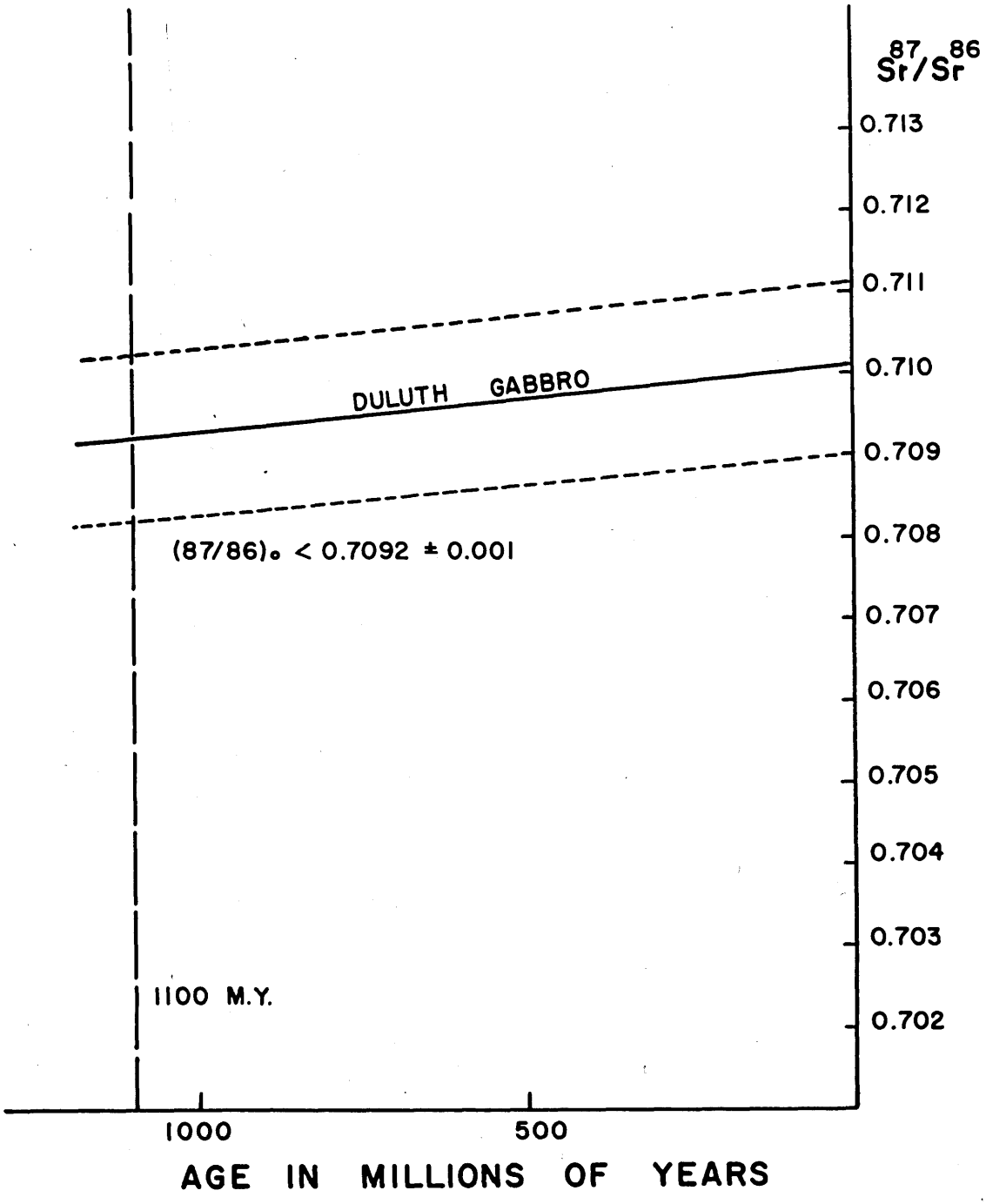


FIGURE 7.3 DULUTH GABBRO

Table 7.2 Duluth Gabbro

Sample Number	Date	87/86	$(87/86)_{corr}$	86/88	84/88	No. of scans	Quality
R1231	1/22/61	.7125	.7101 ± 0.001	.1186	.0067	84	Good

Rb = 6.80 ppm ± 3%, Sr = 349.7 ppm ± 2%, Rb/Sr = 0.0197±0.0007

Discussion.

The K-Ar age of 1100 million years is probably a minimum age for the rock. The initial Sr^{87}/Sr^{86} ratio for the Duluth Gabbro is therefore less than 0.7092 ± 0.001.

Summary and Conclusions.

The analytical results for three basic and ultrabasic igneous rocks from the Bushveld Complex are not inconsistent with an age of 1915 ± 50 million years (Nicolaysen et al. 1958). The best estimate of the Sr^{87}/Sr^{86} ratio at that time is $0.707^{+0.003}_{-0.001}$.

A single gabbro specimen from the Duluth Gabbro was found to have had a Sr^{87}/Sr^{86} ratio of 0.7092 ± 0.001 about 1100 million years ago.

Figure 7.4 is a summary of the results in diagrammatic form. Lack of precision of single determinations

does not allow much confidence in the numerical values of the initial Sr^{87}/Sr^{86} ratios. However the results do not disagree or invalidate the hypothesis that the Sr^{87}/Sr^{86} ratio of the upper mantle has increased throughout geologic time approximately as indicated in Figure 7.4.

The precision errors can be decreased and the results made more meaningful by duplicate or triplicate analyses. Compare analyses of R1292, Chapter 5, Table 5.1.

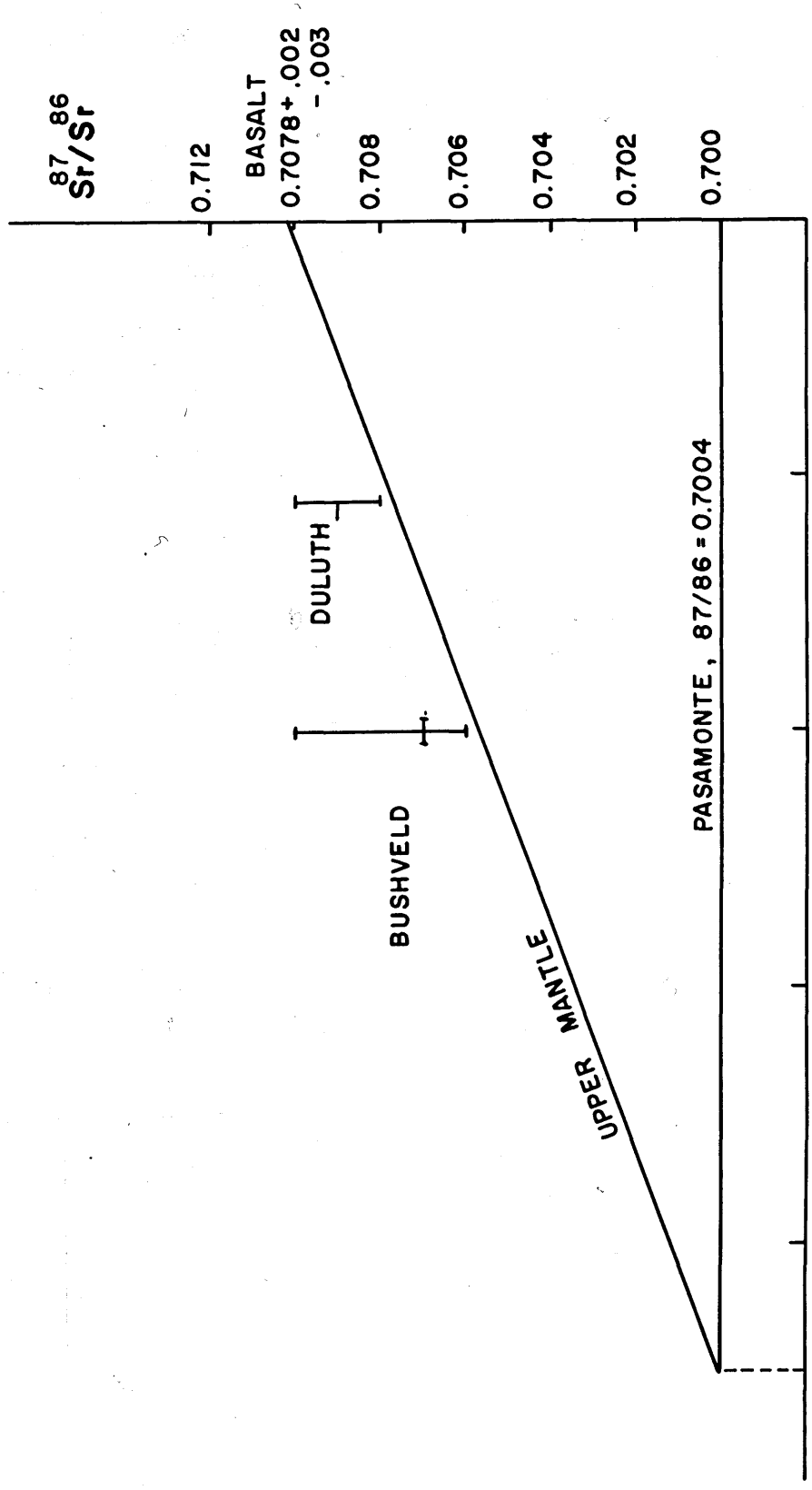


FIGURE 7.4 INITIAL $^{87}Sr/Sr^{86}$ RATIOS IN PRECAMBRIAN BASIC INTRUSIVES

Chapter 8

Part 1

THE AGE OF AN ECLOGITE BY THE Rb-Sr METHOD.

Introduction.

In recent years the hypothesis has been debated in the literature whether the Mohorovicic discontinuity is a phase change from eclogite to basalt or whether it is a chemical and physical boundary between a peridotite mantle and the sialic crust.

The debate was opened by Lovering (1958) who suggested that achondritic meteorites are derived from the mantle of a differentiated parent meteorite body and therefore most closely resemble the mantle of the earth. Pointing to similarities in the chemical compositions of eucritic achondrites, basalts, norites and eclogites he proposed that the upper mantle is composed of eclogite and that the Mohorovicic discontinuity is a phase boundary between eclogite and basalt. From the known depth of the Moho under the continents and ocean basins and from estimates of the pressure and temperature conditions at the Moho he estimated the P - T curve for this trans-

formation. In support of the hypothesis Lovering pointed out that the heat flow measured at the surface of the earth could be accounted for if the upper 200 - 300 kilometers of the mantle are composed of eclogite and the concentrations of U, Th and K decrease with depth. The occurrence of diamonds in eclogite xenoliths found in kimberlite pipes indicates that the source of these eclogites is at a depth of at least 130 - 190 km.

Similar suggestions have been made before by Fermor (1914) and Holmes (1927). Goldschmidt (1922) proposed the existence of an eclogite layer between levels of 120 to 1000 km. Birch (1952) on the basis of studies of incompressibility, density and other parameters of the mantle suggested that the upper mantle could be composed of eclogite to a depth of 300 or 400 km.

Kennedy (1959) discussed the application of this hypothesis to the solution of four important geological problems:

1. Uplift of continental plateaus.
2. Subsidence of geosynclinal sediments into a denser substratum and their subsequent uplift to form mountains.
3. The uniformity of heat flow at the surface of continents and ocean basins.

4. The discrepancy between the rate of erosion and the life-time of continents.

Kennedy concluded that these questions could be explained qualitatively by assuming that the Moho is a phase boundary between eclogite and basalt and that its position is controlled by temperature and pressure conditions.

MacDonald and Ness, (1960) examined the hypothesis in the light of existing experimental evidence. They showed that although the hypothesis could be used to explain many problems connected with orogenies and continental uplift, the experimental evidence is insufficient to either prove or disprove it.

Harris and Rowell, (1960) pointed out that there is no theoretical justification for using the composition of meteorites in quantitative calculations of the composition of the earth. An achondritic mantle in particular would be 60% basaltic which cannot be reconciled with heat flow measurements. Moreover, partial melting of a basaltic mantle would give rise to rhyolitic or phonolitic magma and one should expect these rocks to be more abundant on the continents and in the oceans than they actually are. They favoured a mantle of peridotitic composition citing as evidence the occurrence of ultrabasic nodules

in basalt and the existence of ultrabasic rocks of primary non-differentiated origin. If the upper mantle is composed of eclogite, fragments of eclogite should be found in oceanic basalts. In fact eclogite xenoliths occur only in kimberlite pipes which are restricted to the continents.

According to Powers (1955, p. 93) and Kuno (1959) in Turner and Verhoogen (1960, p. 219) eclogite xenoliths are found in lavas of the Honolulu series of Oahu and the Koloa seris of Kaui, Hawaii.

Application of Abundances of Strontium Isotopes in Basalts To The Eclogite Problem.

Measurements of the Sr^{87}/Sr^{86} ratios of Recent oceanic and continental basalts allow an estimate to be made of the Rb/Sr ratios of their source material. Thus the possibility is here given to compare the Rb/Sr ratios of eclogites to those of the source material of basalts and to determine whether or not eclogites are a suitable source material from which to derive basalt magma. By analyzing the isotopic compositions of strontium and the concentrations of Rb and Sr in several phases of the eclogite it may also be possible to determine the time of its crystallization. An age of 4.5 billions years would be a strong argument in

favour of the existence of an eclogite layer in the mantle. With these considerations in mind a series of measurements was undertaken on an eclogite from a kimberlite pipe at the Robert Victor Mine in South Africa.

Geological Summary.

The diamond-bearing kimberlite pipes intrude the Upper Dwyka shales which are of Mesozoic age. The pipes contain abundant xenoliths of all rocks in the stratigraphic section. The emplacement of the kimberlite magma is believed to have been preceded by a gas explosion following which rock fragments fell back into the cavity in which kimberlite magma carrying diamonds and xenoliths of eclogite welled up. A detailed description of the geology and the occurrence of diamonds in the kimberlite was given by Williams (1932).

Experimental Data.

The experimental results are given in Table 8.1. For a graphical representation and interpretation of these results see Figure 8.1. The samples are described in detail in Chapter 10.

Table 8.1 Experimental Results for the Eclogite.

Number	Date	87/86	$(87/86)_{corr}$	86/88	84/88	No. of scans	Qual.	Rb ppm	Sr ppm	Rb/Sr
Eclogite, whole rock										
R3111	8/25/60	.7088	.7100	.1198	.0066	84	Good	3.42*	131.7*	
"	11/5/60	.7113	.7089	.1186	.0064	78	Good	7.00	148.3	
"	12/13/60	.7083	.7074	.1191	.0067	84	Good	6.82	149.7	
Average		.7095	.7088	.1192	.0066			6.90	149.0	.0463
	$\bar{\sigma}$	±0.0009	±0.0008	±0.0003	±0.00009			±0.09	±0.7	±0.0006
	$\bar{E}$	±0.13%	±0.11%	±0.30%	±1.4%			±1.3%	±0.5%	
Eclogite, pyroxene concentrate										
P3111	9/21/60	.7133	.7112	.1187	.0062	84	Good	12.7	272.7	
"	11/10/60	.7129	.7105	.1186	.0064	90	Good	13.2	257.9	
"	2/15/61	.7095	.7071	.1186	.0066	90	Good	13.0	254.6	
Average		.7119	.7096	.1186	.0064			13.0	261.7	.0497
	$\bar{\sigma}$	±0.0012	±0.0013	±0.00004	±0.0001			±0.147	±5.6	±0.0012
	$\bar{E}$	±0.17%	±0.18%	±0.03%	±1.8%			±1.13%	±2.1%	
Eclogite, garnet concentrate										
G3111	9/5/60	.7176	.7149	.1185	.0064	44	Fair	0.92	17.50	
"	9/22/60	.7145	.7145	.1194	.0070	84	Fair	1.41	21.8	
								1.03	17.7	
Average		.7161	.7147	.1190	.0067			1.12	19.0	.0589
	$\bar{\sigma}$	±0.0016	±0.0002	±0.0005	±0.0003			±0.15	±1.40	±0.0088
	$\bar{E}$	±0.22%	±0.03%	±0.042%	±4.5%			±13.2%	±7.4%	

*omitted from the average, Rb could be 6.94 ppm due to uncertainty how sample was spiked.

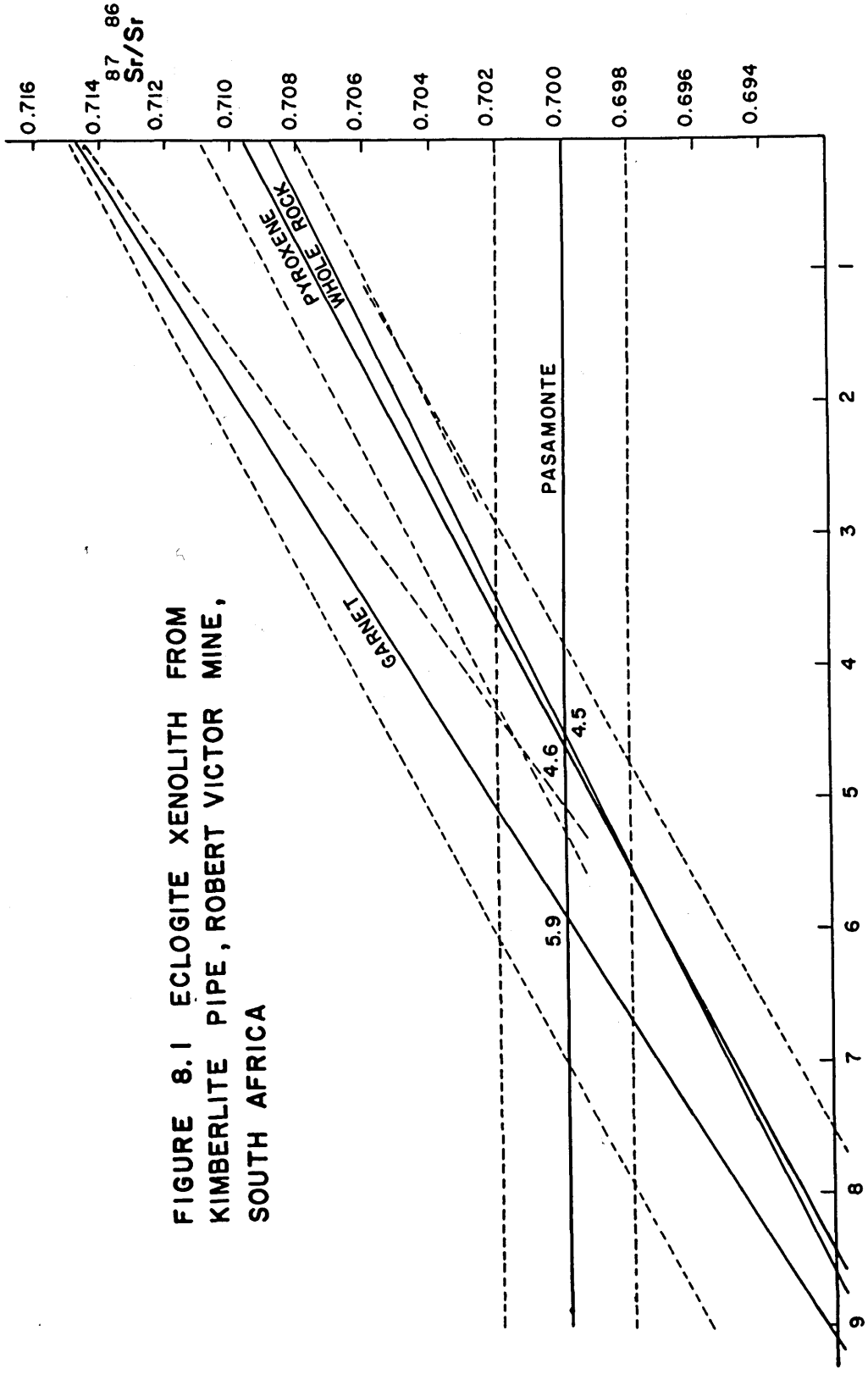


FIGURE 8.1 ECLOGITE XENOLITH FROM KIMBERLITE PIPE, ROBERT VICTOR MINE, SOUTH AFRICA

Discussion of the Results.

The average corrected Sr^{87}/Sr^{86} of the eclogite was found to be 0.7088 ± 0.00075. Gast, (1960) reported a value of 0.711 ± 0.003 for an eclogite from the same locality. The Rb/Sr ratio of this rock is 0.0463 ± 0.0006 while the concentrations of Rb and Sr are 6.9 and 149.0 ppm, respectively. As far as the author is aware this is the first and only determination of the rubidium and strontium concentrations in eclogite from the kimberlite pipes.

The Sr^{87}/Sr^{86} ratios of continental and oceanic basalts range from 0.705 to 0.710 (Chapter 6). If this variation is real, the calculated Rb/Sr ratios of the sub-crustal magmatic source material range from 0.022 to 0.051. These calculated values are based on the assumption that the initial Sr^{87}/Sr^{86} ratio is 0.7004 ± 0.002 and that the age of the earth is 4.5 billion years (Chapter 1). Gast (1960) gave values of 0.014 to 0.060 for this ratio. The Rb/Sr ratio of the eclogite is within the range of values indicated for the upper mantle. This is compatible with the hypothesis that at least some basalts could have been derived from an eclogite layer in the upper mantle. This evidence, however, does not prove that the upper mantle is actually composed of eclogite since peridotites or other

ultrabasic rocks may have similar Rb/Sr ratios.

Assuming that measurements could be made sufficiently accurately and that the distribution of radiogenic Sr^{87} was not changed during the intrusion of the kimberlite magma, the time of crystallization of the eclogite can be determined from the point of intersection of the strontium development lines of the whole rock, the pyroxene, and the garnet (Figure 8.1). Unfortunately, the results are rather indifferent. The following observations can be made:

1. The general pattern of the abundance of Sr^{87} is compatible with the present Rb/Sr ratios of the different phases.

2. The error envelopes for the development lines of strontium in the pyroxene and the whole rock overlap. The two are therefore indistinguishable within experimental error.

3. Although the pyroxene is enriched in Rb (13 ppm) the garnet has the highest Rb/Sr ratio and consequently has the highest Sr^{87}/Sr^{86} ratio.

4. The strontium development line of the garnet intersects those of the pyroxene and the whole rock at 12.6 and 11.05 b.y., respectively.

5. If the initial Sr^{87}/Sr^{86} ratio is assumed to be 0.700 ± 0.002, the following intersections are obtained:

   Pyroxene and whole rock: 4.6 ± 1.8 b.y.

   Garnet: $5.9 \begin{smallmatrix} +2.0 \\ -1.5 \end{smallmatrix}$ b.y.

Conclusions.

The Rb/Sr ratio of the eclogite is 0.0463 ± 0.0006 which is within the range of values of this ratio for the source of basaltic magmas. The possibility that some basalts are derived from an eclogite layer in the upper mantle is therefore not excluded.

The pattern of the radiogenic Sr^{87} developed in the whole rock and the garnet and pyroxene phases does not lead to an unambiguous determination of the time of crystallization. The evidence does seem to indicate a very old age for the eclogite. The difficulty of determining low concentrations of rubidium and strontium causes relatively large experimental errors. Moreover the possibility exists that a re-distribution of radiogenic Sr^{87} between the phases of the eclogite took place during the intrusion of the kimberlite magma, thus destroying the strontium development pattern.

Part 2.

THE AGE OF THE ELY GREENSTONE AND THE SOUDAN FORMATION IN MINNESOTA.

Introduction.

The Ely greenstone and the Soudan iron formation belong to the oldest volcanic and sedimentary rocks of Precambrian age in Minnesota. These rocks have been dated indirectly as being older than the Saganaga granite which intrudes them (Schwartz, 1956, p.1).

An attempt was made to determine the age of the volcanics directly by the Rb-Sr method. For this purpose one specimen of Ely greenstone and Soudan shale have been analyzed. In addition the Sr^{87}/Sr^{86} ratio of calcite segregations occurring between pillows in the Ely greenstone was determined.

This work is not considered to be completed and the present summary is in the nature of a progress report.

Geological Summary.

The Ely greenstone consists of an assemblage of lava flows, tuff and minor basic intrusives. The rocks are frequently altered to chlorite schist and

and have been recrystallized near intrusive igneous contacts. The greenstone outcrops in disconnected belts extending from the Gunflint district, Ontario, westward through Vermilion Lake. According to Goldich et al. (1961) the Ely greenstone belongs to the Keewatin group and has been correlated with the type Keewatin volcanics first described by Lawson in 1888 near the Lake of the Woods.

The Soudan formation is composed of alternating bands of chert and iron oxides. Ferruginous carbonates, chlorite and sulfides also occur in small amounts. Schwartz (1956) considered the Soudan formation to be an upper member of the Ely greenstone. Goldich et al. (1961) prefer to give it formational rank.

The Keewatin volcanics were intruded by the Laurentian granites one of which is the Saganaga batholith on the Ontario - Minnesota border. The age of the Saganaga granite according to K-Ar and Rb-Sr ages determined by Goldich et al. (1961) on mica and feldspar from pegmatites is between 2.5 and 2.6 billion years. However, its age may actually be greater than this because the Laurentian granites are believed to predate the Algoman orogeny which took place approximately

2.5 billion years ago. Accordingly, the age of the Keewatin volcanics including the Ely greenstone should also be greater than 2.5 billion years.

Experimental Results.

Table 8.2 summarizes the analytical data which are reproduced in graphical form in Figure 8.2. The errors assigned to the corrected Sr^{87}/Sr^{86} ratios and the rubidium and strontium analyses are estimates of the reproducibility. Information regarding the localities from which the samples were collected are given in Chapter 10.

Discussion.

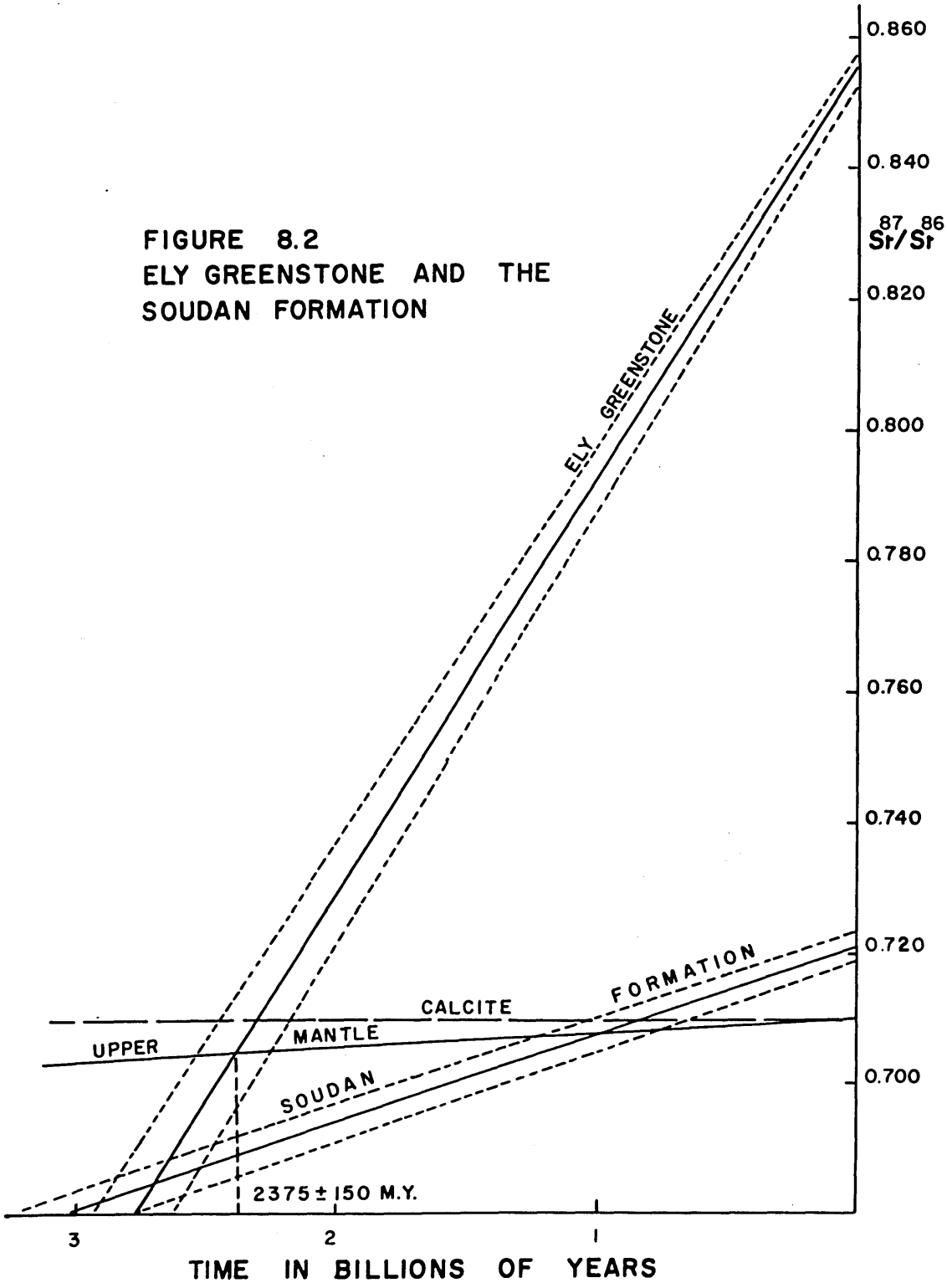
The Ely greenstone specimen has a Sr^{87}/Sr^{86} ratio of 0.8555 and a Rb/Sr ratio of 1.45. This is surprisingly high for a basic volcanic rock. Its strontium development line intersects that of the upper mantle at 2375 $\pm$ 150 million years and $Sr^{87}/Sr^{86} = 0.705$.

The calcite occurs in form of narrow bands between pillows in an outcrop of the Ely Greenstone at the City limits of Ely on Highway 21 enroute to Babbitt. It is not clear whether these segregations formed by precipitation from sea water at the time of eruption of the lava

Table 8.2 The Ely Greenstone and the Soudan Formation.

Sample Number	Date	87/86	$(87/86)_{corr}$	86/88	84/88	No. of scans	Qual.	Rb ppm	Sr ppm	Rb/Sr
Ely Greenstone										
R3357A	1/16/61	.8573	.8555 ±0.001	.1189	.0065	90	Good	36.5 ±3%	25.2 ±3%	1.45 ±0.062
Soudan Formation										
R3354	1/24/61	.7224	.7212 ±0.001	.1190	-	84	Good	105.0 ±2%	332.0 ±2%	0.316 ±0.009
Calcite, leached from Ely Greenstone										
R3358B	1/17/61	.7132	.7099	.1183	-	48	Fair	-	-	

FIGURE 8.2
ELY GREENSTONE AND THE
SOUDAN FORMATION



or whether they are the product of later metamorphic alterations or hydrothermal activity. In any case the Sr^{87}/Sr^{86} ratio of the calcite should be greater than that of the lava at the time of its formation. Assuming that the Rb/Sr ratio in the calcite is negligibly small, an intersection is obtained with the Ely greenstone at t = 2300 ± 125 million years.

The possibility cannot be excluded that rubidium was introduced into the Ely greenstone by metasomatism and hydrothermal solutions originating from the Laurentian Intrusives. In this case the age obtained here dates the time of metasomatism and makes this rock unsuitable for age determination purposes.

The strontium development line for the specimen of the Soudan formation is plotted on the same diagram (Figure 8.2). An intersection with the Ely greenstone will have meaningful co-ordinates only if their Sr^{87}/Sr^{86} ratios were identical at the time of deposition. This is not necessarily true. The Soudan formation gives an age of 2700 ± 250 with the Ely greenstone, the value of the Sr^{87}/Sr^{86} ratio at the point of intersection is 0.685. This almost certainly invalidates the age. On

the other hand an intersection with the development line for the upper mantle gives an age of approximately 1000 million years. This low age is contrary to geological evidence. These discrepancies suggest that the analytical data for the Soudan formation are in error.

Conclusions.

The analytical data are consistent with the conclusion that the age of the Ely greenstone is 2375 ± 150. This value, however, is suspect because of the possibility of metasomatic addition of rubidium to the Ely greenstone at the time of intrusion of the Laurentian granites. This would lower the age value and would make the rock unsuitable for age determination purposes. According to Goldich et al. (1961) the age of the Ely greenstone is definitely greater than 2.5 million years.

The age of the Soudan formation, as indicated by the data, is inconsistent both with geological evidence and the abundances of strontium isotopes as they are known at this date. If the Ely greenstone was enriched in rubidium after its formation, the Soudan formation apparently was not. For this reason it may be more suitable for age determination purposes.

Part 3

EVIDENCE OF SUB-CRUSTAL ORIGIN OF ROCKS FROM THE MONTEREGIAN HILLS.

Introduction.

Isotopic compositions of strontium in four igneous rocks from the Monteregian hills and in one specimen of calcite from a carbonatite at Oka, Quebec, were determined. The purpose of this investigation was to demonstrate a co-magmatic origin for the different igneous rocks and the carbonatite occurrence at Oka and to test the hypothesis that the parent magma was derived from the upper mantle.

Geological Summary.

The Monteregian hills are a series of eight prominent topographic features extending from Montreal eastward across the St. Lawrence lowlands for a distance of about 50 miles. The centers of these hills are composed of alkali-rich igneous rocks which collectively constitute a distinct petrographic province. All but one of the intrusives consist of two or more rock types ranging in composition from ultrabasic and basic essexite and yamaskite to intermediate nepheline syenites and

nordmarkite. A comprehensive bibliography and a summary of the geological information pertaining to the Monteregian hills were given by Dresser and Denis (1944, p.455-482).

Geological evidence suggest that the magma bodies which formed the individual intrusives were derived from a common parent whose composition was that of an alkali diorite or gabbro. The magma reservoir which is believed to have been inside the Precambrian basement was tapped in several places and portions of it were drawn off through pipes located along a fracture system which may be related to the Appalachian orogeny.

Structural and Stratigraphic evidence indicates a post-Upper Devonian age. Osborne proposed a Tertiary age on the basis of similarities of pleochsoic halos surrounding crystals of zircon and titanite and those developed in Tertiary intrusives (Dresser and Denis, 1944). Urry (1936, p.1221) reported a Helium age of 57$\pm$ 1.5 million years for a tinguaite sheet two miles east of Mount Royal. The Geological Survey of Canada (Lowdon, 1960, p.38) obtained an age of 122$\pm$9 m.y. by the K-Ar method using biotite extracted from a nordmarkite from Brome Mountain. This age has been confirmed by the Geochronology Laboratory at M.I.T.

(Eighth Ann. Prog. Rep. 1960). The age of the igneous rocks of the Monteregian hills is therefore Cretaceous.

Experimental Results.

The experimental data are summarized in Table 8.3 and are shown in graphical form in Figure 8.3. The errors assigned to the values of the rubidium and strontium concentrations as well as the corrected Sr^{87}/Sr^{86} ratios are reasonable estimates of the reproducibility. A description of the samples appears in Chapter 10.

Discussion.

The average value of the corrected Sr^{87}/Sr^{86} ratio of the essexite, the yamaskite and the tinguate is 0.7049. This value is considerably lower than that for the nordmarkite which is 0.7156. However, when the strontium development lines with their error envelopes are plotted for the nordmarkite and the yamaskite, an intersection is obtained at $t = 115 \pm 25$ million years and $(Sr^{87}/Sr^{86})_o = 0.7047 \pm 0.001$. This time is identical within experimental error to the age of the biotite from Brome Mountain which was determined by the K-Ar

Table 8.3 Experimental Results for Monteregian Hills.

Sample Number, Locality and Rock Type.	Date	87/86	$(87/86)_{corr}$	86/88	84/88	No. of scans	Qual.	Rb ppm	Sr ppm	Rb/Sr
Mt. Johnson, Quebec										
R4180 Essexite	10/28/60	.7050	.7053 ±.001	.1195	.0064	84	Good			
Mt. Yamaska, Quebec										
R4179 Yamaskite	11/4/60	.7040	.7049 ±.001	.1197	.0066	84	Good	59.6 ±2%	1635 ±1%	.0365 ±.0008
Mt. Royal, Quebec										
R3069 Tinguaite (?)	12/17/60	.7048	.7045 ±.001	.1193	.0067	90	Good			
Oka, Quebec										
C3255 Calcite	12/18/60	.7046	.7067	.1201	.0067	84	Good			
"	1/6/61	.7067	.7057	.1191	.0069	90	Good			
Average calcite		.7057 ±.0011	.7062 ±.0005	.1196 ±.0005	.0068 ±.0001					
Shefford, Quebec										
R4181 Nordmarkite	11/1/60	.7177	.7156 ±.001	.1187	.0066	84	Good	140.0 ±2%	62.4 ±2%	2.24 ±.06

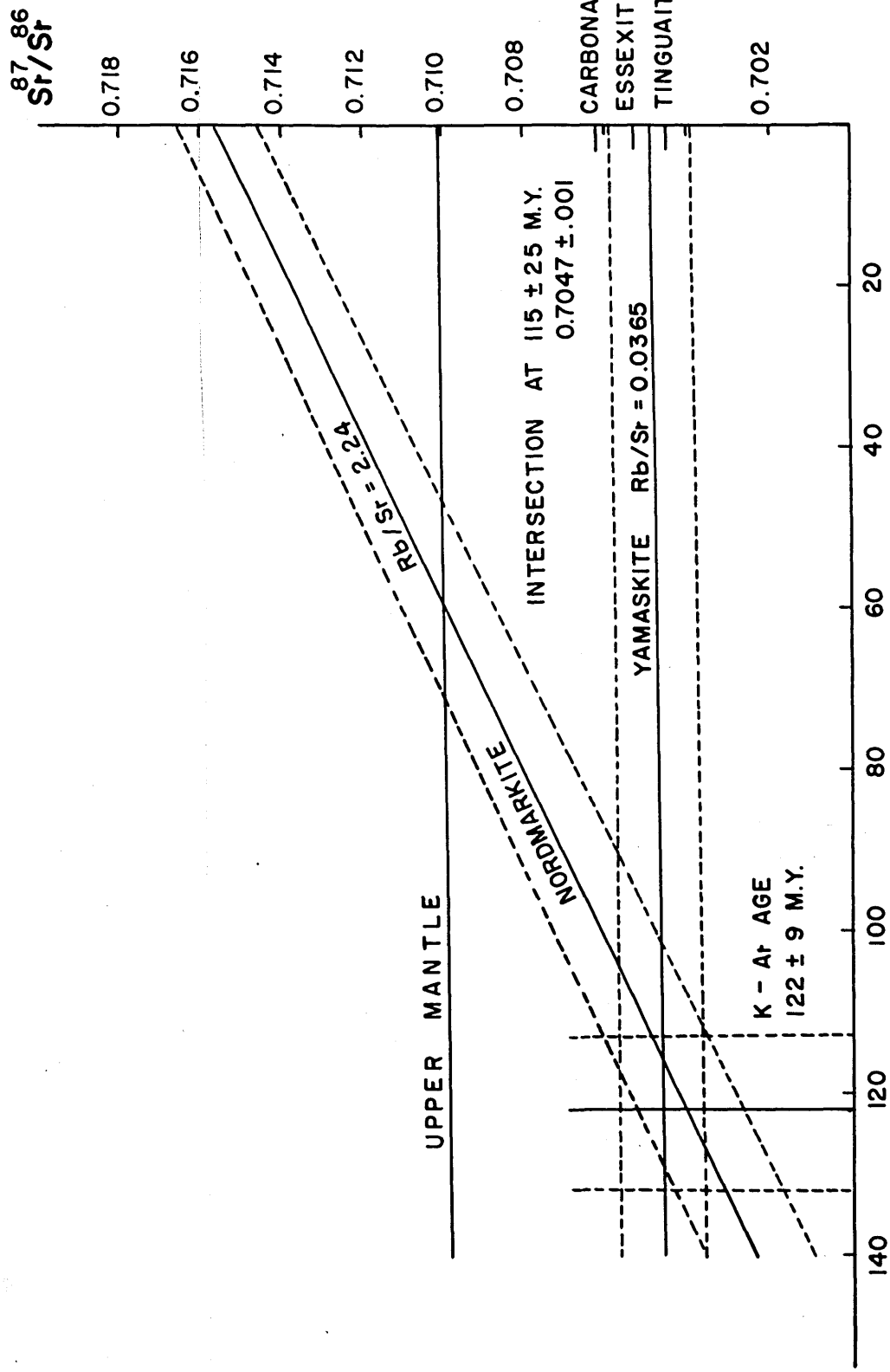


FIGURE 8.3 MONTEREGIAN HILLS

TIME IN MILLIONS OF YEARS

method. The time at which the strontium development lines intersect is therefore also the time at which the different rock types were separated from the parent magma and from each other and began to accumulate radiogenic strontium in accordance with their different Rb/Sr ratios. There is thus strong evidence that the nordmarkite is a magmatic differentiate of the same parent magma which gave rise to the yamaskite and the other rock types. The only way in which the nordmarkite could develop a Sr^{87}/Sr^{86} ratio of 0.7156 in 115 million years is to have had an initial ratio of 0.7047. Had the nordmarkite magma been contaminated at the time of its intrusion with old crustal material, having a Sr^{87}/Sr^{86} ratio much greater than 0.7047, it could not give an intersection with the yamaskite at a time which is known to be the age of these rocks from other evidence.

The Sr^{87}/Sr^{86} ratio of the parent magma was $= 0.7047 \pm 0.001$. This is surprisingly low when compared to the average Sr^{87}/Sr^{86} ratio of eleven Recent oceanic basalts which is 0.7072 (Chapter 6). This low abundance of Sr^{87} indicates that the source material

from which the magma was formed by partial or complete melting had a very low Rb/Sr ratio, even lower than the source material for average oceanic basalts. The Rb/Sr ratio of the source material can be estimated by assuming an age of the earth of 4.5 billion years and an initial Sr^{87}/Sr^{86} ratio of 0.7004 ± 0.002 (Chapter 1). The Rb/Sr ratio calculated in this way is 0.022 ± 0.011. This value is so low that only an ultrabasic rock could qualify as a source for the primary Monteregian hill magma. If the content of alkali elements decreases downward in the upper mantle, this would suggest that the source region for the magma was at considerable depth in the upper mantle.

The isotopic composition of strontium in calcite concentrated from Nb ore from the carbonatite at Oka, Quebec, was determined for comparison with the strontium in the igneous rocks of the Monteregian hills. The relationship of the carbonatite occurrences at Oka to the intrusives of the Monteregian hills is not clear and the general question of the origin of carbonatites is still unanswered. The average of two independent determinations gave $Sr^{87}/Sr^{86} = 0.7062 \pm 0.0005$. As can be seen in Figure 8.3 the errors between

the carbonatite value and those of the essexite, tinguaite and yamaskite overlap. The Sr^{87}/Sr^{86} ratio of the carbonatite is not measurably different from that in the basic igneous rocks. The results are therefore not inconsistent with the conclusion that the calcite of the carbonatite at Oka is of magmatic origin.

This conclusion is strengthened by comparison with a Sr^{87}/Sr^{86} ratio of 0.709 ± 0.002 reported by Gast (1960) for Grenville limestone. An impure Grenville limestone containing a small amount of mica would give a much higher ratio. Gast also reported a value of 0.713 ± 0.003 for an Ordovician limestone from Perry County, Texas.

Conclusions.

The whole-rock Rb-Sr age for a nordmarkite from Shefford and a yamaskite from Mt. Yamaska was found to be 115 ± 25 million years. This age is identical to one determined by the K-Ar method using biotote from Brome Mountain.

The Sr^{87}/Sr^{86} ratio of the parent magma 115 ± 25 million years ago was 0.7047 ± 0.001 indicating that the

source was sub-crustal. The evidence presented confirms the conclusions reached previously on the basis of geologic evidence that the different rock types are products of magmatic differentiation of a common parent magma.

The unusually low Sr^{87}/Sr^{86} ratio of this primary magma indicates that the source region had a lower Rb/Sr ratio than that found for continental basalts, suggesting an unusual depth of origin.

The isotopic composition of strontium in calcite from the carbonatite at Oka is compatible with the conclusion that the calcite is of magmatic, sub-crustal origin and may be related to the igneous intrusives of the area.

Chapter 9.

VARIATIONS OF THE Sr^{86}/Sr^{88} AND Sr^{84}/Sr^{88} RATIOS.

Introduction.

During the course of this investigation a total of 96 strontium isotope ratio determinations have been performed in cooperation with C.C. Schnetzler. The total is composed of 63 analyses of terrestrial rocks most of which are basic igneous rocks of sub-crustal origin, 25 tektite analyses and 8 analyses of a $SrCO_3$ standard. The opportunity is therefore given to compare the abundances of the non-radiogenic isotopes of strontium in the three types of material and to calculate average Sr^{86}/Sr^{88} and Sr^{84}/Sr^{88} ratios.

Experimental Results.

Most of the Sr^{86}/Sr^{88} ratios were calculated from about 80 consecutive scans. The reproducibility expressed as the standard deviation of a single analysis is ± 0.0006 or $\pm 0.5\%$ (Table 9.1). Duplicate runs on the same sample showed that the Sr^{86}/Sr^{88} ratio can vary by

as much as 0.0021 (1.8%) between successive analyses of the same sample (Schnetzler, T3990). This variation is due to isotopic fractionation in the mass spectrometer.

The Sr^{84}/Sr^{88} ratios are generally based on no more than 12 to 18 scans. The precision error is of the order of $\pm$ 0.0002 or 3.0% (Table 9.1) expressed as the standard deviation for a single analysis. This ratio was found to vary by as much as 0.0007 (1%) between successive analyses of the same sample (Faure R1292, Schnetzler T3986).

Average values of the Sr^{86}/Sr^{88} and the Sr^{84}/Sr^{88} ratios were calculated for each of the three types of material as well as for all analyses combined (Table 9.1).

Table 9.1 Average Sr^{86}/Sr^{88} and Sr^{84}/Sr^{88} Ratios.

Material		Sr^{86}/Sr^{88}	Sr^{84}/Sr^{88}	No.of Analyses
$SrCO_3$		0.1195	0.0066(7)	8
	$\bar{\sigma}$	$\pm$ 0.00018	$\pm$0.0001	
	σ	$\pm$ 0.0005	$\pm$0.00027	
Tektites		0.1192	0.0068(18)	25
	$\bar{\sigma}$	$\pm$ 0.00015	$\pm$0.00006	
	σ	$\pm$ 0.00077	$\pm$0.00023	
Terrestrial Rocks		0.1190	0.0066(55)	63
	$\bar{\sigma}$	$\pm$ 0.00007	$\pm$0.00003	
	σ	$\pm$ 0.00055	$\pm$0.0002	
Combined Average		0.1191	0.0066(80)	96
	$\bar{\sigma}$	$\pm$0.00006	$\pm$0.00003	
	σ	$\pm$0.0006	$\pm$0.0002	

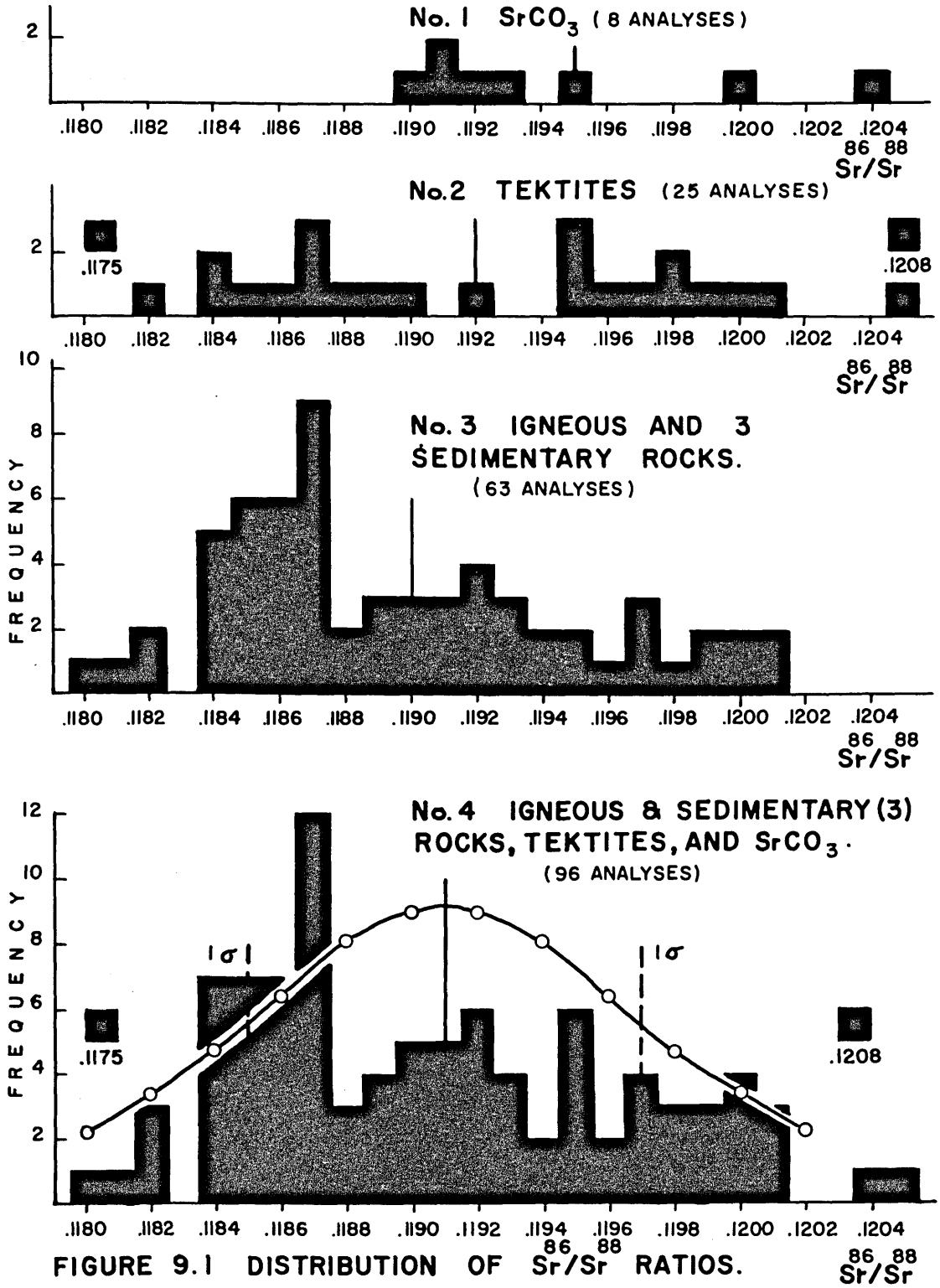


FIGURE 9.1 DISTRIBUTION OF $^{86}Sr/^{88}Sr$ RATIOS.

Discussion of Results.

In order to study the distribution of values of the Sr^{86}/Sr^{88} ratio in the three types of material, a series of histograms was constructed (Figure 9.1). The number of analyses of the $SrCO_3$ and the tektites is not sufficient to show a distinct distribution pattern. The analyses of the igneous rocks, however, do show a tendency toward a normal distribution. The high frequency of values in the range from .1184 to .1187 is striking but is not considered to be significant. An examination of the data shows that no one rock type favours this particular range. It is therefore suggested that this is an instrumental effect and is due to the fact that a large number of analyses was made during a period of time when fractionation processes in the mass spectrometer favoured this range of values. The fluctuations in the measurement of the Sr^{86}/Sr^{88} ratios are well displayed by sample R1292 (Chapter 5, Table 5.1) and the $SrCO_3$ standard (Chapter 5, Table 5.2).

All 96 analyses are combined in histogram number 4, Figure 9.1. A normal distribution curve having the same mean and standard deviation was fitted to the

histogram. The goodness of fit was tested by replotting the data on normal probability paper (Figure 9.2) and by performing a chi square test.

The plot on the probability graph shows some evidence of the presence of two superimposed normal distributions. However, as mentioned before, this is ascribed to instrumental isotope fractionation effects. More data taken over a period of time would be needed to confirm the existence of two normal populations. A single straight line can be fitted to the points indicating that the overall distribution is approximately a normal one.

A chi square test was performed to determine the goodness of fit of the data to a normal distribution (Dixon and Massey, 1957, p.221). The statistic used is defined as

$$\chi^2 = \sum_{i=1}^{k} \frac{(f_i - F_i)^2}{F_i}$$

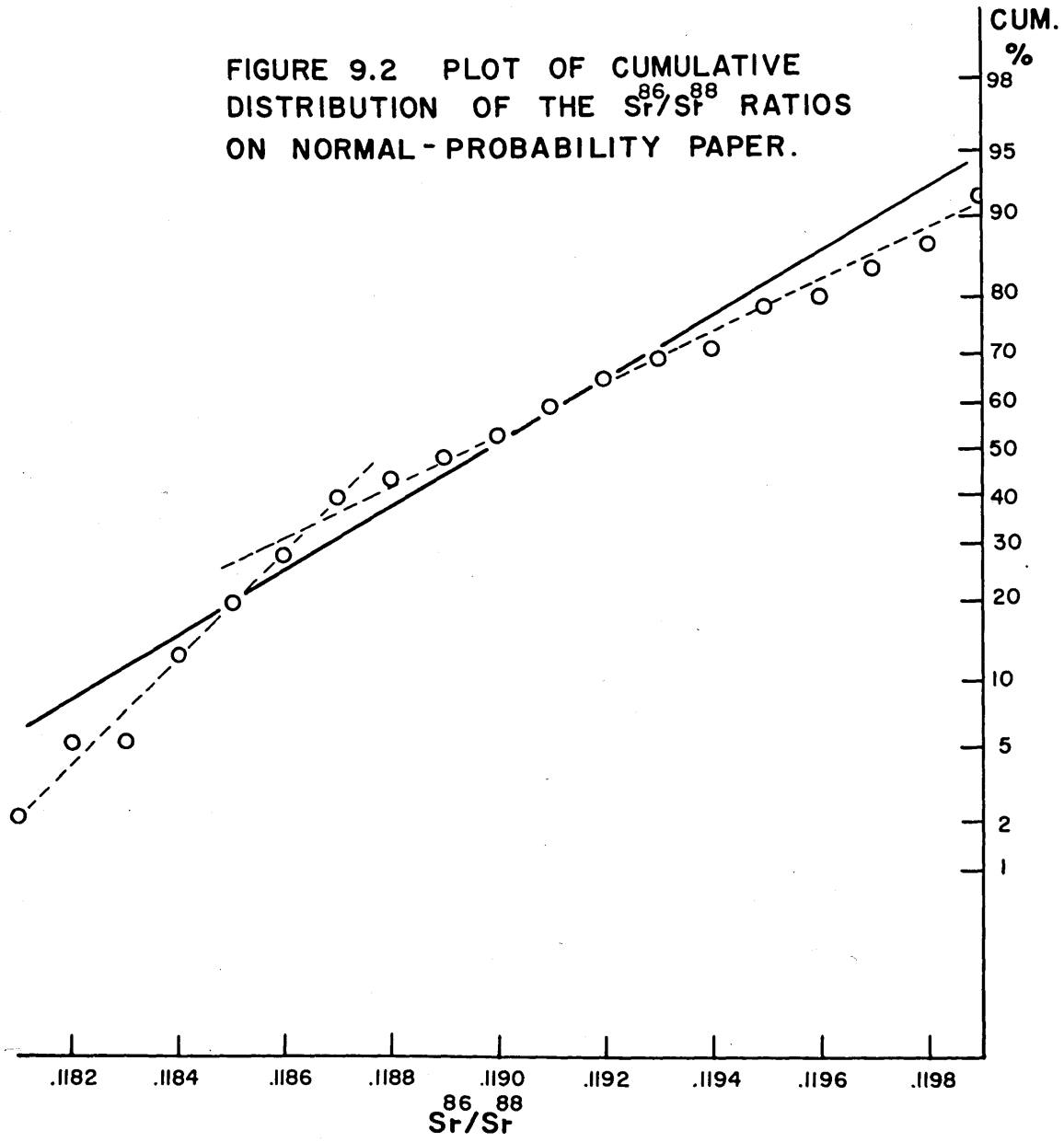
where k = number of categories

f_i = observed frequency for each category

F_i = theoretical frequency for each category assuming normal distribution.

Values of F_i are obtained by calculating the areas under the normal distribution curve between the limits for each

FIGURE 9.2 PLOT OF CUMULATIVE DISTRIBUTION OF THE Sr^{86}/Sr^{88} RATIOS ON NORMAL-PROBABILITY PAPER.



category. The distributions of χ^2 are tabulated for different degrees of freedom. The number of degrees of freedom is determined by

$$df = (k-1) - \text{number of assumptions.}$$

Since the mean and the standard deviation for a given set of data must be known before F_i can be calculated,

$$df = k-3.$$

It is customary to accept the hypothesis that a given distribution is normal when the calculated value of χ^2 is less than its predicted value at the 95% confidence limit.

The value of χ^2 for the distribution of the Sr^{86}/Sr^{88} ratios is 15.50 (Table 9.2). Since this is less than 18.31 for 10 degrees of freedom, the hypothesis that the distribution is normal is accepted at the 95% confidence limit (Dixon and Massey, 1957, Table A-62, p.385).

The average value of the Sr^{86}/Sr^{88} ratio for the entire assemblage of 96 analyses is 0.1191, $\bar{\sigma} = \pm$ 0.0001, $\sigma = \pm$ 0.0006. The spread of the distribution is such that all previously reported averages (Chapter 3, Table 3.1) as well as the averages for the three types of material reported here fall into the band 0.1191 ± 0.0006 (σ) at the 68% confidence limit. The difference between the previously accepted value for the Sr^{86}/Sr^{88} of 0.1194 and the

Table 9.2 Chi Square Test

Interval	F_i	f_i	$(F_i-f_i)^2$	$\frac{(F_i-f_i)^2}{F_i}$
.1180	3.2	1	4.84	1.51
.1180 - .1182	3.2	5	3.24	1.01
.1182 - .1184	5.2	7	3.24	0.62
.1184 - .1186	7.8	14	38.44	4.93
.1186 - .1188	10.2	15	23.04	2.26
.1188 - .1190	12.0	9	9.0	0.75
.1190 - .1192	12.7	11	2.89	0.23
.1192 - .1194	12.0	6	36.00	3.00
.1194 - .1196	10.2	8	4.84	0.47
.1196 - .1198	7.8	7	0.64	0.08
.1198 - .1200	5.2	7	3.24	0.62
.1200 - .1202	3.2	3	0.04	0.01
.1202	3.2	3	0.04	0.01
Totals	95.9	96		15.50

overall average obtained here is statistically not significant. This conclusion is confirmed by comparing the mean reported by Aldrich et al. (1953) to the average reported here.

Aldrich et al (1953): $Sr^{86}/Sr^{88} = 0.1195 \pm 0.0003 (\bar{\sigma})$
This work $Sr^{86}/Sr^{88} = 0.1191 \pm 0.0001 (\bar{\sigma})$
$D = 0.0004, \bar{\sigma}_D = \pm 0.00032$. Since $D < 2\bar{\sigma}_D$, the two means are identical at the 95% confidence limit.

Because the difference between 0.1194 and 0.1191 is not statistically significant, there is no reason to reject or modify the former value.

The distribution of values of the Sr^{86}/Sr^{88} ratio is shown in Figure 9.3. The means is 0.0066 with a standard deviation of 0.0002 (σ). A normal curve was fitted to the histogram (Figure 9.3) and a satisfactory fit was obtained. The data were also plotted on probability paper (Figure 9.4). The experimental points approximate a straight line quite well thus confirming that the distribution is normal.

Conclusions.

The distribution of the measurements of the Sr^{86}/Sr^{88} is normal about the mean at the 95% confidence limit. The average for the total of 96 analyses is 0.1191, $\bar{\sigma} = \pm$ 0.0001, $\sigma = \pm$ 0.0006. Because of the large spread of the data, indicated by a standard deviation of $\pm$ 0.0006 (σ), this value is not significantly different from the previously accepted value of 0.1194 (Nier, 1938) or 0.1195 (Aldrich et al., 1953).

The measurements of the Sr^{84}/Sr^{88} ratios are likewise normally distributed about the mean of 0.0066, $\bar{\sigma} = \pm$ 0.00003,

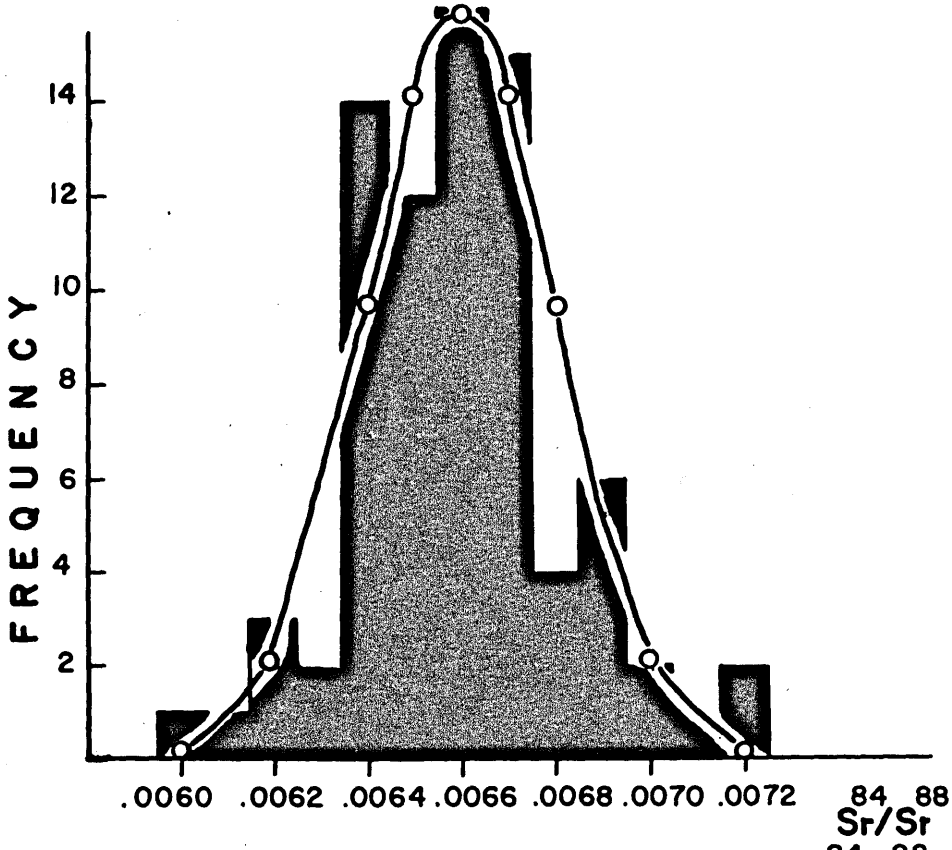


FIGURE 9.3 DISTRIBUTION OF $^{84}Sr/^{88}Sr$ RATIOS IN ROCKS TEKTITES AND $SrCO_3$
(80 ANALYSES)

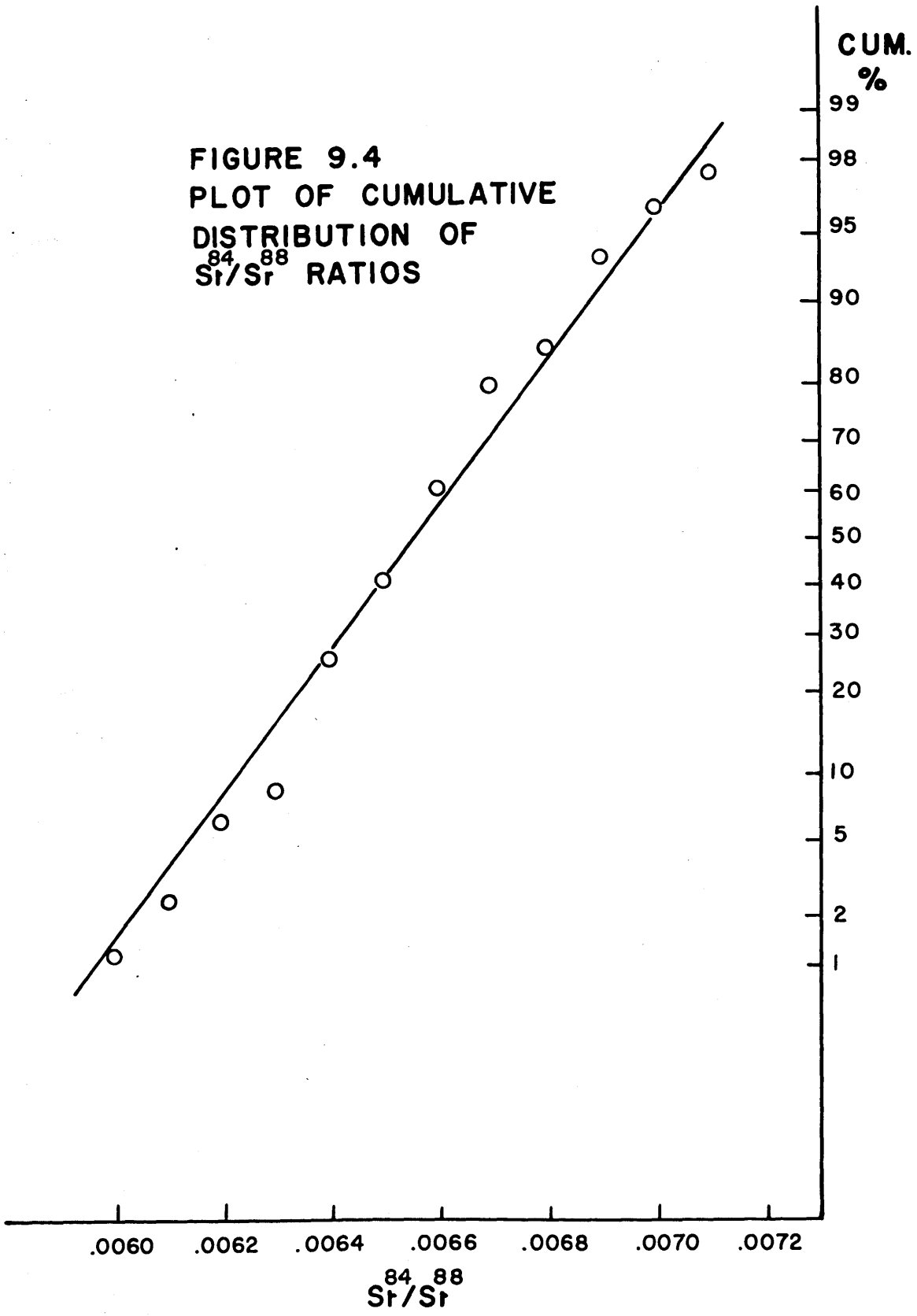


FIGURE 9.4
PLOT OF CUMULATIVE DISTRIBUTION OF Sr^{84}/Sr^{88} RATIOS

$\sigma = \pm$ 0.0002, which is identical to the values previously reported by Nier (1938) and Aldrich et al. (1953).

Even though the distribution of the measurements is approximately normal, the wide spread of the data requires a large number of individual measurements before a statistically reliable mean is obtained.

Chapter 10.

DESCRIPTION OF SAMPLES.

Oceanic Basalts

R1292 Olivine basalt
Aphanitic to glassy, highly vesicular, almost a pumice. Scattered phenocrysts of olivine. Erupted in 1894, Kilauea, Hawaii. Collected by N.E.A. Hinds near Postal Cavern.

R1282 Basalt glass
Glassy, highly vesicular with bubbly surface indicating top of flow. Probably erupted in 1921, Kilauea, Hawaii.

R2001 Olivine basalt
Glassy, highly vesicular, containing scattered phenocrysts of olivine. Recent flow on floor of Kilauea sink (Birch #20).

R1993 Basalt
Aphanitic, vesicular, no olivine phenocrysts observed. Mauna Kea, Hawaii (Birch #H63).

R2002 Basalt
Fine grained, composed of plagioclase and pyroxene. No olivine observed. Maui Island, Hawaii (Birch #H58).

R2029 Olivine basalt
Aphanitic, vesicular with scattered phenocrysts of olivine, Tutuila, Samoa. (Birch #2594).

R1995 Olivine gabbro
Medium grained, containing euhedral phenocrysts of olivine. Volcanic neck on Ofu Island, Samoa (Birch #2661).

R2030 Basalt
Aphanitic, vesicular without observable olivine phenocrysts. Ofu Island, Samoa (Birch #2651).

R2031 Basalt
Aphanitic, vesicular with phenocrysts of plagioclase. Ascension Island (Birch #2751).

R4125 Basalt
Aphanitic and slightly vesicular. Mid-Atlantic Ridge Lat. 31°18.' 8N, Long. 40° 54.' 3W. Collected in "rift" from sloping bottom at depth of about 1250 meters. Echo sounding traces available from Capt. Cousteau. Gift of Lloyd Breslau, 1960.

R4156 Olivine basalt
Horta Fayal, Azores. M.I.T. Petrology Collection #6412.

R4158 Obsidian
San Miguel, Azores. M.I.T. Petrology Collection #6410

Continental Volcanic Rocks

R4161 Hypersthene, augite andesite (bomb)
Fine grained, composed of plagioclase and pyroxene. Erupted in 1909 at Sakurajima, Kyosho, Japan. M.I.T. Petrology Collection #2081. Collected by Sidney Powers, 1915.

R4221 Andesite vitrophyre
Contains hypersthene and augite. Erupted in 1914 at Sakurajima, Kyosho, Japan. M.I.T. Petrology Collection #2082. Collected by Sidney Powers, 1915.

R4244 Dacite
Light grey, fine grained, composed of plagioclase, pyroxene and quartz. Erupted in 1888 at Bandai San, Japan. M.I.T. Petrology Collection #2079. Collected by Sidney Powers, 1915.

R1864 Basalt
Samples from bore holes for Kogna River Project, Bombay State. Map sheet No.47, G/11 and 15, between Pophali (17°26'N, 73°46'E). B.H.T4B, El.200'(M.S.L.)60/922.

R1865 Basalt
Same as above.
B.H.T5, El.978'(M.S.L.)60/937.

R1868 Basalt
Same as above.
B.H.T4, El.1811'(M.S.L.)60/949.

R1428 Basalt
Aphanitic, slightly vesicular. Collected by P.M. Hurley and H.W. Fairbairn along Wahkeenah Trail Rte. U.S. 30 just east of Portland, Oregon. Samples from flow centers only, starting at top of stratigraphic section of about 1000 feet.

R1435 Basalt
Aphanitic, slightly vesicular. No minerals identifiable. Same as for R1428.

R1443 Basalt
Aphanitic, slightly vesicular. Same as for R1428. Bottom of stratigraphic section.

R4209 Diabase
Fine grained, composed of plagioclase and pyroxene. Palisades Interstate Park, top of cliff.

R4210 Diabase.
Palisades Interstate Tourist Camp, 100 ft. above Hudson River.

R4211 Diabase.
Sleeping Giant Quarry, Mt. Carmel, north of New Haven, Connecticut.

R4159 Olivine basalt
Vesicular, aphanitic with olivine phenocrysts. Post-Pleistocene in age, Iceland, from M.I.T. Petrology Collection.

R4243 Tachylite (basalt glass)
Glassy, scoriaceous flow surface. Mt. Vesuvius, Italy, M.I.T. Petrology Collection #459.

R1574 Basalt
Aphanitic, vesicular, Yellowstone Park.

R4245 Basalt
Tertiary age, Squaw Creek, Montana. M.I.T. Petrology Collection #4805.

Precambrian Basic Intrusives

R4193 Anorthosite, with sharp bands of enstatite
Waterkop 602, Bushveld Complex, Shaler Memorial Expedition. Harvard #13444x. Donated by Dr. J.B. Thompson.

R4194 Norite
Mosego Mountain, Bushveld Complex, Hackney 700, Shaler Mem. Expedition. Harvard #13434x. Donated by Dr. J.B. Thompson.

R4195 Pyroxenite - overlying chronite band
Mooihoek 147, Bushveld Complex, Harvard #13452x, Donated by Dr. J.B. Thompson.

R1231 Gabbro (Duluth Gabbro Complex)
Eight miles south of bridge at Island - Orchard Lake, west side of Rte. 4, Minnesota, Specimen taken 6" below glacial surface.

R4186 Anorthosite
Stillwater Complex, Montana.

Monteregian Hills

R4179 Yamaskite
Mt. Yamaska, Quebec. Collected by G.H. Beall, 1960.

R4180 Essexite
Mt. Johnson, Quebec. Collected by G.H. Beall, 1960.

R4181 Nordmarkite
Shefford, Quebec. Collected by G.H. Beall, 1960.

R3069 Tinguaite (?)
St. Joseph's Boulevard, Montreal East, Quebec.

R3253 Carbonatite.
Ore grade Nb concentration. Oka, Quebec. Collected by J.A. Gower.

C3253 Calcite concentrate prepared from R3253 by means of Frantz Isodynamic Separator. Better than 95% pure calcite.

Eclogite

R3111 Eclogite
Composed of pyroxene and garnet. Entire sample ground up, no hand specimen available. Inclusion in kimberlite pipe, Robert Victor Mine, S. Africa. Given by F. Birch.

P3111 Pyroxene concentrated from R3111.

G3111 Garnet concentrated from R3111.

Keewatin Volcanics from Minnesota

R3357A Chlorite schist (Ely greenstone)
Dark Green. Entire specimen was crushed. Collected by P.M. Hurley, 1956, at Soudan Mine, Vermilion Range, Minnesota. Geological Society of America Field Trip Guidebook: Precambrian of Northeastern Minnesota, p.100.

R3358B Greenstone (Ely greenstone)
Pale green, not schistose. Contains calcite occurring in thin bands between pillows. Collected by P.M. Hurley, 1956, at City limits of Ely on Highway 21 enroute to Babbitt. G.S.A. Guidebook 1956, p.104.

C3358B Calcite leached out of R3358B by means of O.S.N. vycor-distilled hydrochloric acid.

R3354 Shale or fine tuffaceous sediment
Soudan formation. Collected at Soudan Mine, Vermilion Range, Minnesota by P.M. Hurley, 1956. G.S.A. Guidebook 1956, p.98.

Shale Composites

R4184 Composite of Appalachian shales of Paleozoic age. Samples were collected from exposures of shale of Pennsylvania Turnpike going east from Harrisburg. Thickness of individual shale beds used to weight proportions of samples in the composite. Prepared by Julian Feiss.

R4185 Composite of Paleozoic shales from the west coast. Prepared by Feiss in same way as described above.

R4132 Gneiss
Labrador trough, eastern gneiss, zone E. Unconformably underlying metamorphozed trough sediments. Collected by Pierre Sauve' (S-42-57) from 58°15'N, 69°14'W.

Chapter 11.

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