Rb-Sr Whole Rock Age in the Imataca Complex, Venezuela

by

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Abstract

The Encrucijada Granite, apparently an intrusion in the Imataca Complex, exhibits an age of 2154±43 m.y. A sample of remelted or granitized Imataca paragneiss exhibits an age of 2.9 b.y.

Acknowledgements

Professor J. Kalliokoski of Princeton University provided six samples used in this work as well as field and petrological data.

The chemical analysis presented in the Appendix were performed in the Cabot Spectrographic Laboratory of M.I.T. by Antonio Quesada.

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Part I - Setting

Introduction

The Imataca Complex is one of the Precambrian units of the Guayana Shield in Venezuela. It outcrops in Bolivar State and Delta Amacuro Federal Territory. It was originally named and described as Imataca Series by Newhouse and Zuloaga (1929), who applied this name to the iron-rich formation of the Guayana Shield. Later on the name was changed to Imataca Formation (Zuloaga and Tello, 1939).

The denomination used here is due to J. Kalliokoski (1965) who prefers this name due to the difficulties offered to the interpretation of the structure, stratigraphy and nature of the original rocks, and it applies not only to the iron-rich formation but to a whole complex of metamorphic rocks of sedimentary origin with extensive areas of acidic intrusions. Chase (1965) also prefers this denomination. The Complex covers most of the area of the Venezuelan Guayana (Bellizia, A. 1957)from the south-west of Cuidad Bolivar almost to the British Guiana border.

Five out of the six samples used for this work come from an acidic intrusion in the Imataca Complex known as the Encrucijada Granite. The other one comes from an outcrop some five miles to the west of the intrusive body and is believed to be a granitized or parly remelted Imataca paragneiss.

A Rb-Sr whole rock isochron has been constructed for the five samples of the Encrucijada granite and its age was calculated. Since only one sample of the possibly Imataca paragneiss has been available for this work, the construction of an isochron for it has been impossible, nevertheless an approximate age has been calculated using the Sr^{87}/Sr^{86} initial ratio obtained for the Encrucijada Granite samples.

Geologic and petrologic features of the Imataca Complex

The highly deformed rocks of the Imataca Complex are folded in asymmetric to equidimensional folds. The equidimensional domes are the dominant structures. The synclines are not so well defined.

The strike of the structures is East-Northeast and usually exhibits steep dips. Two main faults traverse the Complex: El Pao and Cuidad Piar-Guri. Intrusions of granitic and more basic rocks are common. (Martin Bellizia and Bellizia, 1956; Stam, 1963; Chase R. 1965; Kalliokoski j. 1965, Ratmiroff, G. 1965).

The petrological types present in the Complex are: ferruginous quartzites, gneisses and schists, areas of extensive migmatization are common as well as intrusions of granitic materials and also dikes and sills of basic igneous rocks as diabase, gabbro and norite. The iron-rich deposits are of high economical importance. (Martin Bellizia and Bellizia 1956, Kalliokoski, 1965).

The Encrucijada Granite is one of the above mentioned granitic intrusions. It is a plutonic body mainly composed by biotite granite more or less gneissic with medium to coarse grain and also porphiritic phases. A sample of an aplitic dike rock is also included, this rock outcrops near the south border of the pluton.

Previous Work

In a personal communication from Professor P. M. Hurley to the Orinoco Mining Co. gives an age of 2700 m.y. for an Imataca migmatitic gneiss located some 30 miles to the south of the Encrucijada Granite. The method used was Rb-Sr applied to whole rock.

Short and Steenken (1962) give an age of 2340 ±55 m.y. for a biotite with chlorite from a gneiss in what they call "pre Imataca" rocks. The method used was Rb-Sr. They also report an age of 2000±45 m.y. for a biotite from the Encrucijada Granite, and ages of 1540±60 m.y. north of Ciudad Piar (biotite, Rb-Sr) and also two K-Ar ages in a biotite, 800 m.y. and the other in a feldspar, 1070 m.y., both from a small granitic body north of Ciudad Piar.

McDougall et al. (1961) have dated the dolerites intruding the basement rocks and the Roraima formation in the British Guiana. The ages fall in a range of 1.6 to 2.1 b.y. The dolerite intrusions are extensive to all the Guayana Shield area. The determinations were done for whole rock, plagioclase and pyroxene using Rb-Sr and K-Ar methods.

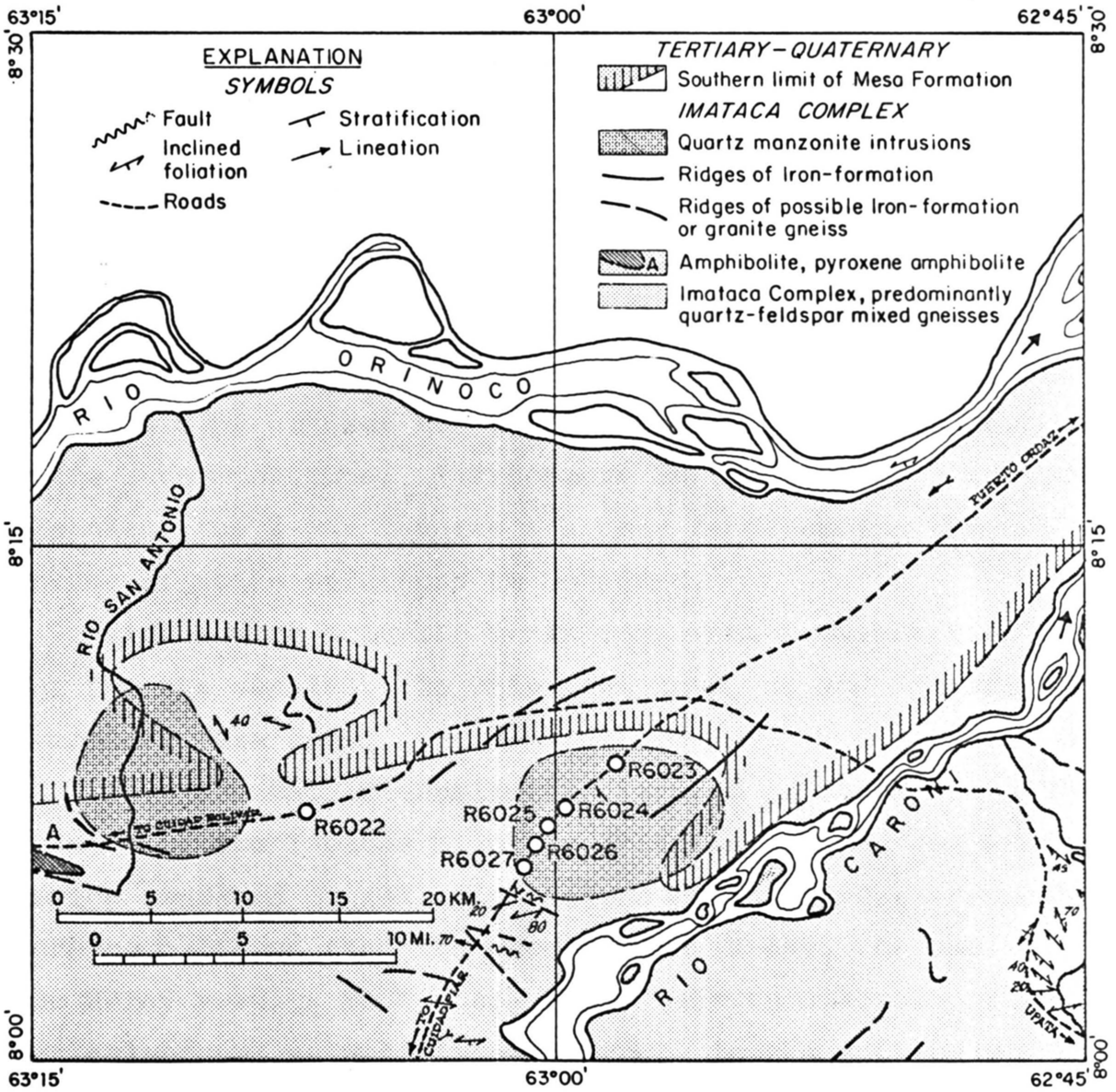
Snelling (1963) also dated the dolerites from British Guiana, using K-Ar for single mineral determinations, the age reported is 1.7 b.y.

Most of this data has been determined for a single sample and since the construction of an isochron is impossible for a single point there is a big uncertainity in the Sr^{87}/Sr^{86} initial ratio. In the work of McDougall et al. isochrons have been constructed for the potassium feldspar and whole rock data, the Sr^{87}/Sr^{86} initial ratio is approximately .703.

The differences in the ages, specially in those from the intrusive bodies suggest the presence of different cycles of magmatic activity. In the case of K-Ar ages or Rb-Sr for single mineral determinations the leakage of Ar or Sr during metamorphic or magmatic activity could explain the discrepancy in the results.

Sampling

The five samples from the Encrucijada Granite and the one from the Imataca paragneiss were fresh looking. The ones from the Encrucijada pluton were taken along a road that crosses the intrusive body in an asymmetrical fashion from NE to SW. The sample from the Imataca complex was also taken from an outcrop along a road.



GEOLOGY OF NORTH-CENTRAL GUAYANA SHIELD, VENEZUELA. KALLIOKOSKI 1959-64.

Part II - Rb-Sr Whole Rock Measurements

X-Ray fluorescence determinations

A previous determination of the approximate Rb and Sr content of the samples was done using G-1 as the comparison standard.

The results of this quick X-ray determination are generally used as the means to decide the best suited samples for mass spectrometric analysis and also in order to determine the most convenient weight of sample on the basis of its Rb and Sr content for both Isotope Dilution and Isotope Ratio determinations. Furthermore in the Isotope Dilution technique the X-ray results are used to determine the volume of spike solutions to be added.

Also a more accurate X-ray measurement was carried on for the six samples. In this case both, Rb and Sr dunite standards were used.

This accurate determination is used to check the results of the Isotope Dilution analysis. Since the arithmetics involved in the calculations of the latter are much more complicated than the ones for the X-ray, the use of the X-ray results as a check could help to discover arithmetical errors as well as main errors in the spiking of the samples. Table IV shows the comparison between Rb^{87}/Sr^{86} data from X-ray and Isotope Dilution analysis.

The Rb/Sr ratio for the X-ray technique is determined on the basis of a known Rb/Sr ratio in parts per million for the standard. This value is known accurately and is equal to 1.20.

The Rb/Sr ratio in parts per million (p.p.m.) in the sample is equal to 1.20 times the Rb/Sr ratio in counts per second (c.p.s.) for the sample divided by the same ratio for the standard.

$$\left[\frac{(\mathrm{Rb/Sr})\,\mathrm{p.p.m.}}{(\mathrm{Rb/Sr})\,\mathrm{c.p.s.}}\right]_{\mathrm{sample}} = \left[\frac{(\mathrm{Rb/Sr})\,\mathrm{p.p.m.}}{(\mathrm{Rb/Sr})\,\mathrm{c.p.s.}}\right]_{\mathrm{std.}}$$

therefore:

$$(\mathrm{Rb/Sr})_{\substack{\mathrm{ppm}\\ \mathrm{sample}}} = 1.20 \times \frac{(\mathrm{Rb/Sr})\,\mathrm{c.p.s.}\ \ \mathrm{sample}}{(\mathrm{Rb/Sr})\,\mathrm{c.p.s.}\ \ \mathrm{std.}}$$

To change the Rb/Sr values into Rb^{87}/Sr^{86} values a conversion factor must be used. This has been plotted versus Sr^{87}/Sr^{86} ratio and is obtained directly from the graph.

The conversion factor is

$$K = 0.003255\ \frac{\mathrm{At.\ Wt.\ Sr}}{\mathrm{At.\ fraction\ Sr}^{86}}$$

and $$(Rb^{87}/Sr^{86}) = K \times (\mathrm{Rb/Sr})\mathrm{ppm}_{\mathrm{sample}}$$

Mass spectrometric determinations

The six samples were analyzed by the Isotope Dilution technique for both Rb and Sr.

Sr^{84} and Rb^{87} spikes were used. The use of Sr^{84} spike permits the correction for instrument fractionation and discrimination as well as eliminates the necessity of running a spiked and an unspiked sample for the determination of Sr^{87}/Sr^{86} ratio (R. van Schmus).

Strontium Computation:

The values for Sr^{84}, Sr^{86}, Sr^{87} and Sr^{88} for the mixture of sample plus spike are obtained from the mass spectrometer runs and from those values the Sr^{84}/Sr^{86}, Sr^{87}/Sr^{86} and Sr^{88}/Sr^{86} ratios are computed.

The values of Sr^{86}/Sr^{84}, Sr^{87}/Sr^{84} and Sr^{88}/Sr^{84} for the spike are known and also the values for "normal" or natural strontium: Sr^{84}/Sr^{88} and Sr^{86}/Sr^{88}, both pairs in those ratios are non radiogenic components of strontium and its value is considered a natural constant.

The whole calculation is carried on in order to determine the original isotopic composition of the sample. This is complicated by the fact that the spike is not pure Sr^{84}, but contains also small amounts of the other isotopic components.

The value of 84/86 ratio in the sample is obtained by means of successive approximations.

All the values in the mixture of sample plus spike must be normalized if the ratio (Sr^{86}/Sr^{88}) normal differs from 0.1194. Therefore the ratios Sr^{84}/Sr^{86}, Sr^{87}/Sr^{86} and Sr^{88}/Sr^{86} are corrected, taking into account that the mass difference between 84-86 is two units and between 87-86 and 88-86 is one and two units respectively, but in the opposite direction.

Once the normalization has been carried on, the 84/86 ratio is recalculated, and from it the 87/86 and 88/86 ratios are determined.

With the 87/86 value, the weight fraction of Sr^{86} in the sample is determined from a graph: Sr^{87}/Sr^{86} vs weight fraction of Sr^{86}.

The concentration of Sr^{86} in the sample in p.p.m. is computed from:

Concentration Sr^{86} in p.p.m. =

$$\frac{(86/86)N \times \text{At.Wt.}86 \times \text{ml spike} \times \mu\text{gm/ml } Sr^{84}\text{spike}}{(84/86)S \times \text{At.Wt.}84 \times \text{sample weight}}$$

where N = normal

S = spike

and the total Sr content in the sample will be:

$$\text{Total Sr p.p.m.} = \frac{\text{Conc. } Sr^{86} \text{ in ppm}}{\text{weight fraction } Sr^{86}}$$

Rubidium Computation:

The Rb^{85} and Rb^{87} values for the mixture of sample plus spike are measured in the mass spectrometer; from those the Rb^{85}/Rb^{87} ratio is computed. From this measured value and the known ratios Rb^{85}/Rb^{87} "normal" and Rb^{85}/Rb^{87} in the spike an equation is set that will permit to compute the ratio N/S (normal to spike).

$$(Rb^{85}/Rb^{87})_{\text{measured}} = (Rb^{85}/Rb^{87})N + (Rb^{85}/Rb^{87})S$$

With the value of N/S ratio the total Rb content in the sample in p.p.m. is computed from:

Total Rb in p.p.m. =

$$\frac{N/S \times \text{weight factor} \times \text{ml spike} \times \mu\text{gm/ml } Rb^{87} \text{ spike}}{\text{Weight of the sample}}$$

From the values obtained for total Rb and total Sr in p.p.m. the Rb/Sr ratio in weight is obtained and the K factor used in the X-ray computation is applied once again here, to obtain the Rb^{87}/Sr^{86} ratio in atoms.

$$(Rb^{87}/Sr^{86})\text{atoms} = (Rb/Sr)\text{Total} \times K$$

Isochron plot

The values of Sr^{87}/Sr^{86} and Rb^{87}/Sr^{86} are now plotted in a suitable scale, the most convenient is that in which the slope of the isochron is as near to one as possible.

If the system has remained as a closed one since the time of consolidation the points must fall on a straight line. The scatter of the points indicates changes in the chemical and/or isotopic composition of the system that could be due to metasomatic processes or diffusion of the radiogenic daughter over a volume greater than the one covered by the sampling.

Even if the system has remained as closed, the points may not fall in a perfect straight line, due to the inherent errors in the analytical techniques, therefore is necessary to determine the best fitted line that passes throughout those points. For this an average of the x and y values of the points is obtained that will give the coordinates of the center of mass of all the plotted points.

The coordinates of all those points are then recalculated taking the center of mass as the new origin of coordinates. This will give positive and negative values for the new X and Y of the points, the sum of which must be equal to zero for Z and Y respectively.

The Coefficient of Correlation r is computed from:

$$r = \frac{(XY)}{\sqrt{(XX)(YY)}}$$

and the slope of the best fitted line a will be

$$a = \sqrt{\frac{\frac{XX}{n(n-1)}}{\frac{YY}{n(n-1)}}}$$

where n = number of determinations

Since the number of determinations for x and y is the same

$$a = \sqrt{\frac{(XX)}{(YY)}}$$

the error in the slope will be:

$$\sigma\bar{a} = a\sqrt{\frac{1-r^2}{n}}$$

where r = coefficient of correlation

n = number of determinations

The equation of the line will be: $X = b + aY$

or $X = aY$ since the line will pass through the origin of coordinates $b=0$

With the value of the slope and suitable values for X or Y two new points are determined, and the best fitted line must pass through those points and the center of mass.

For small sets of numbers (n less than 30)

$$\sigma x = A \cdot R_x$$

$$\sigma y = A \cdot R_y$$

where R_x and R_y are the range of values for x and y and A is found in a table that will give the values of A on the basis of number of determinations and Confidence Limits. (Bauer, E. 1960).

The equation used to calculate the age is:

$$(Sr^{87}/Sr^{86})_p = (Sr^{87}/Sr^{86})_i + Rb^{87}/Sr^{86}\ (e^{\lambda t}-1)$$

This equation has the form:

$$y = a + bx$$

where:

y = is the $(Sr^{87}/Sr^{86})_p$ ratio actually present in the rock and therefore is a measured quantity

a = is the intercept of the line and is the $(Sr^{87}/Sr^{86})i$ ratio initially present in the rock, and is known as the "initial ratio". Therefore $(Sr^{87}/Sr^{86})i$ is directly determined from the intersection of the line with the y axis in the graph

b = $(e^{\lambda t}-1)$ is the slope of the line. is the decay constant for Rb^{87}, and is equal to 1.39×10^{-11} yr^{-1}. t is the age of the rock.

x = Rb^{87}/Sr^{86} ratio and is also a measured quantity

An easier way to visualize the age of the rock t is by writing the above equation as:

$$t(m.y.) = \frac{1 \times 10^5}{1.39} \ln \left[1 + \frac{(Sr^{87}/Sr^{86})_p - (Sr^{87}/Sr^{86})i}{Rb^{87}/Sr^{86}} \right]$$

and the error in the age is calculated by

$$\sigma_t = t \cdot \frac{\sigma a}{a}$$

The envelope of error for the isochron is computed from the value of the standard deviation of all d's

$$d = \sqrt{2(1-r)\ (\sigma_x^2 + \sigma_y^2}$$

and the standard deviation of the mean $\bar{d}$

$$\sigma_{\bar{d}} = \frac{\sigma_d}{\sqrt{n}}$$

With the value of σ_d and the highest and lowest values for the age the envelope is graphically determined around the center of mass of the best fitted line.

The values of the intercept for the envelope are the main possible errors in the initial ratio $(Sr^{87}/Sr^{86})i$

(In the present work, the lower value for $(Sr^{87}/Sr^{86})i$ is below .700, this does not have any geochemical meaning , therefore is assumed that the error in the initial ratio must be lower than the reported one and the high error represented is due to the low number of determinations . The lack of geochemical meaning is due to the fact that such an initial ratio will be below the meteorites value.

Analytical procedure

The samples were surface-cleaned and broken and crushed into small pieces in a steel jaw crusher; the pieces showing some surface alteration were discarded and the rest was stored in sample boxes. A portion of each sample has been selected by quartering it with a spatula and taking successive alternated quarters.

The selected portion was powdered in a Pica blending mill from 20 to 30 minutes.

All the implements used were cleaned and washed before each sample was prepared.

The powdered samples were stored in clean polyethylene bottles.

A quick X-ray determination was performed for each sample, using G-1 as a standard, in order to determine the approximate Rb and Sr content in the samples. G-1 was run twice, once in the middle and once at the end of the run.

On the basis of the above mentioned determination the samples were weighted out in such a way that the approximate content of Sr for each one was around 100 μgm. Also the above determination was used to calculate the mililiters of spike necessary for both Rb and Sr, and the samples were spiked in such a fashion (to the nearest milliliter) to make $Sr^{84}/Sr^{86} = 1$ and normal Rb/spike Rb = 0.85.

The procedure used to dissolve the samples is given in Appendix II, as well as the procedure used to separate Rb and Sr in the chromatographic columns.

The mass spectrometer operation for the Sr samples was: the samples were placed in a clean filament in the form of nitrates and were conditioned in the mass spectrometer at pressures in the 10^{-6} mmHg range and 1.1 to 1.2 amperes for the filament supply for more than 12 hours.

The samples were run at a filament supply of 1.6 to 1.7 amperes. The 100 millivolts scale was used for Sr^{84},Sr^{86} and Sr^{87} and the 1 volt scale for Sr^{88}. The pressure was always lower than 1×10^{-6} mmHg.

An Sr standard plus 84 spike (R. van Schmus preparation) was run at the beginning and after three samples.

The source was completely washed with nitric acid and demineralized water and dried with acetone to avoid Rb contamination of the Sr samples.

To check the presence of possible Rb contaminant, the mass spectrometer was set in the 85 position and in a very sensitive scale. If presence of Rb was suspected the filament supply was raised to 1.9 amperes until no indication of Rb was detected.

For the Rb samples the pressure setting was as low as it was for Sr, but the conditioning time was only from 1 to 2 hours at approximately 0.5-0.6 amperes..

The 100 milivolts scale was used for both Rb^{85} and Rb^{87} and the filament supply was usually 0.7 ampers.

The values for Rb and Sr are averages of 6 lectures for each isotopic component, and usually from 8 to 10 of those sets were run for each sample.

The Rb/Sr ratios were also obtained by means of a Norelco X-ray fluorescence unit (the same used for the "quickies"). These values were used as a cross check for those of the Isotope Dilution results. A portion of the same powdered sample used for the mass spectrometric determination was also used for the X-ray. Each sample was run three times. Rb and Sr standard dunite were run at the beginning, between each sample and at the end of each run.

Results

From the isochron plot (Plate II) is possible to appreciate that the five points representing the samples from the Encrucijada Granite fall in a fairly good line if the errors inherent to the determination are taken into account. The most immediate meaning of this observation is that the Encrucijada Granite body has remained as a closed system since the time of consolidation.

The highest point of the isochron is due to an aplitic differentiation that outcrops in the southern border of the pluton. The high Rb and low Sr content of that sample make the uncertainty of the value bigger than usual and the relative error between the X-ray and the Isotope Dilution values much higher than for the other samples.

From the microscopic observations (Appendix I) is possible to determine the presence of some calcite as well as some sericitic material in some of the samples but in general they are clean and fresh and no signs of high alteration are observed.

The value for the initial ratio for the isochron plot is 0.7010 but the uncertainty is quite big for reasons explained elsewhere in this paper (see pg. 13).

The computed age for the Encrucijada Granite is 2154 ± 43 m.y. which agrees fairly well with the biotite age already mentioned for the same body.

The only sample from outside the pluton and which has been considered as representative of the Imataca paragneiss has not been included in the isochron plot since it belongs to a different geological unit for which a different age is expected.

The sample has been analyzed exactly as the others and its age has been computed using the Sr^{87}/Sr^{86} initial ratio found for the Encrucijada Granite isochron. The value obtained is 2.9 b.y.

Tables I, II, III and IV give the values for the X-ray and Isotope Dilution data.

Precision

The precision of the mass spectrometer in the measurement of Sr^{87}/Sr^{86} ratio is considered to be less than ±0.001 and approximately 2% for Rb^{87}/Sr^{86} ratio.

The Rb/Sr ratio for the X-ray measurements has a precision of approximately 3%.

The normal error for the comparison of the Rb/Sr data for X-ray and Isotope Dilution determinations is around 5% when the samples have been run three times in the X-ray fluorescence. The error is expected to be higher in those samples in which either Rb or Sr shows a much lower concentration respect to the other, this is shown for one of our samples with a fairly high Rb and a low Sr content (higher point in the isochron).

Since no duplicate mass spectrometric analysis of the samples was performed the error represented in the isochron plot for Rb^{87}/Sr^{86} is 3% instead of the usual 2%, but is believed to be lower than that.

The scatter of the points fall pretty well into the limits set by the inherent errors of the determination.

The problem in the uncertainty of the initial ratio has been discussed elsewhere in this work, and the error is expected to be less than the reported one.

The computation of the error in the age of the isochron has been explained in other paragraphs.

No attempt to calculate the error in the age of the single Imataca paragneiss has been made.

Conclusions

Since the geochronological data for the area is quite scarce and most of the ages are referred to single sample, whole rock or single minerals, the present work contributes with a fairly accurate age for a period of magmatic activity that have affected the old basement rocks of the Guayana Shield in early Precambrian times.

The age obtained for the Imataca paragneiss sample, even if it is not as accurate as the one for the Encrucijada Granite, open, together with the 2.7 b.y. reported by Prof. Hurley to Orinoco Mining Co., a wide field of speculation, since some similarly old ages appear in the west of Africa (Sierra Leone).

The 2 b.y. age appears to be common over a wide territory in Africa (Ghana, Ivory Coast) and the north of South America (east of Belem de Para to Venezuela) which besides reassuring the value of the obtained age implies interesting possibilities for a further geochronological work.

Suggestions for further work

Since the data actually available in the Guayana Shield area does not contribute yet to clarify the picture of the relation between the various igneous and metamorphic activities that have affected the area at different times during its long history, the only possible suggestion is a more detailed and intensive geochronological work in the different geological units that make up the whole metamorphic and igneous complex of the Shield.

Also the observed age-coindidences in Africa and South America open a broad field of suggestions regarding the studies in Continental Drift.

Table 1

X-ray Results for the Encrucijada Granite and the Imataca paragneiss

	Rb/Sr intensity	Rb/Sr weight	Ave (wt.)	K	Rb^{87}/Sr^{86}
R6022	0.7448	0.9281			
	0.8009	1.0053			
	0.7780	0.9756	0.9697	2.9260	2.873
R6023	0.3820	0.4784			
	0.4079	0.5120			
	0.4073	0.5112	0.5005	2.9046	1.4538
R6024	0.2213	0.2764			
	0.2335	0.2924			
	0.2189	0.2719	0.2802	2.900	.8126
R6025	0.3355	0.4172			
	0.3449	0.4254			
	0.3442	0.4316	0.4247	2.9038	1.233
R6026	2.5095	3.1078			
	2.6004	3.2436			
	2.6619	3.3312	3.2275	2.969	9.58
R6027	3.2563	4.0284			
	3.6082	4.5384			
	3.3851	4.2313	4.2660	2.998	12.79

Table II

Mass spectrometer results for Sr I.D. analysis

	Sr^{88}/Sr^{86}	Sr^{87}/Sr^{86}	Sr^{84}/Sr^{86}	Ave.		
R6022	8.114	.7964	1.1948			
	8.079	.7972	1.1876			
	8.238	.7976	1.1949			
	8.224	.7962	1.1951			
	8.271	.7981	1.2007			
	8.063	.7947	1.1986			
	8.031	.7945	1.1972			
	8.106	.7930	1.1914			
	8.042	.8007	1.1909			
	8.098	.7960	1.1992	8.127	.7964	1.1950
R6023	8.102	.7231	.9239			
	8.174	.7287	.9141			
	8.184	.7258	.9117			
	8.196	.7307	.9113			
	8.196	.7285	.9102			
	8.205	.7288	.9107			
	8.212	.7282	.9127			
	8.230	.7297	.9110			
	8.221	.7289	.9116	8.191	.7280	.9130
R6024	8.242	.7152	.7800			
	8.256	.7153	.7791			
	8.245	.7167	.7774			
	8.238	.7145	.7779			
	8.230	.7159	.7773			
	8.253	.7157	.7778			
	8.241	.7162	.7772			
	8.251	.7164	.7768			
	8.251	.7163	.7778	8.245	.7158	.7779
R6025	8.050	.7192	1.0059			
	8.024	.7164	1.0094			
	8.079	.7209	1.0099			
	8.041	.7174	1.0164			
	8.104	.7213	1.0088			
	8.221	.7214	1.0103			
	8.156	.7229	1.0035			
	8.180	.7253	1.0054			
	8.080	.7172	.9959			
	8.127	.7232	.9979	8.106	.7205	1.0063

Table II (cont.)

	Sr^{88}/Sr^{86}	Sr^{87}/Sr^{86}	Sr^{84}/Sr^{86}	Ave.		
R6026	8.109	.9479	1.0771			
	8.094	.9427	1.0794			
	8.093	.9412	1.0749			
	8.122	.9439	1.0799			
	8.108	.9440	1.0748			
	8.121	.9453	1.0770			
	8.120	.9442	1.0769			
	8.114	.9441	1.0769	8.110	.9442	1.0771
R6027	8.058	1.0324	1.2586			
	8.079	1.0350	1.2533			
	8.015	1.0280	1.2257			
	8.135	1.0428	1.2441			
	8.063	1.0298	1.2481			
	7.986	1.0243	1.2541			
	7.957	1.0284	1.2489			
	8.018	1.0297	1.2503	8.039	1.0313	1.2479

The value for each ratio and the average of six consecutive scans.

Table III

Mass spectrometer results for Rb I.D. analysis

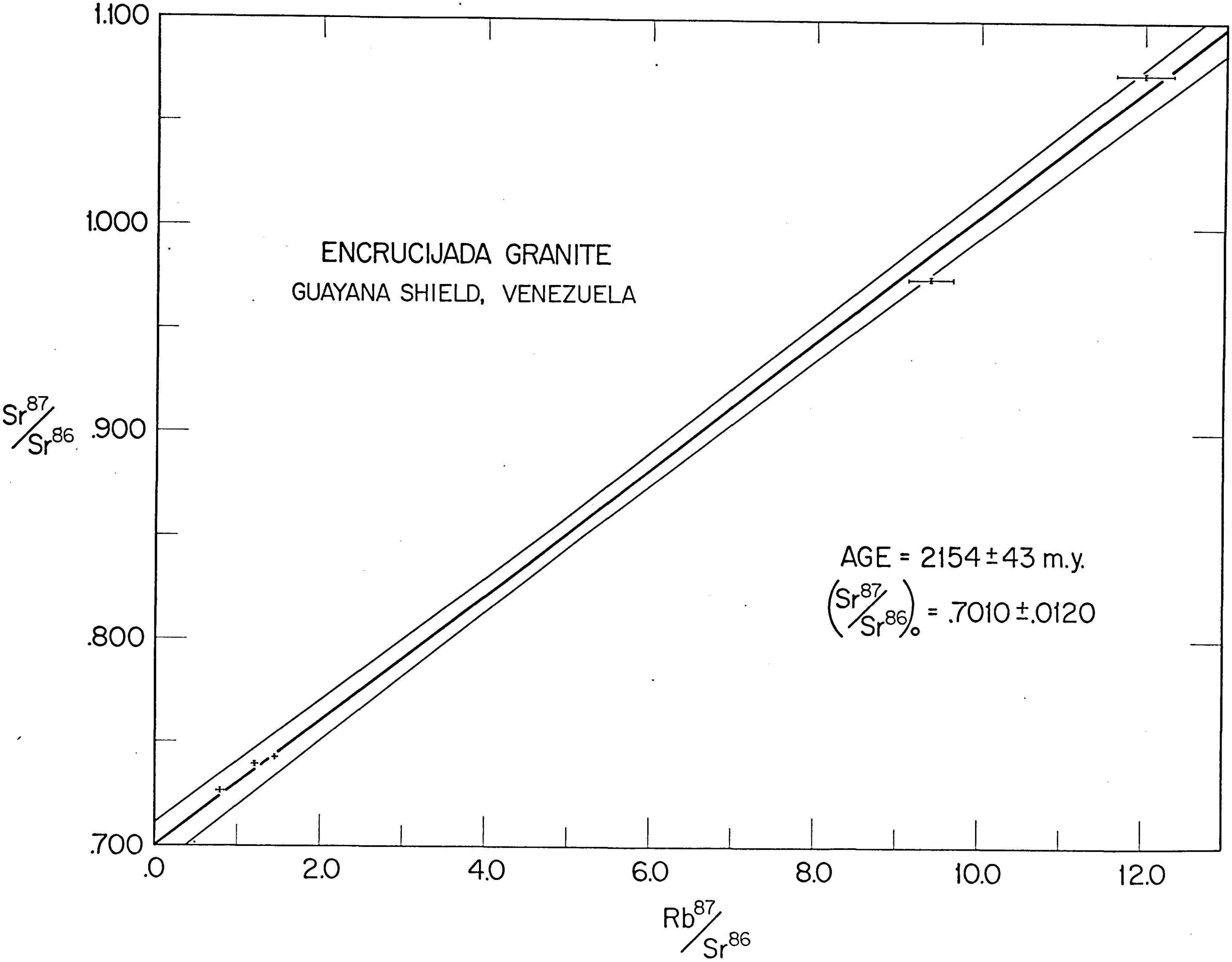
	Rb^{85}/Rb^{87}	Ave.		Rb^{85}/Rb^{87}	Ave.
R6022	.4997		R6026	.5140	
	.4994			.5135	
	.4987			.5144	
	.4974			.5149	
	.4993			.5125	
	.4995			.5146	
	.4977			.5136	
	.4971			.5142	.5140
	.4968				
	.5057	.4991			
R6023	.6673			.4767	
	.6660			.4772	
	.6672			.4767	
	.6675			.4766	
	.6668			.4761	
	.6658			.4788	
	.6666			.4799	
	.6669			.4791	.4776
	.6664	.6665			
R6024	.5717				
	.5637				
	.5664				
	.5652				
	.5657				
	.5681				
	.5651				
	.5682	.5668			
R6025	.6354				
	.6358				
	.6378				
	.6365				
	.6358				
	.6345				
	.6365				
	.6396				
	.6365	.6365			

Table IV

Comparison of Rb^{87}/Sr^{86} data from X-ray and I.D. Analysis

Sample	Sr^{87}/Sr^{86}	K factor	Rb/Sr I.D.	Rb/Sr X-ray	Rb^{87}/Sr^{86} I.D.	Rb^{87}/Sr^{86} X-ray
R6022	.8204	2.926	.9720	.9697	2.844	2.8373
R6023	.7428	2.9046	.5047	.5005	1.4659	1.4538
R6024	.7266	2.900	.2733	.2802	.7926	.8126
R6025	.7396	2.9038	.4199	.4247	1.2193	1.233
R6026	.9749	2.969	3.1675	3.2275	9.40	9.58
R6027	1.0750	2.998	4.0031	4.2663	12.00	12.79

The error is from 1 to 2% in all samples except for R6027 where it is 6%, therefore exceeding the admitted 5% discrepancy between X-ray and I.D. values.



ENCRUCIJADA GRANITE
GUAYANA SHIELD, VENEZUELA
AGE = 2154 ± 43 m.y.
$(Sr^{87}/Sr^{86})_o$ = .7010 ± .0120
Sr^{87}/Sr^{86}
1.100
1.000
.900
.800
.700
.0
2.0
4.0
6.0
8.0
10.0
12.0
Rb^{87}/Sr^{86}

Appendix I

Description of the samples

R6022: a) Pink granitic gneiss with some fine dark laminae.
b) Quartz, perthitic microcline, biotite, some chloritic material and zircon. This sample is believed to be granitized or remelted Imataca paragneiss.

R6023: a) Gray biotite granitic gneiss, with medium to coarse grain and some pegmatitic microcline crystals.
b) Quartz, microcline, biotite, hornblende, plagioclase, zircon, sphene, apatite. Some sericitic alteration and some calcite.

R6024: a) Gray porphyritic biotite granite, slightly gneissic.
b) Quartz, microcline, plagioclase, hornblende, zircon, magnetite sphene.

R6025: a) Gray, porphyritic quartz-monozonite
b) Quartz, microcline, plagioclase, biotite, hornblende, magnetite, apatite, zircon.

R6026: a) Pink, medium grained biotite granite.
b) Mostly quartz, perthitic microcline, plagioclases, biotite (some chloritic alteration), magnetite, zircon, and hematitic material.

R6027: a) Aplitic dike-rock near the south border of the Encrucijada pluton.
b) Mainly quartz, perthitic microcline, plagioclase and a few crystals of hornblende and biotite.

Note: a) hand specimen
b) thin section

Appendix II

a) Disolution of the silicate samples

The samples were weighed out in a precision balance up to the tenth of a milligram and placed in platinum dishes.

The disolution procedure is rather similar for both Isotope Dilution and Isotope Ratio analysis. The steps followed were:

1. Wet the sample in the platinum dish with several milliliters of demineralized water.

2. Add the calculated milliliters of Rb and Sr spike solutions being careful in order to avoid contamination.

3. Add 10 ml of HF acid for each 0.5 gm of sample (HF is the main Sr contaminant, therefore is necessary to avoid its superfluos use specially if the sample is low in Sr).

4. Add 1.5 ml of concentrated H_2SO_4 (Vycor dist.) for each 0.5 gm of sample (The use of H_2SO_4 instead of $HClO_4$ is preferred to avoid the formation of a precipitate of alkaline perclorates, in this case $RbClO_4$). The previous dilution of H_2SO_4 with demineralized water in a 1:1 proportion is recommended to avoid splattering of the sample.

5. Place on steam bath and stir frequently, USE RUBBER GLOVES. Evaporate.

6. Add approximately 150 ml of 2N HCl (Vycor dist.), stir. Evaporate to almost dryness.

7. Add 20 ml of 2N HCl, stir plus 20 ml demin. water.

8. Allow to cool and filtrate.

b) Rb and Sr separation in the chromatographic columns

The ion exchange columns are prepared with Dowex 50W-X8, 200-400 mesh, ionic form H^+. The height is about 25 to 30 cm. and the diameter 2½ cm. The columns are washed with 2N HCl and while not in use are mantained closed and with a head of the same acid.

Steps followed in the separation:

1. Add Sr^{85}, carrier free, tracer to the liquid samples obtained by the above mentioned procedure, in such volume as to have and activity from 3 to 4 times higher than the background level. Control with a Gamma scintillation detector and counter.

2. Place the samples in the columns avoiding to disturb the resin surface. In this work the samples were added to the columns drop by drop with a pipette.

3. Once the sample is well into the column add small volumes (40ml) of 2N HCl, without disturbing the resin, before adding a new volume of acid allow the previous one to disappear into the resin.

4. Once the iron ring is almost at the bottom of the column add a head of acid and connect the column authomatic.

5. Test for Na, and when the Na flame is almost gone start collecting in numbered beakers. Continue collecting until all the activity due to Sr^{85} is gone.

6. Detect the beakers with Rb using an Atomic Absorption Spectrophotometer and Sr with the aid of a Gamma detector.

7. Evaporate those beakers with Rb and combine them for each column. Do the same for the ones with Sr.

8. Once the volume is less than 5 ml place the samples in numbered Vycor beakers with 2-3 drops of $HClO_4$. Evaporate to dryness in hot plate and ignite.

9. Add HNO_3 1:1 (vycor dist.) and evaporate to dryness.
10. Cover and label.

Note: The spike solutions used for the present work were:

Sr^{84} intermediate spike (Sr^{84}/65B)

4.85 ugm Sr^{84}/ml = 6.01 ugm total Sr/ml

Rb^{87} intermediate spike

14.35 ugm Rb^{87}/ml = 14.47 ugm total Rb/ml

Appendix III

Spectrographic Analysis

The analyses were performed by Antonio Quesada in the Cabot Spectrographic Laboratory, M.I.T. with a Hilger Emission Spectrograph. For the analytical procedure see: Dennen, W. H. and Fowler, W. C. (1955): Spectrographic Analysis by use of Mutual Standard Method. Bull., G.S.A., V. 66, p. 655-662.

Results

Oxides	R6022	R6023	R6024	R6025	R6026
SiO_2	37.37	62.48	77.13	65.05	72.41
TiO_2	0.17	0.38	0.73	0.58	0.10
Al_2O_3	2.80	8.9	10.1	16.6	15.1
Fe_2O_3	60.0	3.47	5.25	5.1	1.29
MnO	0.08	0.09	0.07	0.08	0.03
MgO	0.10	1.6	1.36	1.5	0.27
CaO	-	2.31	2.02	3.4	0.91
Na_2O	-	8.9	1.44	3.7	3.10
K_2O	-	11.57	1.76	3.9	6.71
Total	100.5	99.8	99.9	99.9	99.9

Note: Results for R6027 are not presented here since the lack of iron in the sample has not permitted an accurate analysis

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