ACTIVATION ANALYSIS FOR SILICA IN IGNEOUS ROCKS

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ABSTRACT

The possibility of analyzing igneous rocks for silica and aluminum by a radio-activation method is discussed. The relevant data for the occurrence of elements in igneous rocks and the activation conditions of these elements are presented. It is shown that the detection of induced activity due to silicon after exposure to fast neutrons and aluminum after exposure to thermal neutrons is possible and that analysis for these elements is feasible.

The amount of sample material required, the sample preparation, the irradiation period, the time required for an analysis and the methods of neutron bombardment are considered and are found to be satisfactory for practical applications. A simplified procedure for such analysis is outlined.

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INTRODUCTION

The importance of silicate analysis is widely recognized in industry and in pure science. Analyses provide the petrologist with accurate data which add precision to his descriptions of the analyzed rocks and so enable him to interpret the relationships, history, and mode of origin of the materials concerned. In the task of determining and describing rocks, the petrologist may not always find the microscopic examination sufficient for his purpose. This limitation is particularly felt when poorly or incompletely crystallized volcanic rocks or metasomatically altered rocks are considered.

The analysis of igneous rocks by chemical methods is a costly and time consuming process. The chemical similarity of several of the rock forming elements increases the difficulty and decreases the accuracy of chemical methods. A method of rock analysis for some of the rock forming elements by radioactivation is described herein.

Research in activation analysis has been carried out by Eichholz,[1] and Gaudin, Sentfle and Freyberger.[2] These experimenters used Geiger Müller counters and proportional counters. A scintillation counter, which has a much higher efficiency and is thus a much better detecting device, was used in the following experiments. Preliminary investigations using the same apparatus were carried out by K. Bramadat.[3]

The main principle of activation analysis rests on the detection of induced activity from the test sample after it has been exposed to bombardment by neutrons for a suitable length of time. Such analysis is feasible if the following conditions are satisfied.

1. The elements to be tested must be easy to activate with the bombarding source available.

2. The activity produced must be readily detected and of sufficient intensity.

3. The activated elements must have a long enough half ~~life~~ lives to be handled and transported easily from the source area to the detector, but short enough to provide a rapid analysis.

4. All elements existing in the same rock must have such activation properties to make it a simple matter to distinguish between them. This condition is satisfied if the elements concerned have different half lives, if the activation cross-sections (ie activation probabilities) differ and if certain elements emit lower energy radiation than others.

Although a large number of elements may be present in igneous rocks only eight are generally present in amounts greater than one per cent. These are O, Si, Al, Fe, Mg, Ca, Na and K. The above mentioned conditions apply in the case of several of these elements and also in the

case of some of the minor elements such as manganese.

Tests have been carried out with a polonium-beryllium neutron source having a strength of about 2 Curies. The writer has restricted his investigations to the quantitative detection and differentiation of silica and aluminum in igneous rocks. Results show that neutron activation analysis of these elements is feasible. Preliminary investigations indicate that Na and K may also be detected by activation analysis.

The method is simple and requires very little sample preparation or handling. In most analyses only coarse crushing is required. Since a large sample (300 grams) is used weighing errors are very slight. The sample is not destroyed in the course of the analysis.

ACTIVATION CONDITIONS

The activation of any element irradiated in a beam of particles is given by the following equation:[1]

$$A = \frac{m\ No}{M}\ F\sigma\ (1 - e^{-0.7\ \frac{T}{\tau}})\ e^{-0.7\ \frac{t}{\tau}} \quad (1)$$

Where A = activity, ie number of particles emitted per second.

No = Avogadros number 6.02×10^{23} $mole^{-1}$

M = Atomic weight of the element.

m = Mass of bombarding substance in grams.

F = Bombarding flux, ie number of bombarding particles per cm^2 per second.

σ = Activation cross-section, ie the probability that a bombarding particle interacts with a target nucleus (expressed in cm^2).

τ = half life of the active nucleus.

T = time of irradiation.

t = time elapsed since irradiation.

This equation shows that the activity of an element is directly proportional to the amount of element used, the neutron flux available and the activation cross section for the reaction. There is, therefore, no theoretical limit for the counting rate attainable as one can simply use a larger sample of the rock if the element considered is present in lower concentration. In practice the size of the sample is limited by requirements of uniform detector geom-

→ self absorption will limit size.

etry and bombardment conditions.

The cross sections for the (n,γ) and (n,p) reactions for the different rock forming elements vary from relatively small values for fast neutron reactions to larger ones for thermal neutron reactions. The isotopes formed have characteristic properties of initial activation, decay and half life, and γ-ray energies. If it is possible to determine and distinguish these properties experimentally, then it should be possible to make a qualitative and quantitative analysis of some of the rock forming elements.

The general procedure in activation analysis is to calibrate the detector by exposing a standard sample to the flux F of the bombarding source and compare the resultant initial activation with that of the unknown sample exposed under identical conditions. In that case the mass of the desired element in the unknown sample is given by

$$m_1 = m_o \frac{A_1}{A_o}$$

Where the suffix "o" refers to the standard sample and 1 to the unknown sample.

The Detector

The scintillation counter used in the following experiments employs a solid Na I (TL) scintillator 2 inches in diameter, which is placed on the face of a photomultiplier tube. When subjected to gamma radiation, electrons released in the crystal excite centres of fluorescence in

the crystal lattice which are subsequently detected by the photomultiplier. The pulse from the photomultiplier is transmitted by a cathode follower circuit to a linear amplifier. From the linear amplifier the pulse is transmitted directly to a cathode ray oscilloscope and through a discriminator to a scaler unit.

The scintillation counter has the desirable property of acting as a proportional devise, so that it is essentially a gamma ray spectrometer[4-6] in which a measure of the energies of the gamma rays is obtained from the pulse height distribution of the voltage pulses of the photomultiplier. It is assumed that a strict proportionality exists between the total light per scintillation in the phosphor and the energy imparted by the gamma ray to the crystal. The interaction between the gamma ray and the crystal may take place according to three processes: the photoelectric effect, the Compton effect, and the pair production effect. It is therefore possible to identify in the voltage pulse height distribution curve for a given gamma ray energy, either a photoelectron line, or a pair production line or a distribution corresponding to the Compton effect, or a combination of these. Using a differential discriminator and photographic storage methods employing a cathode ray tube rapid analysis of distributions of this type is possible. The value of this proportional property of the scintillation counter in activation analysis lies in the ability of the device to identify a particular pulse in the terms of the

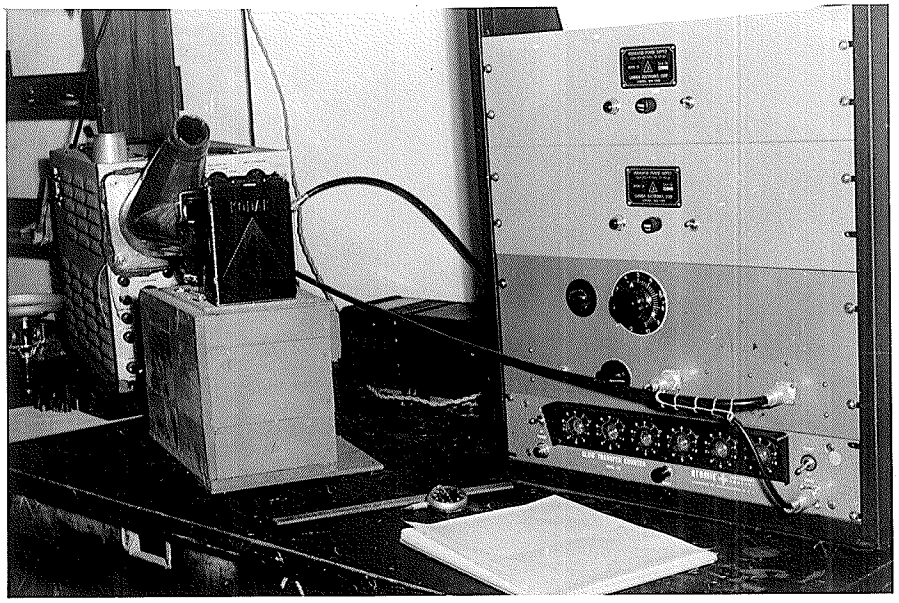

Fig. 1--Photograph of apparatus

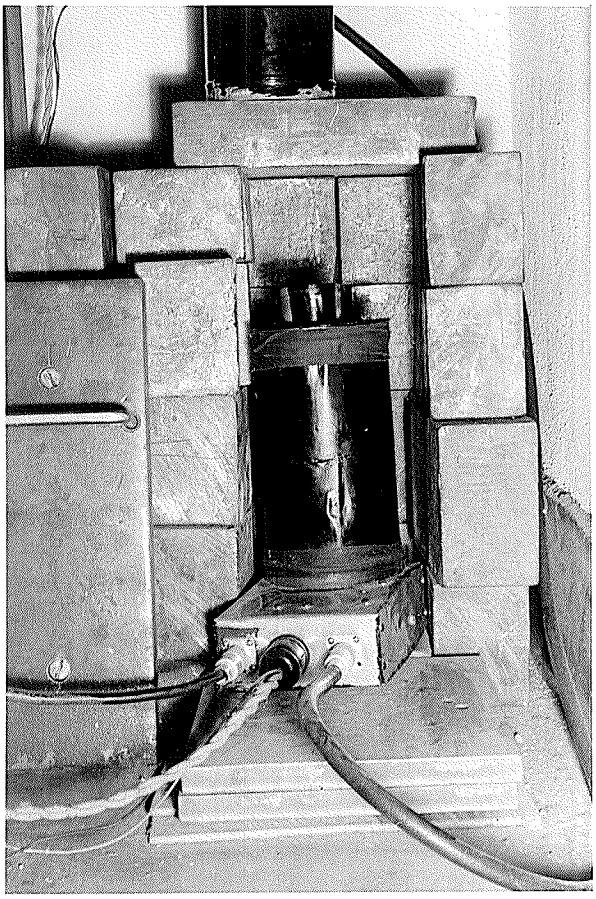

Fig. 2--Photograph of cathode follower

spectrum, as well as the intensity of the gamma radiation involved, and thus indicate the nature of the radioactive elements responsible.

A discussion of the electronics and a detailed description of the apparatus used in the following experiments is given by Bramadat[3]. Figures (1) and (2) are photographs of the apparatus. Figure (1) shows the scaler unit, discriminator amplifier units, the power supply, the cathode ray oscilloscope and the camera. Figure (2) is a photograph of the castle and the cathode follower unit. The crystal can be seen projecting above the shielding of the cathode follower.

Occurrence of the Elements

The elements will be considered in order of relative abundance in the earth's crust, attention being confined to those which may be detected in the course of activation analysis. The results of Clarke and Washington's computations (Prof. Paper 125 U.S.G.S., 1924, 32) as to the composition of the "ten-mile crust" as calculated from chemical analyses, are given in Table I. The figures in Table I were used because they are given as a percentages and because the relative abundance of the oxides are also given.

Table I

Element	Per Cent	Oxide	Per Cent
Oxygen	46.71	SiO_2	59.07
Silicon	27.69	Al_2O_3	15.22
Aluminum	8.07	Fe_2O_3	3.10
Iron	5.05	FeO	3.71
Calcium	3.65	MgO	3.45
Sodium	2.75	CaO	5.10
Potassium	2.58	Na_2O	3.71
Magnesium	2.08	K_2O	3.11
Titanium	0.62	H_2O	1.30
Hydrogen	0.14	CO_2	0.35
Phosphorus	0.13	TiO_2	1.03
Carbon	0.094	P_2O_5	0.30
Manganese	0.09	MnO	0.11
Sulphur	0.052	SrO	0.02
Barium	0.05	BaO	0.05
Remaining elements	0.244	S	0.06
		Rest	0.31
	100.00		100.00

Despite their wide range in chemical composition igneous rocks are predominantly composed of eight of the elements in Table I. They are essentially multicomponent systems of O, Si, Al, Fe, Mg, Ca, Na, and K. These elements combine to form seven principal mineral groups, the silica minerals, feldspars, feldspathoids, olivine, pyroxenes, amphiboles, and micas. In addition to these, magne-

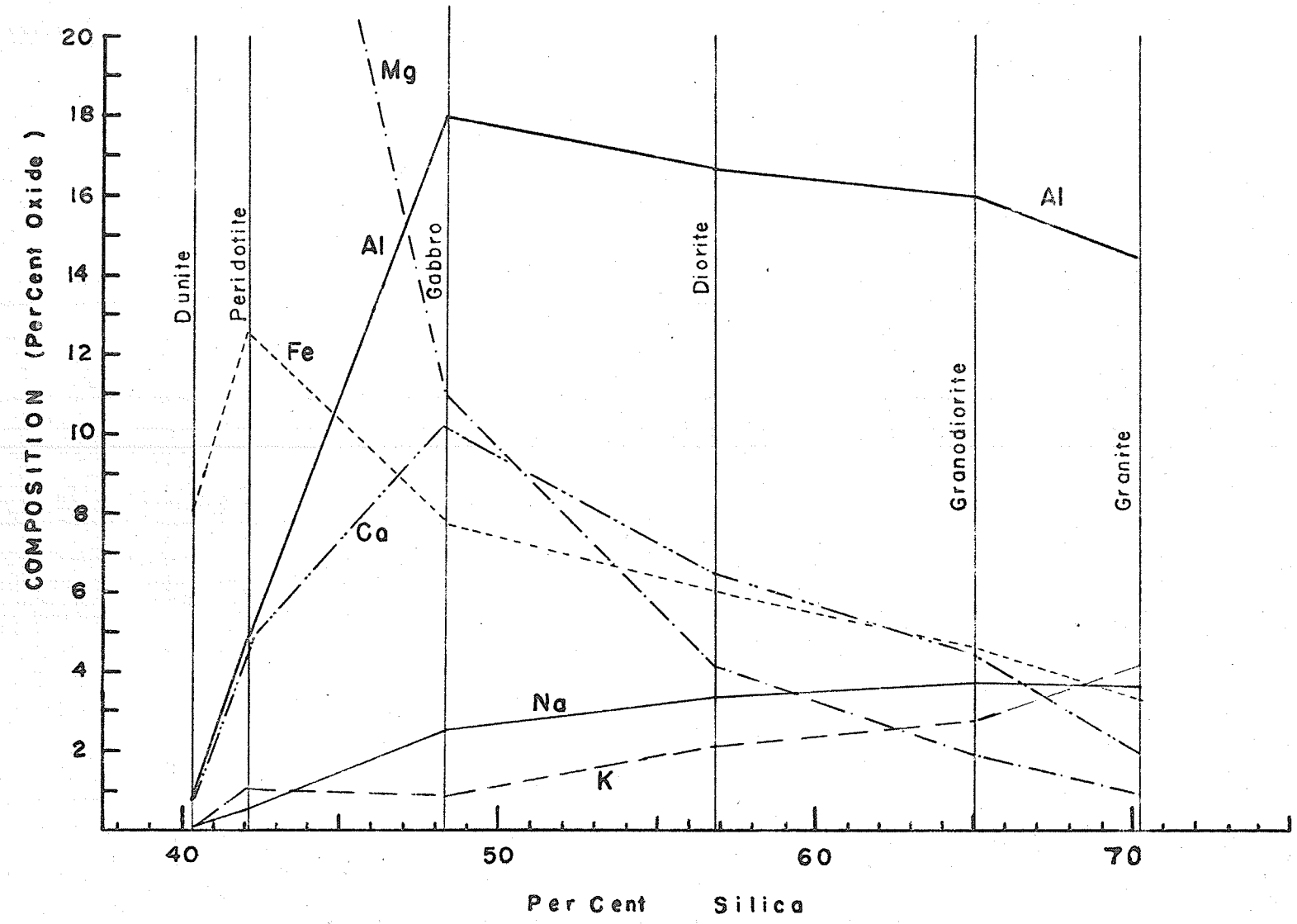

Fig. 3 - Silica variation diagram showing the average major element composition of the principal igneous rocks. From averages of Daly's analyses (7).

tite, ilmenite, and apatite are commonly found in very small amounts.

The above mentioned elements do not vary randomly but are interdependent. Because of its great variability silica is often used as a reference substance and all other oxides are plotted as dependent variables of the silica content. Figure (3) is a silica variation diagram of the common plutonic rocks taken from Daly's average analyses.(7)

Silicon after oxygen is the most abundant element in the earth's crust and is present in all igneous rocks either as silica or a silicate. The silica content of igneous rocks varies from 30% to 80% and this fact forms the bases of classification of igneous rocks. It is common to refer to the granitic rocks as acid, the gabbroic rocks as basic and those between as intermediate. This nomenclature has been adopted in this paper.

Aluminum is the most abundant of the metals in igneous rocks and is third in abundance in the lithosphere after oxygen and silica. It is an essential constituent of most igneous rocks and as can be seen from Figure (3) reaches a maximum of about 18% in the intermediate to basic rocks and a minimum in ultrabasic rocks.

Iron, after aluminum, is the next element in order of abundance in the outer portions of the lithosphere, but considering the earth as a whole, it is probably the most abundant metal. It occurs in the bivalent (ferrous) and trivalent (ferric) state in practically all rocks. However

since only total iron could be detected by activation analysis it is shown in this way in Figure (3). Iron shows a maximum of about 12% in the ultrabasic rocks and minimum (4%) in the acidic rocks.

Magnesium is the eighth most abundant element in the earth's crust. It is present in almost all igneous rocks where it forms ferromagnesium minerals. The magnesium content of igneous rocks shows a maximum in the ultrabasic rocks and decreases exponentially towards the acid end.

Calcium is one of the most widespread metals, coming fifth on the list of elements but third among the oxides of the outer lithosphere. It is an essential constituent of a great many of the rock forming minerals. Like aluminum the maximum amount of calcium occurs in gabbroic rocks.

The two principal alkali metals, sodium and potassium take sixth and seventh places in relative abundance in the lithosphere. They are essential to several of the most ubiquitous groups of rock forming minerals such as the feldspars, the feldspathoids, the micas, pyroxenes and the amphiboles. They are both most abundant in the acid rocks and decrease to minor amounts in the ultrabasic rocks.

In addition to those elements already discussed C, Ti, P, Mn, Sr, Ba, are also found in minor amounts in most igneous rocks. Carbon generally occurs in amounts less than 1%. The only rock-forming silicate of importance containing carbon as an essential constituent is cancrinite which occurs in association with nepheline; however carbon may be intro-

duced during such processes as scapolitization. Titanium is most common in rocks of less than 50% silicon. It is generally found in amounts less than 1.5% but in the more basic rocks may reach 4% or more. Phosphorus is an essential element of apatite. In igneous rocks the quantity of $P_2 O_5$ usually lies between 0.10 and 0.5 per cent, and is more abundant in basic rocks. The Mn O content of a great majority of igneous rocks lies between 0.05 per cent and 0.20 per cent, the higher figure being encountered in more basic rocks. It is held principally by the various ferromagnesian minerals. In the great majority of igneous rocks Ba O varies from zero to 0.25 per cent and is found among the silicates. The minerological location of strontium is still doubtful but it appears to be associated with the ferromagnesian minerals. The average for Sr O in igneous rocks is about 0.05 per cent.

Uranium and thorium and very minor amounts of radium occur in most igneous rocks. Many granites and related rocks contain about 0.003 per cent uranium or thorium oxide. The amount in the basic rocks is appreciably less. Due to the radioactive nature of these elements their presence will be detected with the scintillation counter. The concentrations and occurrences of the minor elements have been obtained from Groves.(8)

It is not expected that these minor elements will be detectable by activation analysis methods, however, they are mentioned here because they might interfere with the

detection of the more abundant elements. Manganese, which has a large cross section for thermal neutrons and can be present in igneous rocks in amounts up to 1 per cent, could, however, interfere with the detection of elements such as sodium since they both possess long lived isotopes.

Activation Conditions in Igneous Rocks

All the elements listed in Table I might be expected to contribute to the final activity of the bombarded rock sample. In order to estimate the magnitude of this contribution the relevant characteristics of the elements involved have been listed in Tables 2 and 3. Table 2 shows the nuclear data for thermal neutron activation and Table 3 for fast neutron activation. Most of the figures quoted have been taken from the National Bureau of Standards Circular 499, Nuclear Data.[9] The list does not include oxygen or carbon as their most abundant isotopes are transformed to other stable isotopes by neutron bombardment. The neutron capture cross section σ is expressed in "barns", 1 barn = 10^{-24} cm^2. This expresses the probability of interaction between the bombarding particle and the target nuclei by giving the effective target area.

From Nuclear Data, N.B.S. Circular 499 the reactions for aluminum 27 and silicon 28, 29 and 30, for fast and thermal neutrons are:-

Al^{27} - abundance 100%.

Reactions		Cross Section (Barns)	
(1) Al^{27} (th n, γ) 2.3 min. Al^{28}		0.21	
(2) Al^{27} (~1mev.n, γ) 2.3 min. Al^{28}		0.41	millibarns
(3) Al^{27} (~1mev. , γ) 4.6 min. Mg^{27}		2.80	millibarns
(4) Al^{27} (~1mev. n, γ) 14.9 hours Na^{24}		0.60	millibarns

TABLE 2

Nuclear Data for Thermal Neutron Activation

Element	Target Nucleus	Abundance %	Cross Section in barns	Isotopes Produced	Half Life	Energy of γ-ray mev.
Si	$_{14}Si^{30}$	3.12	0.12	Si^{31}	2.7^{h}	--
Al	$_{13}Al^{27}$	100.00	0.21	Al^{28}	2.3^{m}	1.8
Fe	$_{26}Fe^{54}$	5.9	--	Fe^{55}	2.9^{y}	--
	$_{26}Fe^{58}$	0.33	0.8	Fe^{59}	47^{d}	1.1, 1.3.
Mg	$_{12}Mg^{26}$	10.97	0.05	Mg^{27}	9.6^{m}	0.8, 1.0
Ca	$_{20}Ca^{44}$	2.13	0.6	Ca^{45}	152^{d}	--
Na	$_{11}Na^{23}$	100.80	0.6	Na^{24}	14.9^{h}	2.758 1.38
K	$_{19}K^{39}$	93.08	3	K^{40}	$1.6X10^{9y}$	1.45
Ti	$_{22}Ti^{50}$	5.34	0.14	Ti^{51}	6^{m}	--
Mn	$_{25}Mn^{55}$	100.00	13.00	Mn^{56}	2.59^{h}	$2.13\ {}^{1.81}_{0.845}$
P	$_{15}P^{31}$	100.00	$^{0.2}_{0.15}$	P^{32}	14.3^{d}	--
Sr	$_{38}Sr^{86}$	9.86	1.3	Sr^{87}	2.75^{h}	0.37
Ba	$_{36}Ba^{138}$	71.66	0.5	Ba^{139}	85^{m}	0.165

TABLE 3

Nuclear Data for Fast Neutron Activation

Element	Target Nucleus	Abundance %	Cross Section Millibarns	Isotopes Produced	Half Life	Energy of γ-ray mev.
Si	$_{19}Si^{28}$	92.19	3.0	Al^{28}	2.3^m	1.80
	$_{14}Si^{29}$	4.7	2.7	Al^{29}	6.7^m	1.2, 2.3
	$_{14}Si^{30}$	3.12	0.12	Si^{31}	2.7^h	-- --
Al	$_{13}Al^{27}$	100	0.4	Al^{28}	2.3^m	1.80
	$_{13}Al^{27}$	100	2.8	Mg^{27}	9.6^m	1.01, 0.84
Mg	$_{12}Mg^{26}$	10.97	0.6	Mg^{27}	9.6^m	1.01, 0.84
K	$_{19}K^{41}$	6.91	2.9	K^{42}	12.44^h	1.51
Mn	$_{25}Mn^{55}$	100.00	3.5	Mn^{56}	2.59^h	2.13, 1.81, 0.845
Ba	$_{56}Ba^{138}$	71.66	2.6	B^{139}	85^m	1.65

S^{28} abundance 92.2%

Reaction			Cross section
(5) Si^{28}	($\sim$1mev n,p)	2.3 min. Al^{28}	3.0 millibarns

Si^{29} abundance 4.7%

(6) Si^{29}	($\sim$1 mev.n,p)	6.7 min. Al^{29}	2.7 millibarns

Si^{30} abundance 3.1%

(7) Si^{30}	(th n, γ)	2.7 hr. Si^{31}	0.12 barns
(8) Si^{30}	(1 mev n, γ)	2.7 hr. Si^{31}	1.1 millibarns

The associated gamma ray energies are given in tables 2 and 3.

Reactions (1) and (7) show that aluminum and silicon have only one reaction with thermal neutrons. The half-life of Si^{31} is sufficiently long to provide a means of differentiating between these two elements in an activated sample.

Experimentally, however, it was found impossible to thermalize all neutrons emitted from the source. The source, in the tank, is almost completely surrounded by transformer oil, neutrons could therefore be deflected and be incident on the sample. These deflected neutrons would be only partially thermalized. In such a case reaction (5) would take place and would provide a small but significant contribution to the initial activity of the aluminum component. It would therefore be necessary to analyze for silica first and apply a correction factor for this contribution.

Reactions (2) and (5) show that aluminum Al^{27} and silicon Si^{28} both produce Al^{28} when bombarded with fast neutrons. The cross section for Al^{27} in reaction (2) is only 0.41 millibarns whereas that for Si^{28} is 3.0 millibarns or 7.5 times larger. The relative abundance of Al^{27} is 100 per cent and that of Si^{28} is 92.2% a difference of only 7.8 per cent. Thus the major part of the initial activity of a mixture of silicon and aluminum in equal proportions would be due to the silicon reaction. The aluminum contribution to a silica analysis of a rock is not as serious as it first appears. Figure (3) shows that the alumina content of igneous rocks is fairly constant, varying only a few per cent from acid to basic rocks. Therefore by using chemically analysed rocks as standards and comparing the initial activities of the standard samples and an unknown sample the error introduced to the silica analysis would be due to variation in alumina from the norm established by the stand-

ard rather than from the total alumina content of the rock. In most cases this error would be very slight and well within the limits of statistical error.

Thus it is proposed to show by the following experimental results that the activation analysis of rocks for silica is feasible.

Experimental Procedure

In the course of the following experiments a 2 curie polonium-beryllium neutron source was used. The neutron flux of a curie of polonium is 2.5×10^6 neutrons per second per cm^2. This neutron source has a definite period of decay due to the decay of Po^{210}, which has a half life of 138.9 days. The actual neutron flux thus changes daily. This change was corrected for by determining a standard silica sample with each series of experiments.

Before proceeding with experiments on silicon analyses the following preliminary considerations were made:-

1. Calibration of the discriminator was accomplished by plotting a differential curve of a Cs^{137} source. All counts taken throughout the experiments were integral counts. The 665 kev. energy peak for Cs^{137} occurs at a dial setting of 24 volts. From this relationship the dial was calibrated in terms of energy. The dial was set at 6 volts thereby eliminating all pulses less than 166 kev.

2. The grain size and size of the samples were standardized. Bramadat[3] found that the activity of a speci-

fic element was independent of the grain size of the mineral in which it occurs provided the detector geometry is constant. To maintain uniform detector geometry from sample to sample, 300 gram samples, crushed to minus 1/4 inch mesh were used. In the case of the higher specific gravity ultrabasic rocks larger samples would be necessary to maintain a uniform geometry. The use of standard amounts of sample greatly facilitated the comparison of the initial counting rate and therefore the percentage of silica in the various samples.

3. In silica and alumina determination we are dealing with an Al^{28} isotope which has a half life of 2.3 minutes. The irradiation time for these determinations should therefore be proportional to 2.3 minutes. In the following experiments a six minute irradiation period was allowed. A six minute irradiation period decreased the error due to starting or stopping the stop watch when the sample was placed in or removed from the source area.

4. When an igneous rock was placed on the detector an increase in the normal background count occurred due to the presence of U, Th and K^{40} in the rock. This increase was termed the natural radioactivity of the rock. The total background count of a specific sample was subtracted from the counts per unit of time after irradiation. In this way only the counts due to activated elements in the sample were obtained.

5. A thirty second time lag was allowed after the sample was removed from the source area before the counting period was started. This period allowed sufficient time to place the container on the detector crystal, to replace the necessary cover and shields and to start the counting period at a precise moment in each case. The graphs, showing the decay curves of the isotopes formed after irradiation, were extrapolated to correct for this time lag. Thus the initial activity or the number of counts at time = 0 were obtained.

6. Cumulative counts were taken, the counter being read every 30 seconds for the first 6 minutes and every minute for the remainder of the decay period. The counting rate for any specific time is the difference between the reading at that time and the one immediately preceding. The minute counts were divided by 2 and plotted as 30 second counts. The counts per 30 seconds were plotted as ordinate against time on semi-logarithmic graph paper. The count after the first half minute was plotted at .25 minutes on the graph, the count after 1 minute at 0.75 minutes etc., up to six minutes. The 30 second count after 7 minutes of decay was plotted at 6.5 minutes etcetera.

7. A thirty second check count was taken with a small Cs^{137} source in a standard position before and after every determination. If the difference in the two checks amounted to more than 2 per cent of the total it was assumed that an instrumental fluctuation occurred during the determination. The results were, therefore, discarded.

Fast Neutron Irradiation

Fast neutron irradiation was accomplished by placing the neutron source on a pedestal about five feet in height situated in the centre of the laboratory. The arrangement used is shown diagrammatically in Fig. (4). The location and height of pedestal were intended to keep the source as far away from thermalizing substances as possible. The sample, in a plastic container such as is shown in Fig. (5), was irradiated by placing it over the bare neutron source. The cylindrical opening in the centre of the container was originally intended to surround the detector crystal. The container was, therefore, very suitable for fast neutron irradiation. It was found that this method of fast neutron irradiation afforded excellent bombardment geometry since the source was almost completely surrounded by the sample. The neutron source was transported by means of long handled tongs. The sample was placed on and removed from the source by means of a special hook arrangement on the handle of the tongs. The only difficulty encountered during the experiments was one of timing since a few seconds were required to remove the tongs from the sample after it had been placed on the source before the stop watch was started. A more mechanical method of placing the sample on the source would eliminate this difficulty. As a safety precaution the source was removed to the tank in the first thirty seconds after the counting period was started.

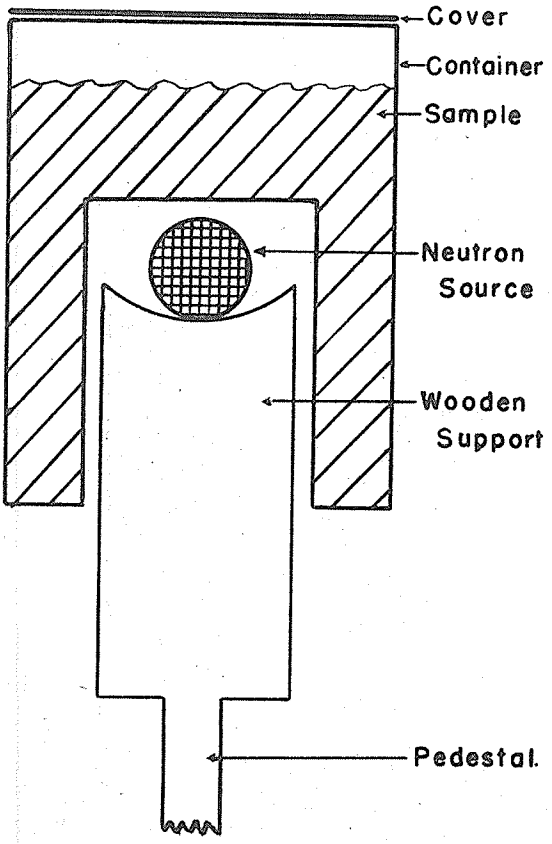

Fig. 4 - Diagram of method of fast neutron bombardment.

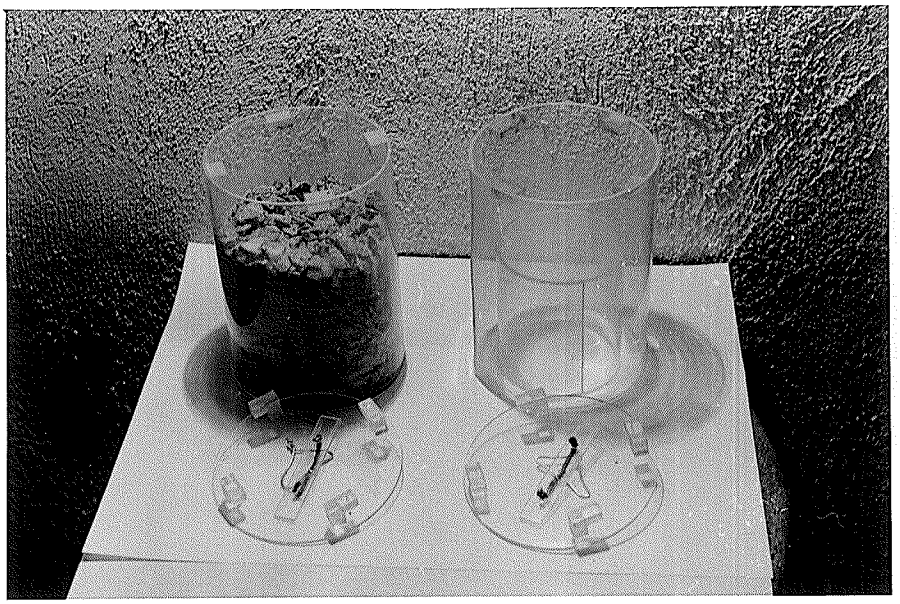

Fig. 5--Photograph of containers

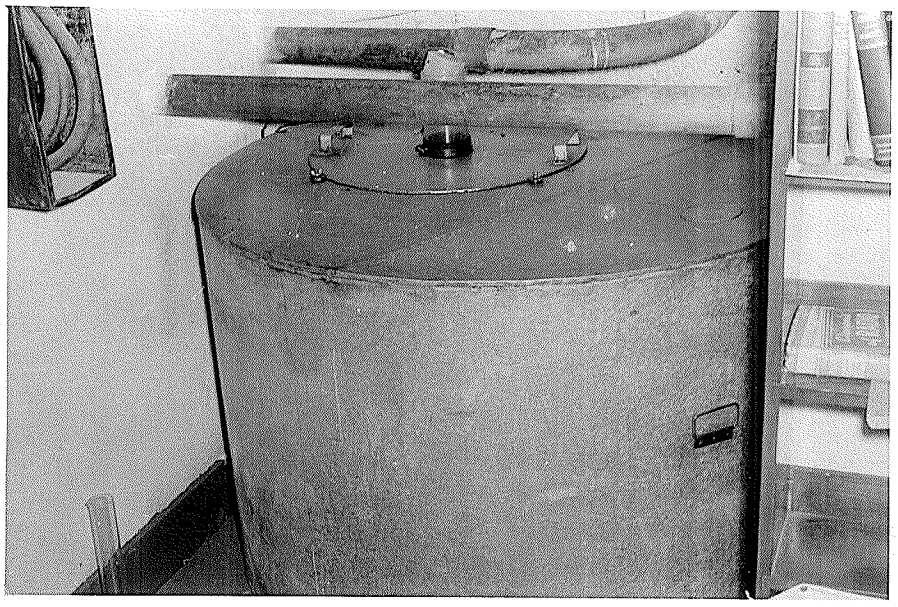

Fig. 6--Photograph of tank

Thermal Neutron Irradiation

The method of thermal neutron irradiation is essentially that used by Bramadat.[3] The neutron source was housed in a cylindrical tank 4½ feet in diameter by 3 feet high. Figure (6) is a photograph of the tank. The outre tank, which contains water, encloses an oil filled inner tank 2 feet in diameter by 2½ feet high. The neutron source was contained in a plastic cylinder, 18 inches long, 4 inches in diameter, sealed at one end and inserted to a depth of 10 inches in the centre of the inner tank. The source was then covered by 5.75 cm. of paraffin. The fast neutrons emitted by the source were thermalized by the paraffin, the hydrogenous oil of the inner tank and water of the outre tank. The sample to be irradiated was placed in the container and lowered into the paraffin covering the source.

Experimental Results

Experiments were carried out with chemically analysed rock samples and with relatively pure silica sand to determine the precision and accuracy of the method. No synthetic samples were used since it is impossible to simulate the exact condition under which the elements occur in igneous rocks.

An excellent series of very accurately analysed igneous rocks were obtained from the Rock Analysis Laboratory of the University of Minnesota. The analyses of these rocks are shown in Table 4. These rocks cover the complete range of igneous rocks from very acid (Granite R-1883 containing 77.75 per cent silica) to very basic (Ultramafic gabbro

R-1767 containing 38.91 per cent silica). The silica used as a standard was a naturally occurring sand found on Black Island, Lake Manitoba. The sand samples used and the analysis were obtained from the Manitoba Mines Branch. The chemical analysis of the sand was:

Silica (SiO_2) - - - - - - - - -	99.33%
Iron Oxide (Fe_2O_3) - - - - - -	0.03%
Alumina (Al_2O_3) - - - - - - -	0.28%
Lime - - - - - - - - - - - - -	0.12%
Magnesia - - - - - - - - - ---	0.15%
Traces of soda, potash and loss on ignition - - -	0.09%

TABLE 4

Chemical Analyses of Rock Standards.

Rock Number	R-1883	R-1737	R-1738	R-1751
SiO_2	77.75	65.49	64.13	58.45
Al_2O_3	12.71	14.49	16.77	15.71
Fe_2O_3	0.39	2.11	1.96	1.61
FeO	0.47	2.90	1.69	6.76
MgO	0.34	2.45	1.29	1.34
CaO	0.68	4.29	2.72	4.97
Na_2O	6.24	2.80	3.92	4.08
K_2O	0.40	3.66	5.77	3.98
H_2O^+	0.38	0.56	0.39	0.31
H_2O^-	0.13	0.05	0.19	0.08
CO_2	0.40	0.05	0.02	0.23
TiO_2	0.21	0.65	0.52	1.46
P_2O_5	0.01	0.21	0.23	0.61
MnO	0.01	0.10	0.05	0.14
SrO		0.04	0.02	--
BaO		0.05	0.10	0.14
S		0.01	0.01	0.07
Rock Name	Soda Clase Granite	Granod-iorite	Monso-nite	Syenite Gneiss

Rock Number	R-1803	R-1982	R-1987	R-1767
SiO_2	54.75	49.65	41.31	38.91
Al_2O_3	12.20	13.22	12.12	6.98
Fe_2O_3	6.48	1.58	3.52	4.93
FeO	8.78	11.76	14.57	29.07
MgO	2.97	5.44	6.58	3.85
CaO	4.08	8.98	11.07	6.55
N_2O	4.18	2.71	2.06	1.00
K_2O	1.17	0.97	0.16	0.42
H_2O^+	1.61	0.59	0.44	0.34
H_2O^-	0.15	0.18	0.06	0.07
CO_2	1.52	0.04	0.05	--
TiO_2	1.50	3.93	7.04	4.70
P_2O_5	0.15	0.53	0.63	1.61
MnO	0.16	0.21	0.21	0.52
SrO	--	--	--	--
BaO	0.05	--	--	--
S	0.34	0.08	0.10	FeS_2 - 0.98
Rock Name	Granophyric Diabase	Basalt Dike	Basalt Hornfels	Garnetiferous Ultramafic Gabbro

Chemically pure alumina (Al_2O_3) and a cylinder of aluminum metal, machined to envelope the crystal were used as aluminum standards.

(a) Natural radioactivity

The causes of natural radioactivity in rocks may best be studied by examination of the spectrum displayed on the cathode ray oscilloscope. Photographs of the spectrum of similar amounts of four unactivated rocks are shown in Figures (7, 8, 9 and 10). These photographs required a four hour exposure and Kodak Contact Process Ortho film was used. A standard Cs^{137} spectrum is shown on each photograph for comparison purposes. In addition to the photographs the background count due to natural radioactivity was determined. The rock name, the figure number of its spectrum, its silica content and its natural radioactivity background count are

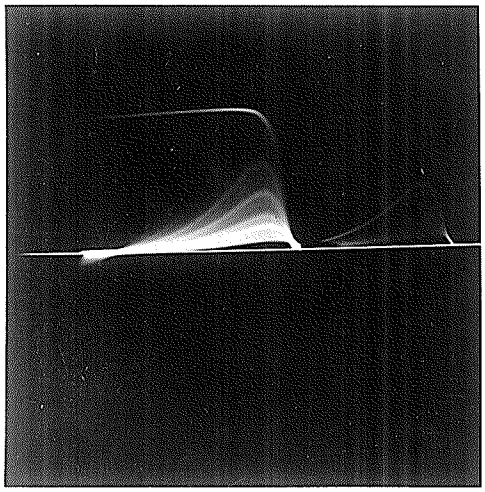

Fig. 7--Spectra of Cs^{137} and Granite R-1883.

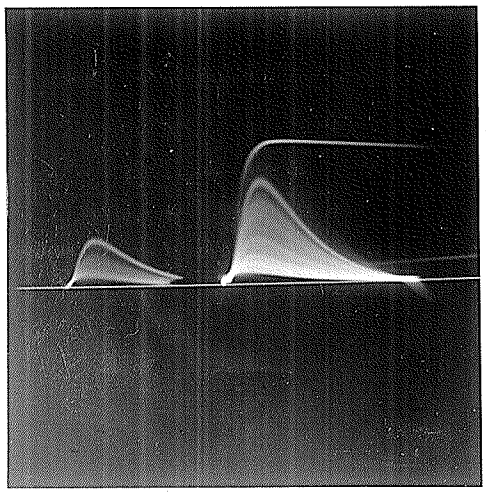

Fig. 8--Spectra of Cs^{137} and Monzonite R-1738.

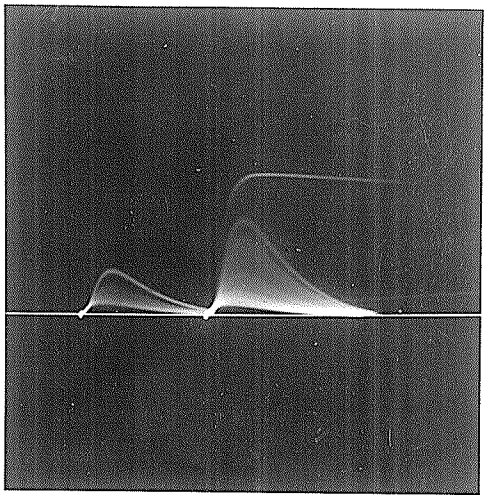

Fig. 9--Spectra of Cs^{137} and Syenite R-1751.

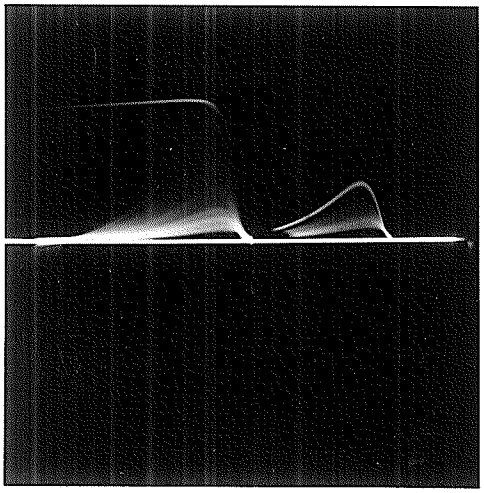

Fig. 10--Spectra of Cs^{137} and Basalt R-1982.

shown in Table 5.

TABLE 5

Rock Name & Number	Figure No. of Spectrum	Silica content	Natural Radioactivity
Granite - R1883	(7)	77.75%	380 c.p.30 sec.
Monzonite - R1738	(8)	64.45%	260 c.p.30 sec.
Syenite - R1751	(9)	58.45%	155 c.p.30 sec.
Basalt - R1982	(10)	49.65%	105 c.p.30 sec.

The most prominent lines of each of the above mentioned spectrum was measured on a reading screen and compared with the standard Cesium^{137} line (.665 Mev.). All four spectra exhibited a prominent line at .60 Mev. (Ra) Examination of N.B.S. Circular 499 showed that thorium has a gamma ray of this energy. The spectrum for granite R-1883 Fig. (7) has a line at .96 Mev. which corresponds to a reported gamma ray of uranium. (Th) The potassium K^{40} line at 1.45 Mev. (1.459) is evident in all the spectra except that of granite R-1883 Fig. (7) which contains only 0.40 per cent potassium oxide (Table 4). This line is also very weak in Fig. (10) basalt R-1982 which contains 0.97 per cent potassium oxide. Lines representing energy levels lower than 0.60 Mev. are probably present but there values were unobtainable. Similarly the blocked pulse in each spectra may be partially due to a higher energy gamma ray of thorium.

Since the spectrum shown in Figures (7, 8, 9 and 10) and others examined, represented a relatively wide range of igneous rocks it was assumed that they were fairly repre-

sentative of igneous rocks in general. Further examination of the spectra indicated that there was no line within about 0.1 Mev. of the K^{40} line at 1.45 Mev. This suggested a possible method of analysis for potassium by employing a differential discriminator. By adjusting the bias on the differential discriminator to count pulses greater than 1.42 Mev. and setting the gate width at about 0.06 Mev. only counts due to potassium (K^{40}) would be counted. Comparison of the number of counts obtained from the same mass of a known rock with that of an unknown rock would produce a quantitative estimate of the potassium content. Unfortunately time did not permit further experimentation in this field.

(b) Fast and thermal bombardment of Aluminum and Silicon.

Before proceeding with the experimental results obtained by irradiating silicon and aluminum with fast and thermal neutrons it might be appropriate to rewrite the major reactions.

Si^{28} abundance 92.2%

(1) Reaction, Si^{28} ($\sim$1 mev. n, p) 2.3 min Al^{28}, cross section 3.0 mb. Al^{28} has one associated gamma ray with an energy of 1.8 mev.

Si^{28} has no reported cross section for thermal neutrons.

Al^{27} - abundance 100%.

Reactions (Cont'd)

Reactions	Cross section	Gamma Ray Energy
(2) Al^{27} (thn, γ) 2.3 min Al^{28}	0.21 mb	1.8 mev.
(3) Al^{27} ($\sim$1 mev. n, γ) 2.3 Min. Al^{28}	0.41 mb	1.8 mev.
(4) Al^{27} ($\sim$1 mev. n, p) 9.6 min. Mg^{27}	2.8 mb	1.01, 0.84, 0.64 mev.

A 300 gram sample of silica sand was irradiated with fast and thermal neutrons for 6 minutes. After the necessary corrections were made on the number of counts obtained, the decay curves shown in Fig. (11) were plotted. The major component and subsequently the initial activities of these decay curves were determined. A photograph of the spectra, displayed on the oscilloscope, was also taken and is shown in Fig. (12).

Despite the fact that Si^{28} has no reported cross section for thermal neutrons decay curve A-Fig. (11) was obtained on irradiation. The half life of the isotope formed was 1.8 minutes which is very close to that of Al^{28} (2.3 minutes). The 0.84 grams of Al_2O_3 present in the sample was insufficient to account for this initial activity. The initial activity of the sample was 137 counts per 30 seconds or .45 counts per 30 seconds per gram of silica. The very weak spectrum shown in Fig. (12) is that obtained with thermal neutron irradiation. Because of the low intensity of the line produced it was impossible to compare it to the Ce^{137} standard.

The activity detected was obviously due to silica and it was assumed therefore that all the neutrons emitted

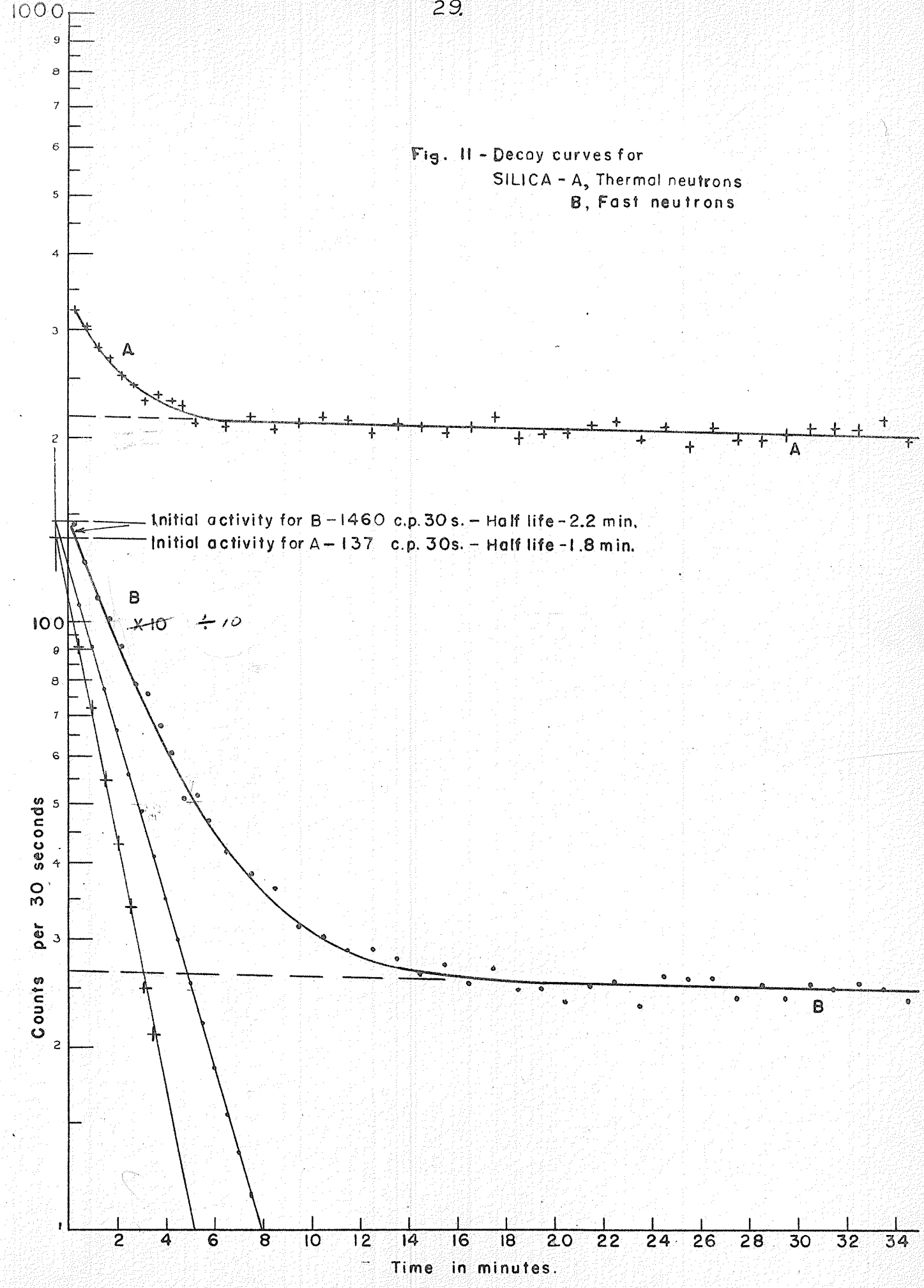

Fig. 11 - Decay curves for
SILICA - A, Thermal neutrons
B, Fast neutrons

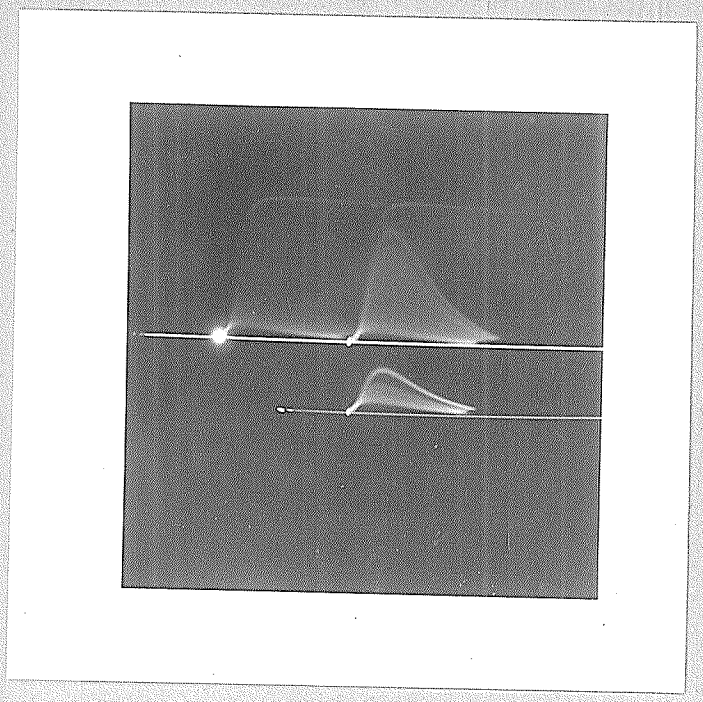

Fig. 12--Spectra of silicon irradiated with thermal neutrons, fast neutrons; and Cs^{137} standard.

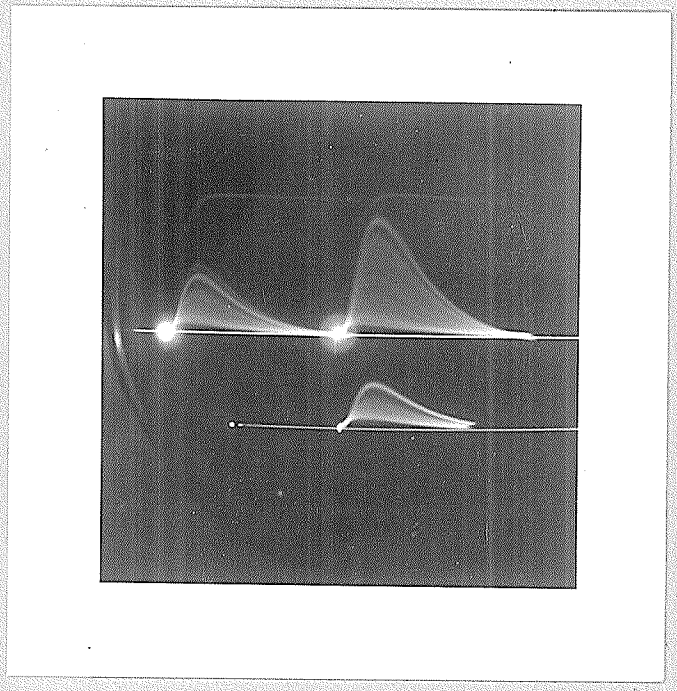

Fig. 13--Spectra of aluminum irradiated with fast neutrons, thermal neutrons; and Cs^{137} standard.

by the source when in the tank were not thermalized and reaction (1) took place. Since igneous rocks contain between 30 and 80 per cent silica the silica contribution to an alumina determination by thermal neutron irradiation would be appreciable. One method of overcoming this difficulty will be discussed in a later section.

Curve B Fig. (11) was the decay curve obtained when silica was irradiated with fast neutrons in the manner already described. The centred spectrum of Fig. (12) is the spectrum displayed on the oscilloscope after fast neutron irradiation. The half life of the major component of Curve B Fig. (11) is 2.2 minutes and is therefore equal to that of Al^{28}. The spectrum Fig. (12) exhibits a distinct line at 1.8 mev. which is the energy level of the Al^{28} gamma ray. These facts provided sufficient proof that the reaction Si^{28} ($\sim$ 1 mev. n, p) 2.3 min Al^{28} took place when silica was irradiated with fast neutrons in the manner previously described. Despite the low cross-section (3.0 millibarns) of Si^{28} for fast neutrons a relatively high initial activity of 1460 c.p. 30 seconds or 4.9 c.p. 30 seconds per gram of silica was obtained.

The relatively high initial activity and the comparatively short half life of the isotope formed on bombarding silica with fast neutrons indicated a possible method of quantitative silica determination. The method suggested a relatively high degree of accuracy because of the high initial activity and a rapid analysis because of the short half

life. Silica determinations by this method were carried out on the igneous rocks whose analyses are shown in Table 4. The results of these determinations will be discussed in a later section.

A 300 gram sample of alumina (Al_2O_3) was irradiated with thermal and fast neutrons for a 6 minute period. The resulting decay curves are shown in Fig. (14). The spectra, displayed on the oscilloscope, were photographed on the same film and are shown in Fig. (13).

Curve B, Fig. (14), was the decay curve resulting from the thermal neutron irradiation of the alumina sample. The half life of the major component of the decay curve was found to be 2.3 minutes. The initial activity of this component was 830 c.p. 30 seconds or 2.7 c.p. 30 seconds per gram of Al_2O_3. The centred image of Fig. (13) was the spectrum obtained with thermal neutron irradiation. This spectrum shows a line at 1.80 mev. which corresponds to the gamma ray energy for Al^{28}. Thus the gamma ray energy of the line in the spectrum and the half life of the major component indicated that reaction (2) had taken place and Al^{28} had been formed.

These results indicated that it should be possible to determine the alumina content of a rock quantitatively by means of activation analysis. However, it has been shown that silicon is activated when irradiated in the thermalizing unit available. The observed characteristics of the silicon component were identical to those of the aluminum

component and the two could not be distinguished from each other. Since all igneous rocks contain large amounts of silica the silica contribution would constitute a major error in an alumina determination. Time did not permit further investigation of this problem, however, a procedure for aluminum determination and a method of correcting for silica contribution will be proposed in a later section of this paper.

The decay curve obtained from the alumina sample with fast neutron irradiation is shown as curve A in Fig. (14). The image on the right in Fig. (13) was the spectrum obtained for the same procedure. Curve A was resolved into two components. Component A-1 has a half life of 2.3 minutes and an initial activity of 315 c.p. 30 seconds or 1.05 counts per 30 seconds per gram of Al_2O_3. The energy level corresponding to the isotope formed does not appear in the spectrum due to its short half life. The half life, however, indicates that the reaction Al^{27} (~1mev. n,γ) 2.3 min. Al^{28} has taken place.

The second component A-2 indicated the half life of the isotoped formed to be 9.8 minutes. The initial activity of this isotope was 220 c.p. 30 seconds. The half life and energy levels shown in the spectrum Fig. (13) are very nearly those of Mg^{27}. The measured spectral lines indicated gamma ray energies of 0.96 mev. and 0.83 mev. corresponding with the 1.01 mev. and .84 mev. levels of Mg^{27}. It was apparent therefore that the predicted reactions had taken place

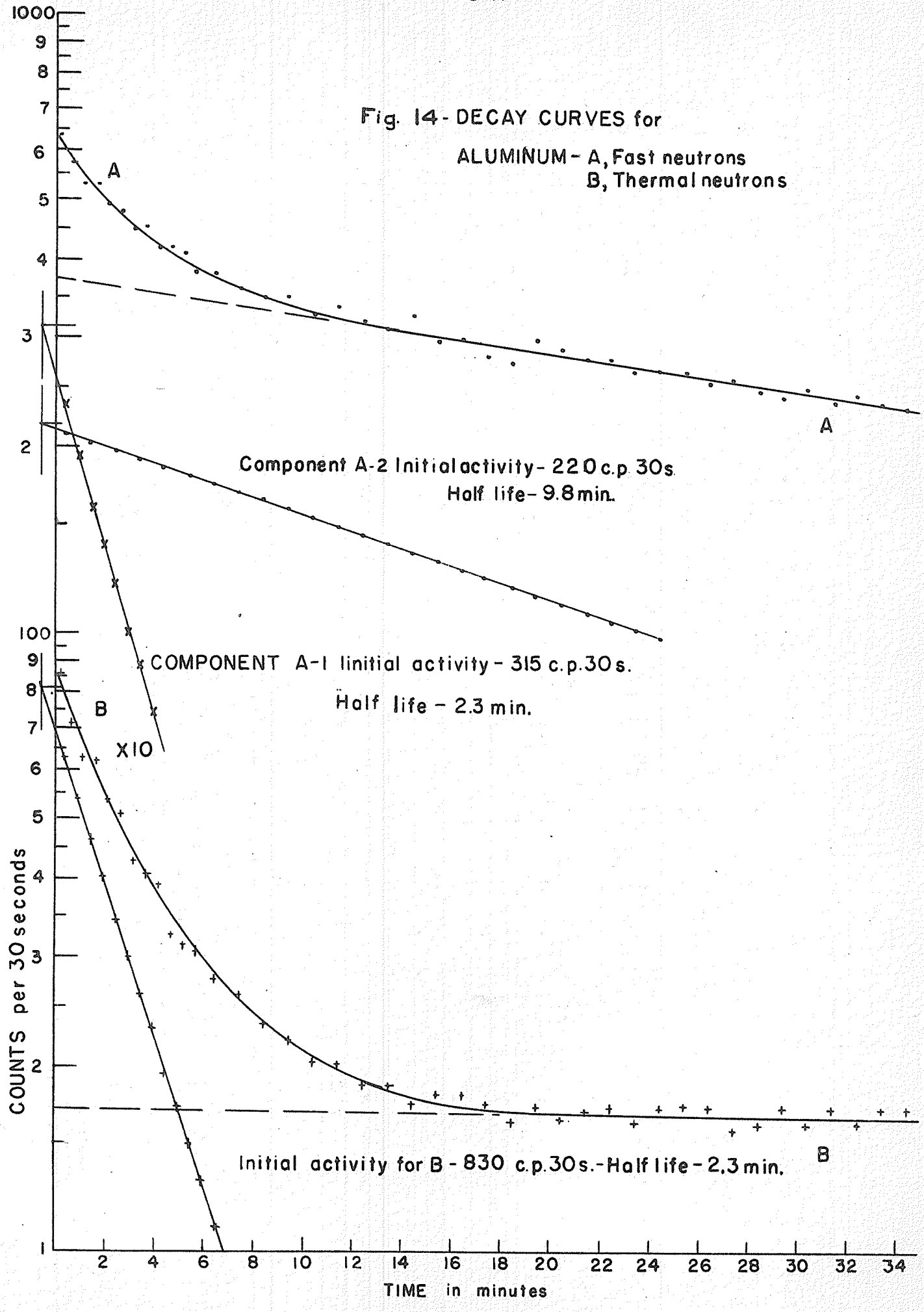
Fig. 14 - DECAY CURVES for
ALUMINUM - A, Fast neutrons
B, Thermal neutrons
A
A
Component A-2 Initial activity - 220 c.p. 30s.
Half life - 9.8 min.
COMPONENT A-1 linitial activity - 315 c.p.30 s.
Half life - 2.3 min.
B
X10
Initial activity for B - 830 c.p.30s. - Half life - 2.3 min.
B
COUNTS per 30 seconds
TIME in minutes
1000
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
1
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34

when alumina was irradiated with fast neutrons.

The silica content of igneous rocks varies from 30 to 80 per cent. The initial activities due to silica of igneous rocks irradiated with fast neutrons, determined from the initial activity of pure silica (Curve B, Fig. (11)) would vary from 441 c.p. 30 sec. to 1180 c.p. 30 seconds. The alumina content of the averages of igneous rocks shown in Fig. (3) varies from 1 per cent in a dunite to about 17 per cent in a gabbro. Thus the initial activity due to alumina in a 300 gram sample of an igneous rock could vary from 3 counts per 30 seconds to 52 counts per 30 seconds. This contribution would, therefore, introduce an appreciable error in a silica determination if the initial activity of a rock sample were compared to a standard silica activity. However, if the initial activity of the rock sample were compared to the initial activity of a similar rock standard the error introduced would be due to the difference in alumina in theknown and unknown samples and not the total alumina content. In most rock types this difference would amount to about 2.5 per cent Al_2O_3 or $\pm$7.5 counts per 30 seconds. Silica analyses of chemical analysed rocks were carried out in order to determine the precision and accuracy of themethod.

(c) Silica analysis of igneous rocks

The eight rock samples, the analyses of which appear in Table 4, were irradiated with fast neutrons for a standard period of time and the resulting decay curves plotted.

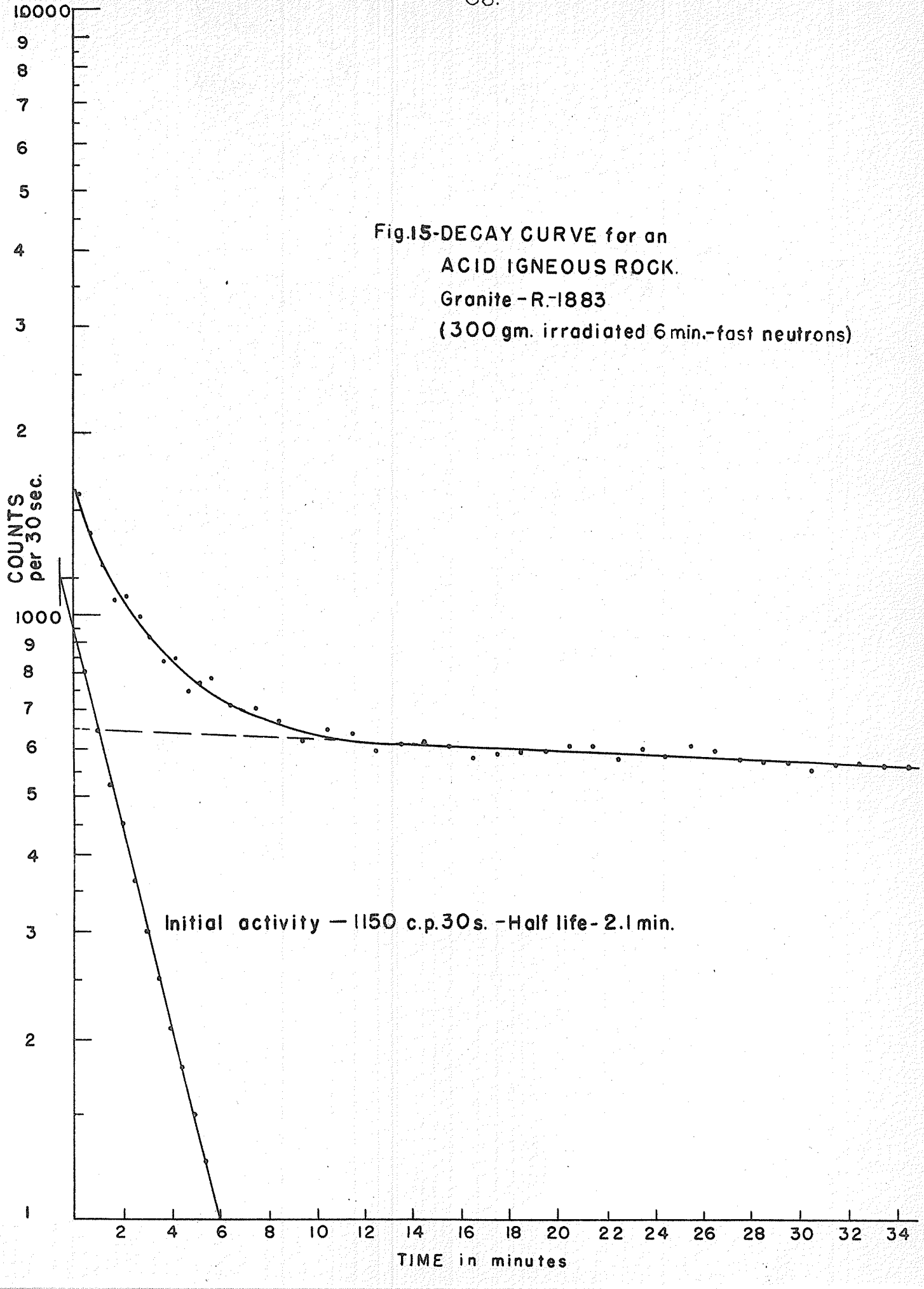

Fig.15-DECAY CURVE for an
ACID IGNEOUS ROCK.
Granite - R.-1883
(300 gm. irradiated 6 min.-fast neutrons)

The 2.3 minute component was determined for each curve and its initial activity, extrapolated to zero, was obtained. Examples of the decay curves obtained upon irradiation of an acid, intermediate and basic igneous rock are shown in Figures (15) (18) and (19) respectively. Photographs of the spectrum, displayed on the oscilloscope, for two of these rocks are shown in Figures (16) and (17). The 1.8 mev. energy level for Al^{28} is visible in both spectra.

The results of a series of samples determined on the same day are shown in Table 6.

TABLE 6

Fig. No. of Decay Curve	Sample Number	Per Cent Silica	Initial Activity counts per 30 seconds	Counts per 30 sec. per gram Silica.
(15)	R-1883	77.75	1150	4.94
(21)	R-1738	64.13	960	4.98
(18)	R-1751	58.45	860	4.93
(19)	R-1982	49.65	739	4.95
	R-1767	38.91	640	5.48
(11)	Silica Sand	99.33	1460	4.91

The values per gram silica (Column 5) are from .5 to 1.5 per cent higher than that obtained for silica sand, with the exception of R-1767. The higher counts per gram of silica in the rocks is to be expected since the rocks contain alumina. The large increase in counts per gram silica of R-1767 over the standard silica value cannot be accounted for by its alumina content and must, therefore, be attributed

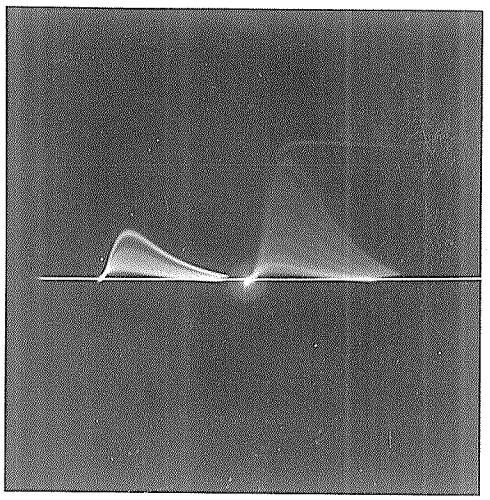

Fig. 16--Spectra of Cs^{137} and activated Granite R-1883.

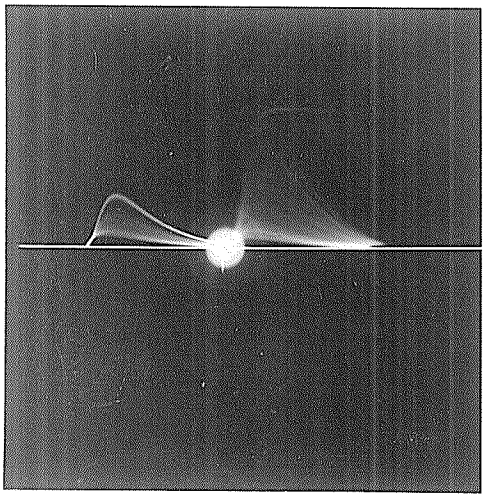

Fig. 17--Spectra of Cs^{137} and activated Monzonite R-1738.

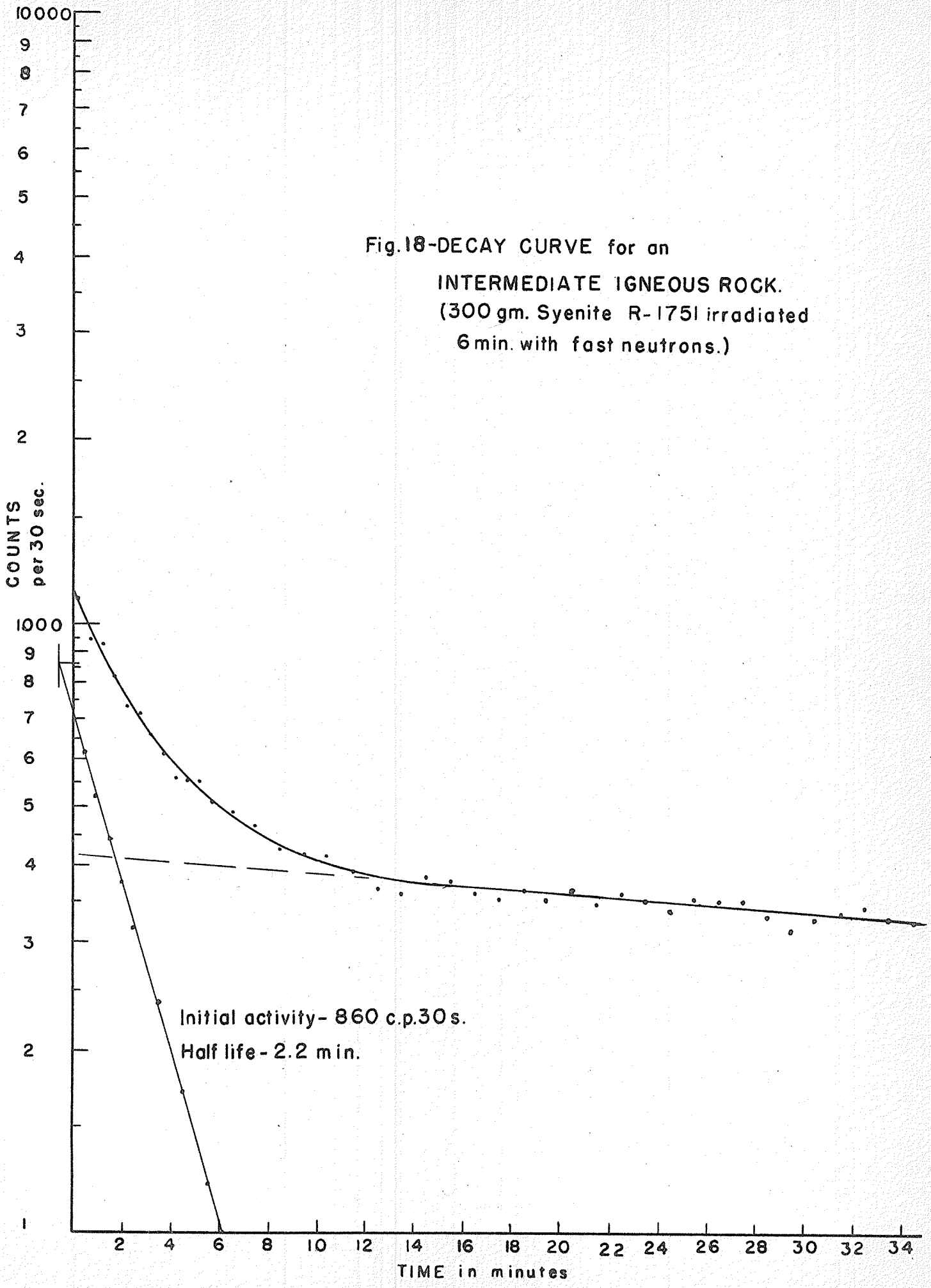

Fig. 18-DECAY CURVE for an INTERMEDIATE IGNEOUS ROCK. (300 gm. Syenite R-1751 irradiated 6 min. with fast neutrons.)

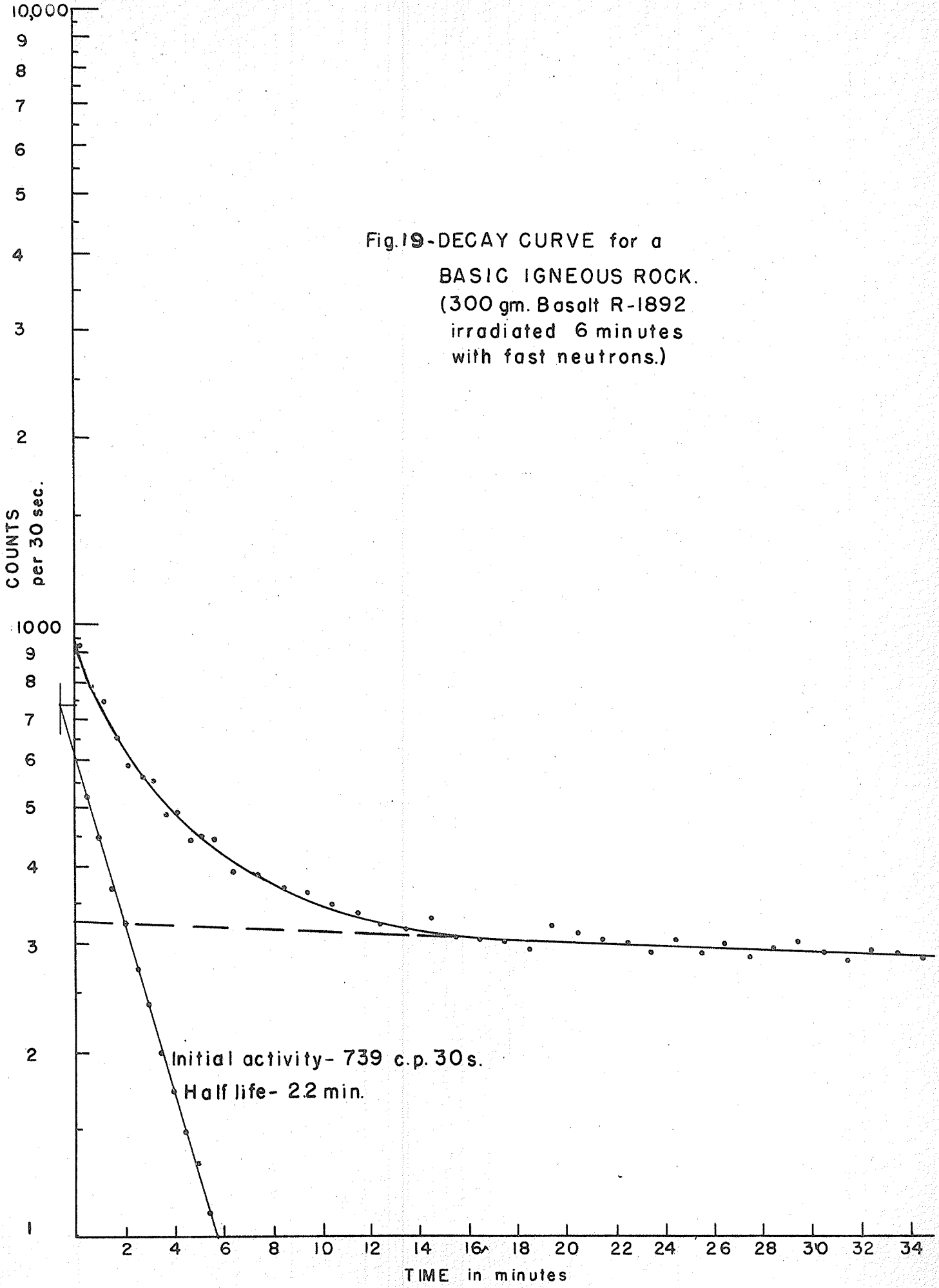

Fig. 19-DECAY CURVE for a BASIC IGNEOUS ROCK. (300 gm. Basalt R-1892 irradiated 6 minutes with fast neutrons.)

to instrumental fluctuations or personal errors in procedure or both.

The initial activities of these rocks were plotted as ordinate on linear graph paper against the percentage silica (SiO_2). This graph is shown in Fig. (20) and the results of Table 6 are indicated thus (+). By drawing the best line to fit the values obtained a perfectly linear relationship was found to exist. Previous silica analyses, extrapolated to fit the linear plot of the analyses of Table 6, are shown as dots, circles and X's in Fig. (20). Assuming the best line obtained in a series of analyses to represent the correct value it is possible to assign an error to each value obtained. The error in a determination of a known rock would be the difference in the value obtained by projecting the initial activity to the best line and true value and can be expressed as per cent silica or as per centage error.

The limits of error of themethod can be calculated. The statistical fluctuation of each count is equal to plus or minus the square root of the count. Figure (21) shows a decay curve of an activated rock with the possible statistical fluctuation of each point plotted on the point. In order to ascertain the possible error of the initial activity, the statistical fluctuation of each point of the 2.3 minute component was plotted; the best line was drawn and the initial activity determined. In addition to the best line a maximum and minimum best line was drawn and the resultant initial

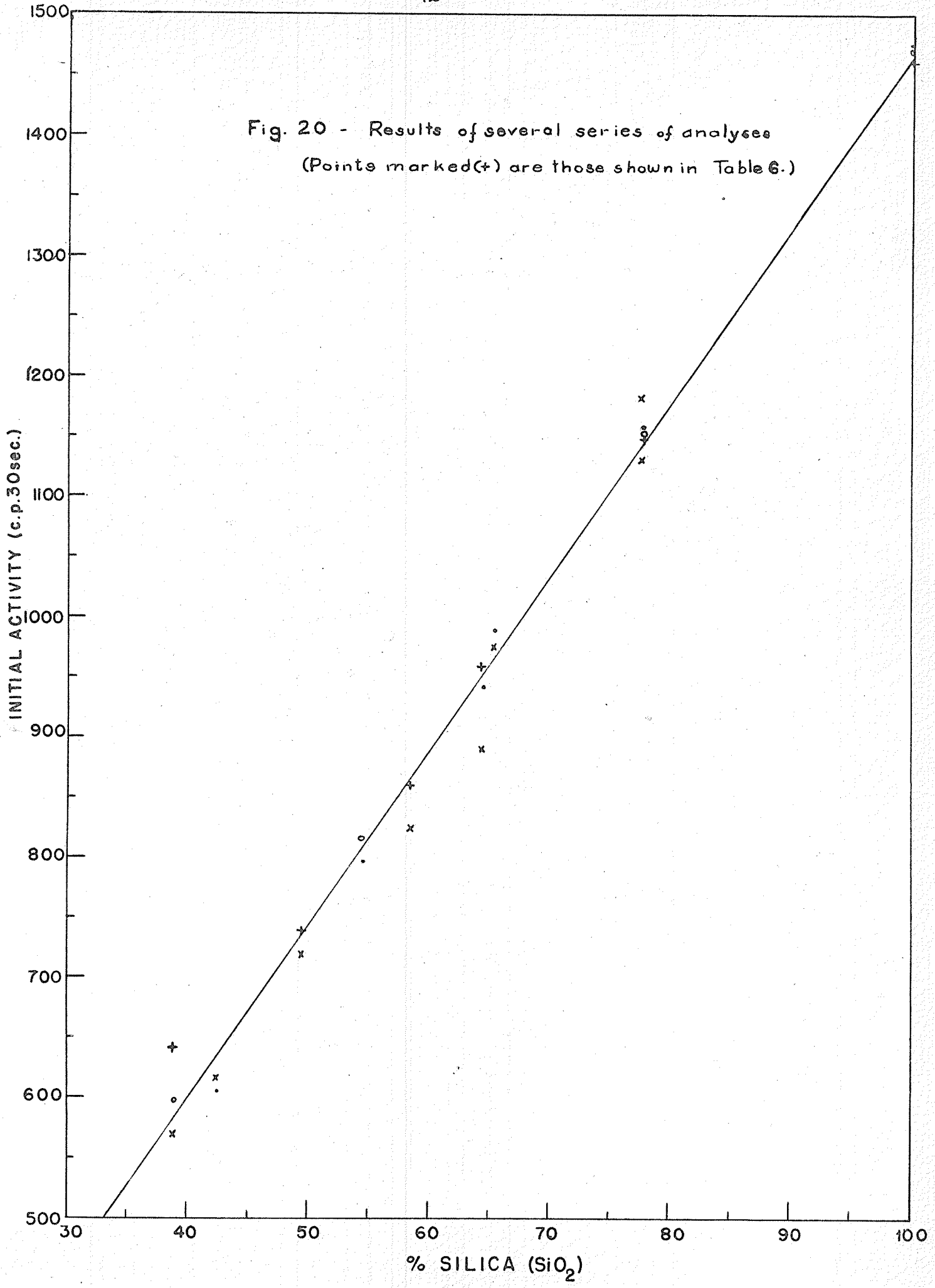

Fig. 20 - Results of several series of analyses
(Points marked(+) are those shown in Table 6.)

activities determined. The maximum initial activity was found to be 980 counts per 30 seconds, the normal initial activity 960 counts and the minimum 940 counts per 30 seconds. The error, therefore, was found to be $\pm$ 20 counts per 30 seconds or $\pm$ 2.08 per cent.

The balance used in weighing out samples was found to weigh accurately to about 0.1 gram. The weighing error therefore, would be $\pm$ 0.03 per cent. In terms of initial counts this would be $\pm$ 0.30 counts per 30 seconds.

It was found that the initial activity of a sample increases very little after a 4.5 minute irradiation period. The error due to timing would, therefore, be very small or negligible if a 6 minute irradiation period is used. The total error on the results of a determination are, therefore, the sum of the statistical error and the weighing error which is $\pm$ 2.11 per cent. In the case of Syenite R-1738 this would amount to $\pm$ 1.35 per cent silica.

Syenite R-1738 contains 64.13 per cent silica and 16.77 per cent alumina. Consider a rock which contains the same amount of silica but 18.77 per cent alumina. In a 300 gram sample the additional 2 per cent alumina would represent 6 grams Al_2O_3 which would increase the initial activity 6.3 counts since the initial activity of alumina was found to be 1.05 counts per 30 seconds per gram Al_2O_3. The silica analysis of this sample would be 0.45 per cent greater than the correct value if compared to R-1738. Similarly if the rock sample contained only 14.77 per cent alumina the

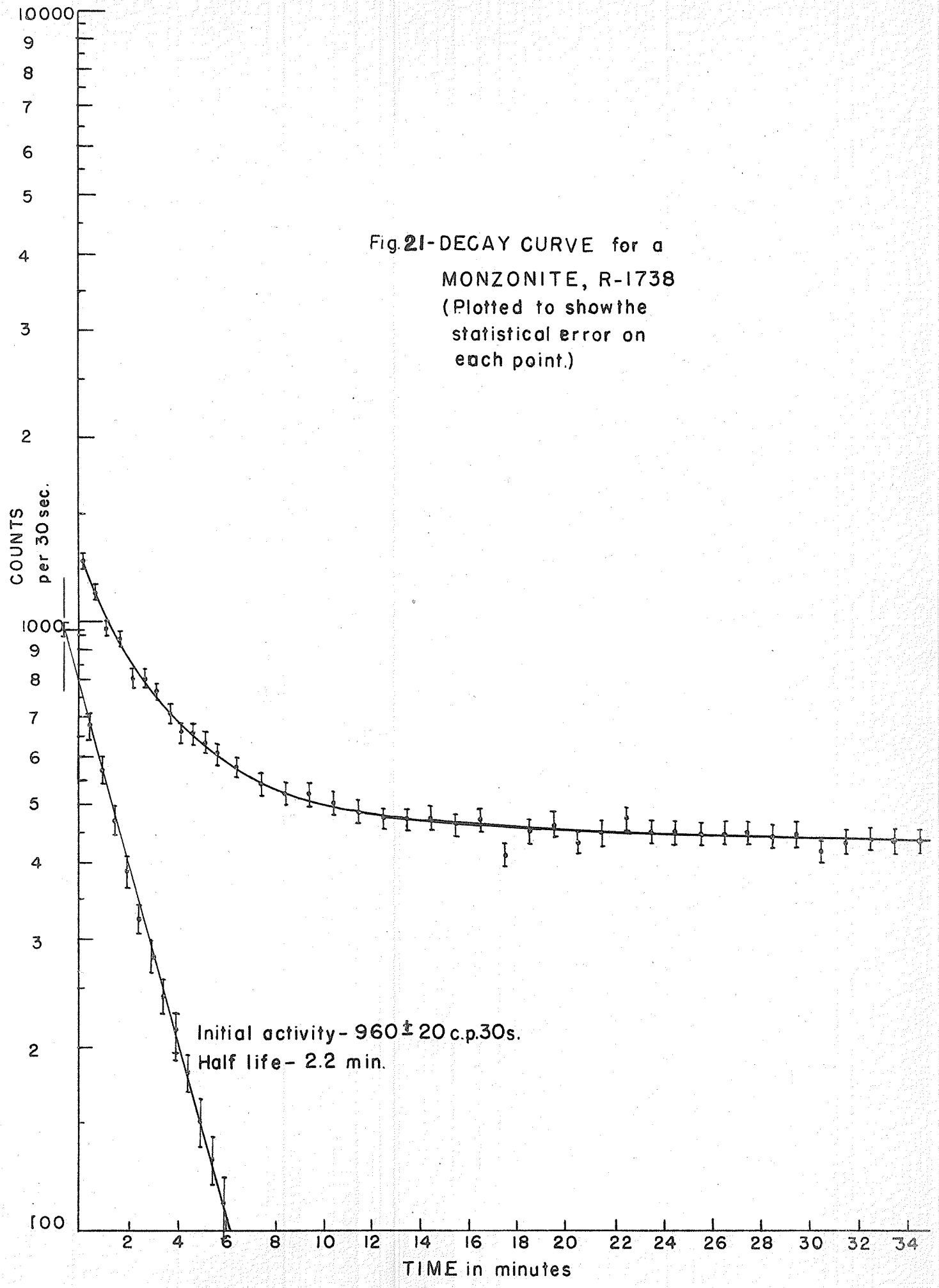

Fig. 21 - DECAY CURVE for a MONZONITE, R-1738 (Plotted to show the statistical error on each point.)

silica analysis by activation methods would be 0.45 per cent lower than the correct value. Since it is unlikely that the alumina percentage in a particular rock type would vary $\pm$ 2 per cent the error due to the alumina contribution would probably be less than $\pm$ 0.45 per cent. Thus the maximum error in a silica determination of an unknown sample compared to R-1738, considering the statistical error, the weighing error, and the possible error due to alumina would be about $\pm$ 1.80 per cent silica. It is possible, however, that these errors would be compensating and the net probable error is, of course, less than the amount stated.

The results of several series of silica determinations shown in Fig. (20) indicate that the values obtained fall for the most part within the limits of error of the method.

The analysis procedure for silica analysis can now be summarized as follows:

1. Coarse crush the rock sample to a grain size of minus $\frac{1}{4}$ inch mesh.

2. Weigh out 300 grams of the sample into the plastic container.

3. Take a 30 second check count with the Cs^{137} source in a standard position.

4. Check the background counting rate with crystal bare and with the sample on the crystal and determine the natural radioactivity of the sample.

5. Irradiate the sample with fast neutrons for a six

minute period.

6. Remove the sample from the source, place it on the crystal and after 30 seconds has elapsed measure the activation count. Thirty seconds counts are taken for the first six minutes of the decay period and one minute counts for the remaining time. The counts obtained are plotted as counts per 30 seconds against time in minutes on semi logarithmic paper. The 2.3 minute component of the curve is determined and the initial activity is obtained by extropolating to zero. The percentage silica is obtained by comparing the initial activity obtained with that of a known sample or by means of a graph such as is shown in Fig. (20)

7. A Cs^{137} 30 second check count is taken at this point and compared with that taken in step 3. If the difference is greater than $\pm$ 2 per cent the analysis is disgarded.

Proposed methods of analysis for other elements.

The method of aluminum analysis would be identical to that of silica analysis except that thermal neutron irradiation would be used. It is essential that the silica content of the rock and the initial activities of fast and thermal neutron irradiation for equal amounts of silica be known in order to correct for the silica contribution with thermal neutron irradiation. The ratio of counts obtained with fast and thermal irradiation would establish a silica equivalent. The initial activity for silica in the sample and the silica equivalent would then be used to correct for the silica contribution with thermal neutron irradiation.

The precision and accuracy of aluminum determinations was not established, however, the errors involved should be similar to those in a silica determination.

Analysis of a rock for sodium might be possible if a long irradiation period and a differential discriminator are used. Sodium has a distinctive gamma ray energy of 2.75 mev. This method would involve a long counting period but by taking relatively long counts at definite intervals, use of the instrument would not necessarily be restricted to sodium determination alone.

Conclusions

The experiments reported here indicate that the initial activities due to silica when irradiated with fast neutrons bear a linear relationship to one another. The results obtained on irradiating a series of analysed rock samples indicate that activation analysis for silica is feasible within the limits of error of the method. The maximum probable errors in silica and aluminum determinations were found to be about $\pm$ 1.75 per cent silica and about $\pm$ 1.00 per cent alumina. The probable error could be significantly reduced if a stronger neutron source were used. Although the accuracy of the method does not approach that of a good chemical analysis, less time and sample preparation are required for an activation analysis for silica. The analysis time would be reduced considerably if several samples of the same rock type were analysed and compared to the same rock standard. It would be convenient to arrange the analyses so that

a standard could be analysed between every second or third unknown.

The analysis of a rock for silica, alumina, and sodium by activation analysis and potassium by natural radio activity would provide a means of classification through the use of triangular or quadrangular diagrams.

Acknowledgments

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