

Thesis
67538
O.S.
C.2

THE GALLIUM AND ALUMINUM CONTENT AND THE GALLIUM-ALUMINUM
RATIO IN SELECTED ROCKS FROM NEW MEXICO

by

K. A. GRACE

A Thesis
Submitted in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE IN GEOLOGY

NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY

JUNE 1965

N. M. I. M. T.
LIBRARY
SCHOOL OF MINING

LIBRARY
N. M. I. M. T.
SCHOOL OF MINING

MAY 26 1982

8464242

CONTENTS

	Page
LIST OF FIGURES	iii
LIST OF TABLES	iv
ACKNOWLEDGMENT	v
ABSTRACT	vi
INTRODUCTION.	1
Previous Work.	5
SAMPLE LOCATION AND DESCRIPTION	7
Zuni Mountains Area.	7
Gallinas Area.	9
Hatchet Gap Area	9
New Mexico Granites.	11
ANALYTICAL PROCEDURE.	15
Introduction	15
General Sample Preparation	17
Film Calibration	18
Spectrographic Procedure	18
Aluminum.	18
Gallium	21
RESULTS	28
Gallium Content and the Ga/Al Ratio in Sedimentary and Source Rocks	28
Zuni Mountain Area.	28
Gallinas Area	30
Hatchet Gap Area.	30

	Page
Gallium Content and the Ga.1000/Al Ratios in New Mexico Granites.	32
CONCLUSIONS AND RECOMMENDATIONS.	36
APPENDIX A.	37
APPENDIX B	38
REFERENCES.	39

LIST OF FIGURES:

	Facing Page
1 Solubility of Gallium and Aluminum	3
2 Dispersion of Gallium in igneous rocks	4
3 New Mexico - Index Map	5
4 Zuni Mountains Area - Sample Location.	7
5 Gallinas Area - Sample Location.	9
6 Hatchet Gap Area - Sample Location	9
7 New Mexico Granites - Sample Location.	11
8 Film Calibration Curve	18
9 Working Curve for Al_2O_3	20
10 Working Curve for Gallium.	27
11 Frequency distribution for Gallium in New Mexico Granites	32
12 Frequency distribution for Aluminum in New Mexico Granites.	32
13 Frequency distribution for Ga.1000/Al in New Mexico Granites.	34

LIST OF TABLES

		Page
I	Atomic and ionic data for Aluminum and Gallium	1
II	Abundances of Aluminum and Gallium.	2
III	Zuni Mountains Samples - Description.	8
IV	Gallinas Samples - Description.	10
V	Hatchet Gap Samples - Description	10
VI	New Mexico Granites - Description	11
VII	Replicate Determinations for Al ₂ O ₃	22
VIII	Replicate Determinations for Gallium.	26
IX	Zuni Mountains Samples - Aluminum and Gallium content, and Ga.1000/Al ratios.	29
X	Gallinas Samples - Aluminum and Gallium content, and Ga.1000/Al ratios.	31
XI	Hatchet Gap Samples - Aluminum and Gallium content, and Ga.1000/Al ratios.	31
XII	New Mexico Granites - Aluminum and Gallium content, and Ga.1000/Al ratios.	33

ACKNOWLEDGMENT

The writer wishes to thank Dr. Lawrence R. Hathaway who originally suggested this research topic and who gave much useful aid and advice throughout the period during which the work was carried out. Thanks are also due to Dr. Clay T. Smith, who served as co-advisor and also assisted in the collection of certain samples, and to Drs. Frank Kottowski and Edward Bingler for reading the manuscript.

Special thanks are due to Roy W. Foster who served as a continuous source of New Mexico geological information and provided many of the granite samples, and without whose assistance this thesis would never have been written.

A grant in aid from the New Mexico Geological Society, to defray certain incidental expenses, is gratefully acknowledged.

ABSTRACT

The close association of gallium and aluminum in rocks is examined. Emission spectrographic analysis is used to determine the gallium and aluminum content of arkosic sediments and related source rocks. Results suggest a relative increase in the Ga/Al ratio in the derived sedimentary rocks. Determinations are also carried out on granites from several locations in New Mexico to compare the Ga/Al ratio in these rocks. The frequency distribution plot of the granite analyses are positively skewed for gallium, but are normal for aluminum. This lack of parallelism between the elements may be the result of dual origin for the granites, variation in mineral composition, or the effect of other ions.

THE GALLIUM AND ALUMINUM CONTENT AND THE GALLIUM-ALUMINUM
RATIO IN SELECTED ROCKS FROM NEW MEXICO

INTRODUCTION

The element gallium forms no simple or discrete mineral during magmatic crystallization, but tends to be closely associated with aluminum and is contained in the crystal lattices of the aluminum minerals. This type of major-minor element association is common and it depends mainly upon ionic size, ionic charge, and ionization potential. Relative data for gallium and aluminum are given in Table I:

Table I: Atomic and ionic data for Aluminum and Gallium*

	Al	Ga
Atomic Number	13	31
Atomic Weight	26.98	69.72
Ionic Radius (+3)	0.57	0.62 Å
Ionic Structure (+3)	Noble gas	"18-electron"
Ionization Potential (3rd)	28.4	30.7 ev.

*(Ahrens, Goldschmidt, and others)

Since Ga^{+3} is slightly larger than Al^{+3} , a relative increase of gallium is expected in the late differ-

entiates. Nockolds and Mitchell (1947) however, in an investigation of major-minor element associations in the Caledonian plutonic rocks, found a practically constant value for Ga.1000/Al of 0.2 for rock compositions ranging from pyroxenite to aplite.

Bell (1953) gives a detailed description of the behavior of gallium in magmatic processes, and finds a very close association between gallium and aluminum during differentiation and crystallization. He notes that aluminum may possibly be slightly enriched in the ultra-basics and gallium slightly enriched in the pegmatitic phase.

The relative abundances of the two elements are given in Table II:

Table II: Abundances of Aluminum and Gallium

	Al (%)	Ga (ppm)
#Earth's crust	8.23	15
#Basalt (average)	8.76	12
#Granite (average)	7.70	18
*Clays and Shales	10.45	30

(#Taylor, 1964
*Vinogradov, 1962).

Using dissociation constants, the solubilities of aluminum and gallium can be calculated as a function of

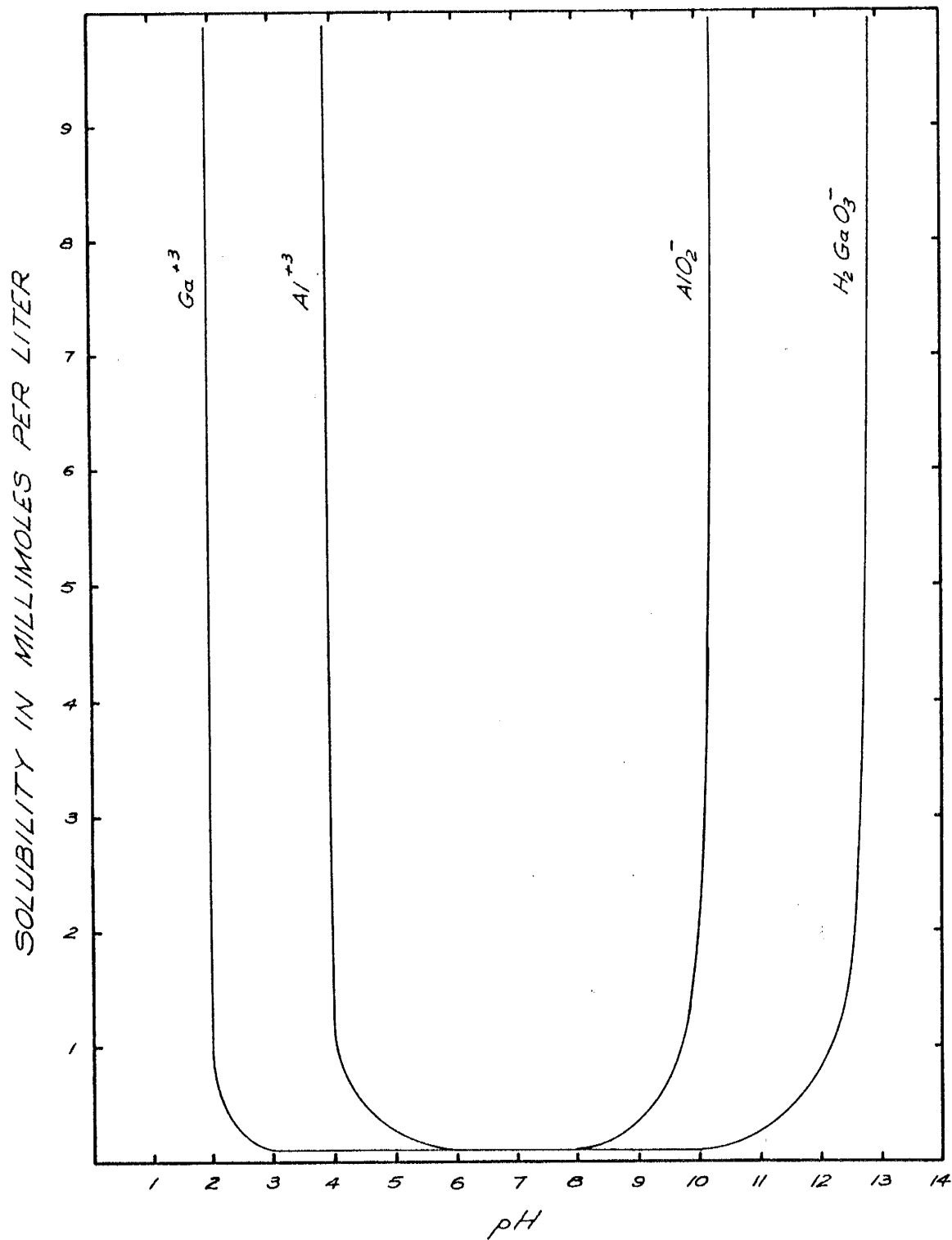
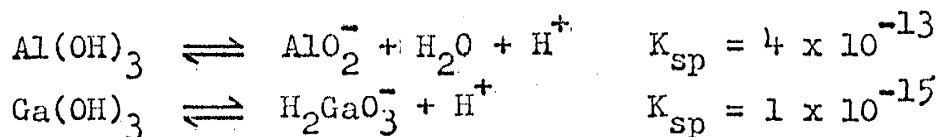


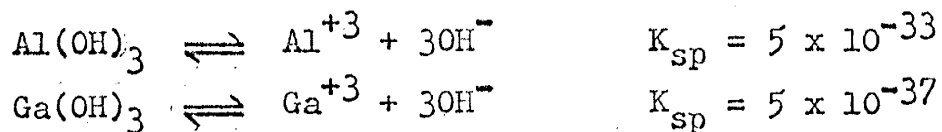
FIG. 1. SOLUBILITY OF GALLIUM AND ALUMINUM AS A FUNCTION OF pH

pH. The available data are comparatively old and remarkably poor; the value for the dissociation constant of $\text{Al}(\text{OH})_3$ in alkali solution, for example, varies from 6×10^{-12} to 1.3×10^{-14} . Similar variations exist in the reported values for gallium. Latimer (1952), taking into consideration all thermodynamic data, gives the following preferred values:

In alkali solution:



in acid solution:



The solubilities of aluminum and gallium, as calculated from the above data, are plotted against pH in Figure 1. From this plot it is seen that, due to their different solubilities, there exists a definite mechanism for the separation of these two elements. The +3 ion is the stable form for both elements and the chemistry (and geochemistry) is mainly determined by this ion.

During the weathering of igneous rock and the transportation of the resultant debris, minerals are in contact with aqueous solutions for sufficient time for any mechanism of separation as stated above to take effect,

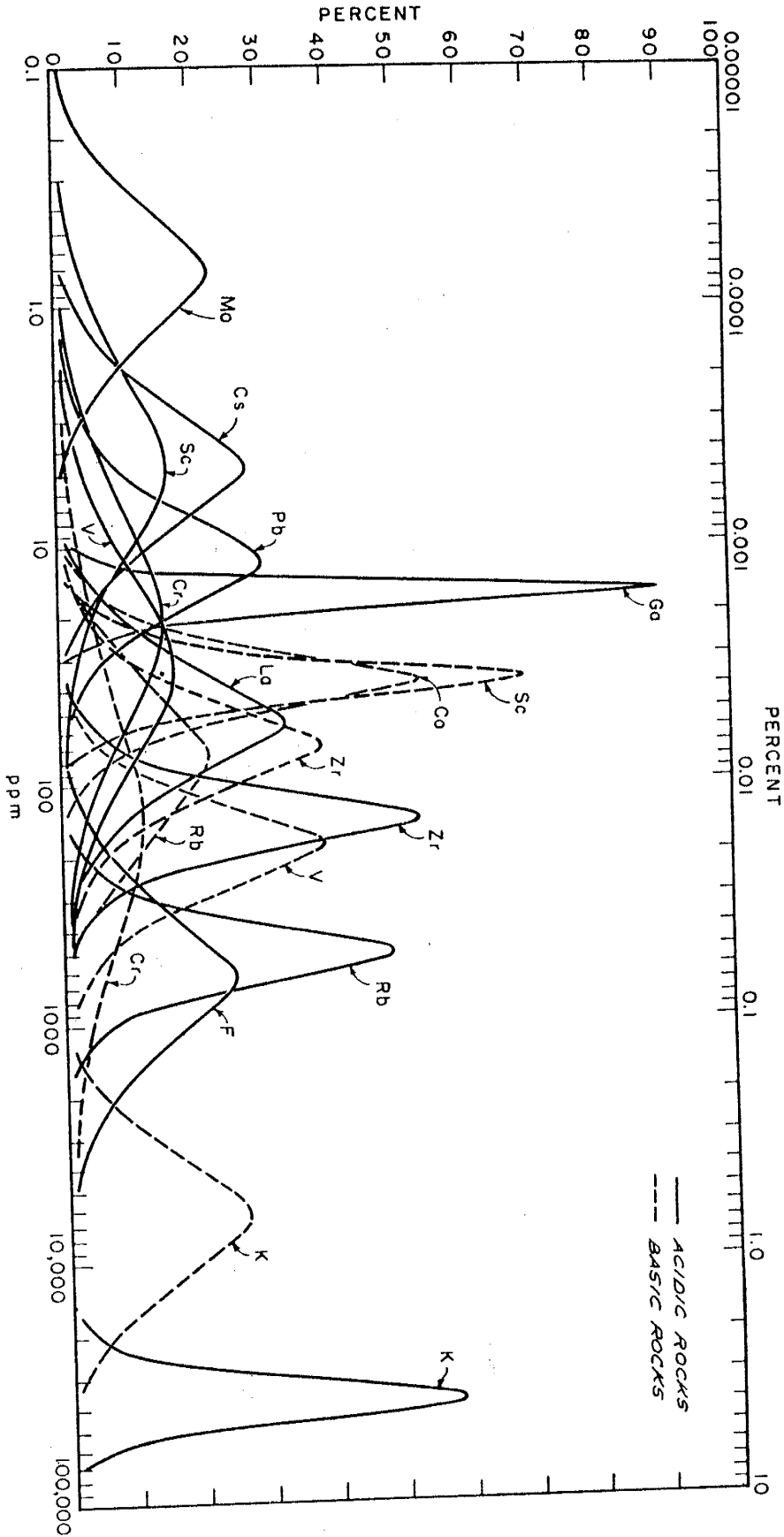


FIG. 2. DISPERSION OF GALLIUM IN IGNEOUS ROCKS (AURENS, 1954)

provided the conditions are favorable. Thus, the more soluble elements will decrease in concentration relative to the less soluble ones with increasing distance from the source rock. It is, therefore, expected that a more soluble element, in this case aluminum, will show a decrease in concentration when compared to a less soluble element, gallium, in a sedimentary rock relative to the concentrations found in the parent rock.

Should a measurable separation of aluminum and gallium take place during weathering, resulting in increased Ga/Al ratios, it is conceivable that this ratio may persist during metamorphism. In such a case the Ga/Al ratio may be a useful indicator as to the origin of granitic rocks, distinguishing between a "true" granite and one with an original sedimentary origin. It may be noted here that the dispersion of gallium in igneous rocks is extremely small as shown in Figure 2 (Ahrens, 1954).

The work here described develops suitable methods for the analysis of gallium and aluminum in rocks, and determines the amounts of these elements and their ratio in selected rocks. The analyses are carried out on a number of feldspathic sandstones and their known igneous source rocks, from the three areas shown on the index map (Figure 3), and on several granites from New Mexico. The purpose of this investigation is to compare

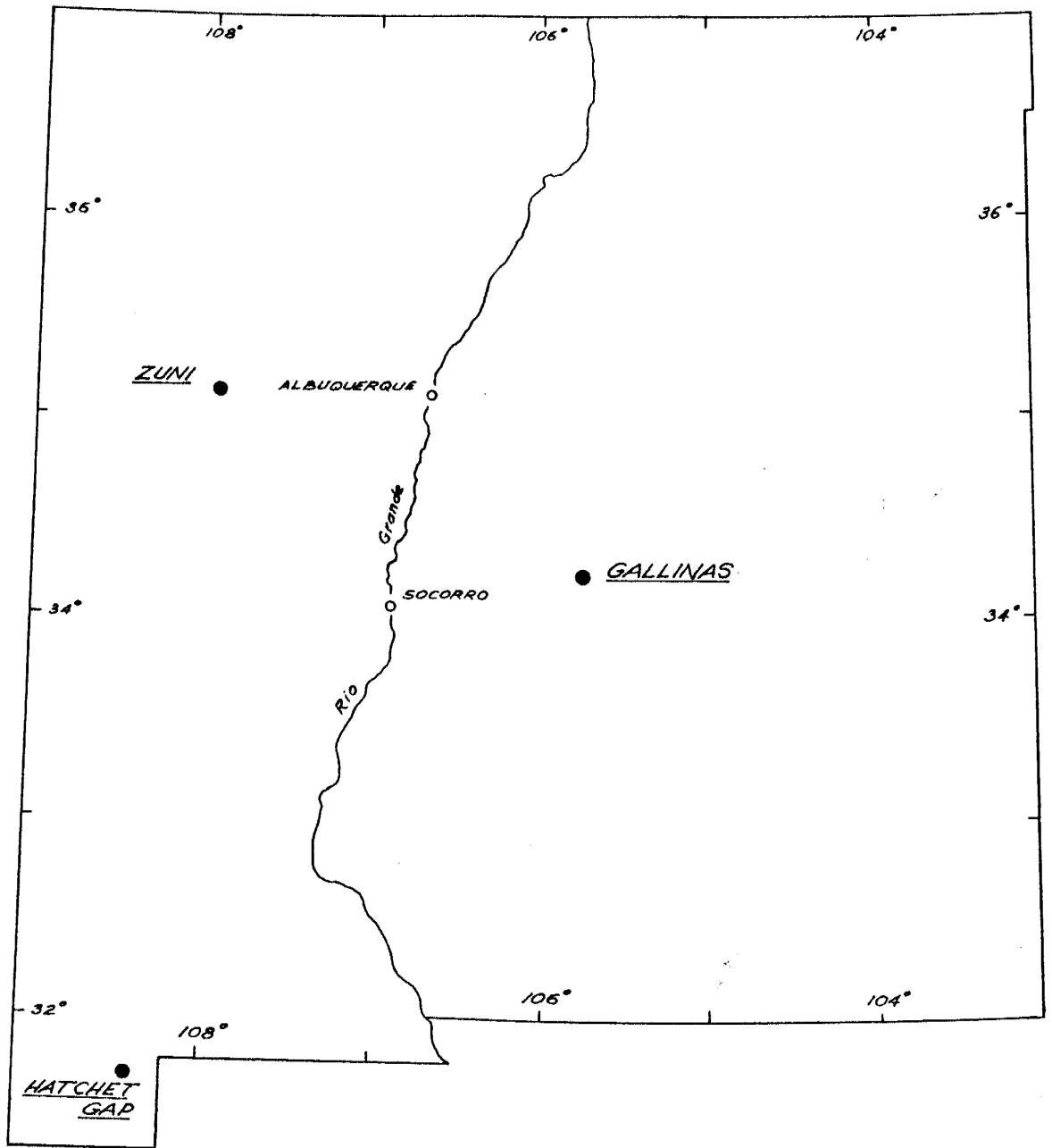


FIG. 3. NEW MEXICO - INDEX MAP

the Ga/Al ratio between sedimentary and source rocks, and to examine and investigate this ratio in granites. The possibility of using this ratio for correlation purposes is also examined.

Previous Work

Many investigations have been carried out on gallium and its mode of occurrence in nature since its discovery in 1875 by de Boisbaudran. Even before the actual discovery, the element ("eka-aluminum") and its properties were predicted by Mendeleev in 1869.

Bell (1953) investigated the gallium content of a large number of igneous rocks and minerals, and gives an extensive bibliography of the element. Although he made no aluminum determinations, he compares the gallium content to the aluminum content where the latter is available. He gives the following approximate values for the Ga.1000/Al ratios:

Granites	0.22
Sandstones	up to 0.6
Shales	0.23

Recently, Booke (1964) investigated the Ga/Al ratio in selected African acidic igneous intrusives and finds that the plot of Ga vs Al can be divided into two fields

with respect to age, the older rocks having the lower Ga/Al ratio.

As far as is known, no intensive investigation of the gallium content and the Ga/Al ratio has been done for rocks from New Mexico.

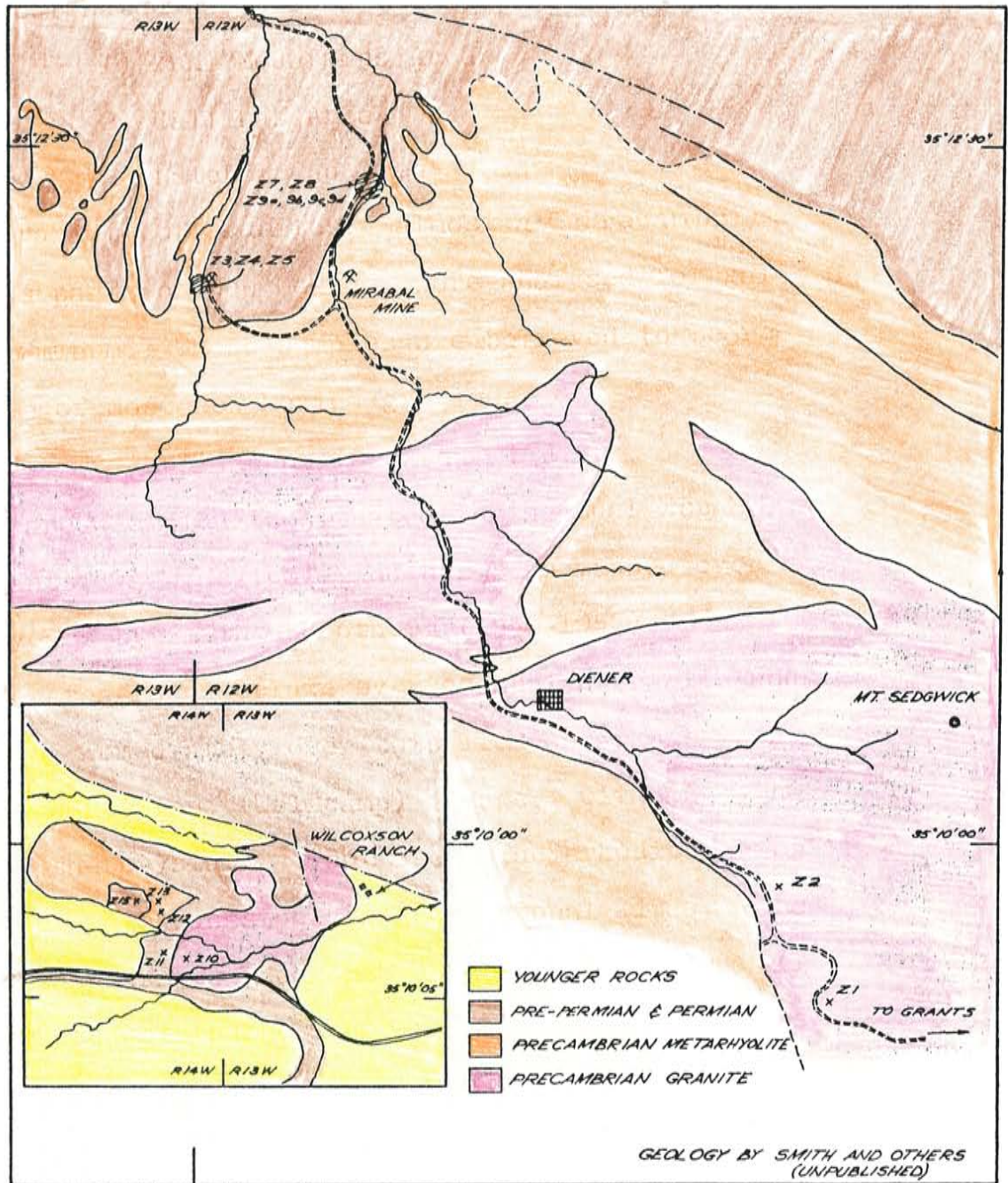


FIG. 4. ZUNI MOUNTAINS AREA - SAMPLE LOCATION
(GEOLOGY SIMPLIFIED)

SAMPLE LOCATION AND DESCRIPTION

Three areas where arenitic sedimentary rocks and parent source rock can be sampled were selected (Figure 3). These are designated as follows:

- 1) Zuni Mountains Area
- 2) Gallinas Area
- 3) Hatchet Gap Area

A variety of granites, almost all Precambrian from various parts of New Mexico, were analysed for gallium and aluminum. These samples are believed to be representative of most New Mexico granites.

Zuni Mountains Area

The area sampled is situated in the Zuni Mountains west of Grants, New Mexico, and has been mapped over a period of years by Smith and others (1954-1957).

The area is underlain by Precambrian granite and metarhyolite. Immediately over this lies an arkose, identified as pre-Permian (Wolfcamp) in age, with many inclusions of the crystalline rocks. The arkosic facies grades upward into sandstones and occasional limestone beds, and disappears to the north as determined from well samples. These data suggest derivation of the sediments from the immediately adjacent crystalline rocks.

Samples were collected north and west from Mount Sedgwick (Figure 4) and are described in Table III.

Table III: Zuni Mountains Samples - Description

Sample

- Z 1 Gneiss. Precambrian, fine-grained, leucocratic. South flank of Mount Sedgwick.
- Z 2 Granite. Precambrian, slightly gneissic. On continental divide at Mount Sedgwick.
- Z 3 Arkose. Five feet above contact with Precambrian schist at copper prospect near Mirabal mine.
- Z 4 Schist. Precambrian, muscovite -- rich. Below Sample Z3.
- Z 5 Gneiss. Precambrian, with biotite. Below arkose near Z4.
- Z 7 Metarhyolite. Precambrian, coarse-grained. North of Mirabal mine.
- Z 8 Metarhyolite (?). Precambrian, fine-grained. Near Z7.
- Z9a Arkose. Overlying Z7.
- Z9b Arkose. Twenty feet above Z9a.
- Z9c Arkose. Twenty feet above Z9b.
- Z9d Arkose. Very coarse-grained. Ten feet above Z9c.
- Z10 Granite. Precambrian. West of Wilcoxson Ranch. (T11N, R14W, Sec. 13)
- Z11 Arkose. Above Z10.

Table III (Continued):

Sample

Z12	Metarhyolite. Precambrian. Three to four miles west of Wilcoxson Ranch.
Z13	Sedimentary (sandstone?) "inclusion" in meta-rhyolite near Z12.
Z15	Arkose. Overlying Z12.
Z16	Granite. Precambrian. Pink, fine-grained. McGaffy Lake.

Gallinas Area

The Gallinas mountain range is an isolated complex of intrusive and extrusive rocks just west of Highway 54, near Corona, New Mexico. A faulted block of presumably Precambrian granite, overlain by Abo (?) Sandstone derived from it, occurs within the area (Perhac, 1960).

Samples are described in Table IV, and locations are shown in Figure 5.

Hatchet Gap Area

Hatchet Gap is the name given to the break between the Little Hatchet Mountains and the Big Hatchet Mountains through which Highway 81 passes, about twelve miles south of Hachita, New Mexico.

The geology of the area is described in detail by Lasky (1947). To the north of Hatchet Gap one large

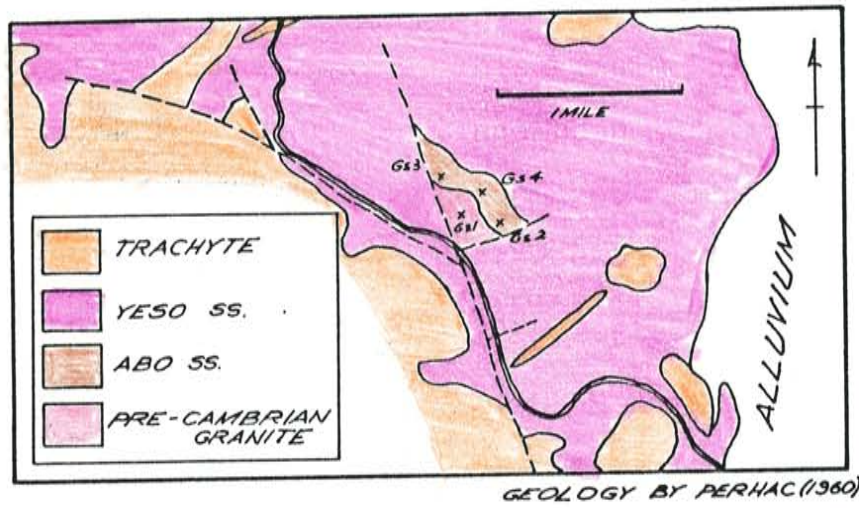


FIG. 5. GALLINAS AREA - SAMPLE LOCATION

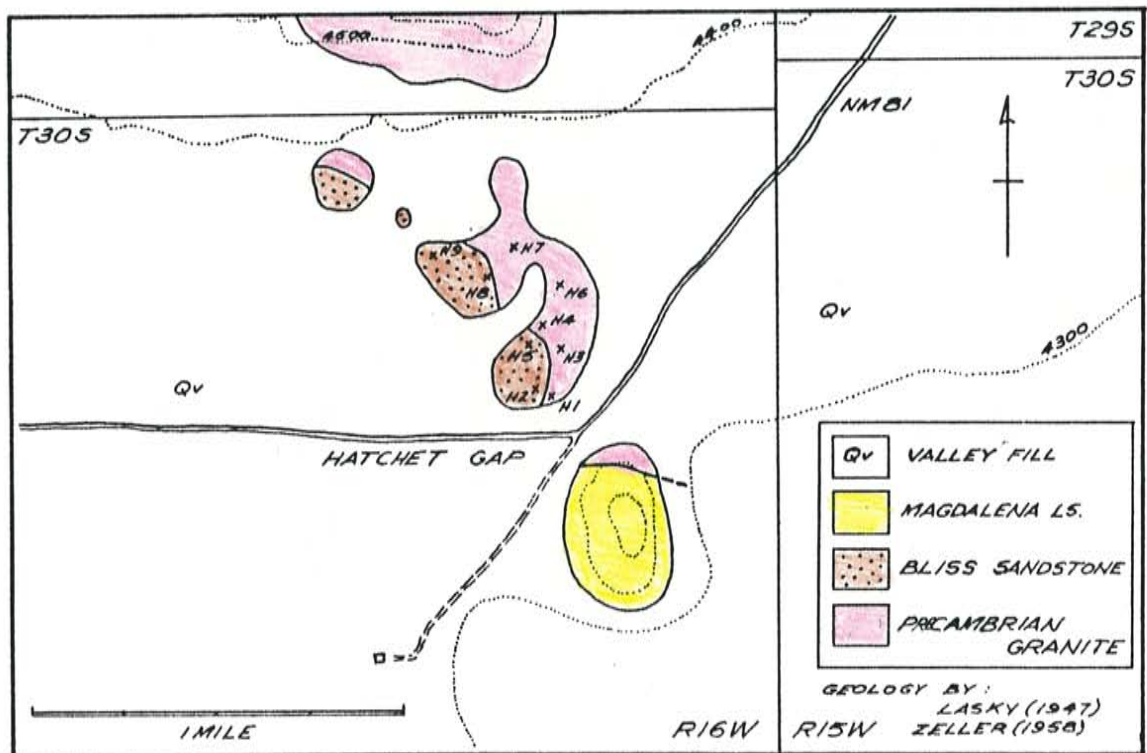


FIG. 6. HATCHET GAP AREA - SAMPLE LOCATION

mass and three smaller masses of granite form the southern end of the Little Hatchet range. This granite, originally mapped by Lasky as Tertiary, has since been identified by Zeller (1958) as being of Precambrian age. Immediately overlying the granite, and forming three outlying hills, is a feldspathic sandstone described by Zeller as Bliss. This contains occasional fragments of the underlying basement rock.

Sample locations are shown in Figure 6 and descriptions are given in Table V. Sample No. H1 is of a granite distinctly different from, and apparently intrusive into, the main body of granite.

Table IV: Gallinas Samples - Description

Sample

Gs1	Precambrian (?) granite.	Near road east of Red Cloud Campground.
Gs2	Abo Sandstone.	Overlying granite 1000 feet west of Gs1.
Gs3	Abo Sandstone.	Overlying granite at Gs1.
Gs4	Abo Sandstone.	Overlying granite 1000 feet east of Gs1.

Table V: Hatchet Gap Samples - Description

Sample

H 1	Precambrian, leucocratic granite.	Near contact with Bliss Sandstone.
-----	-----------------------------------	------------------------------------

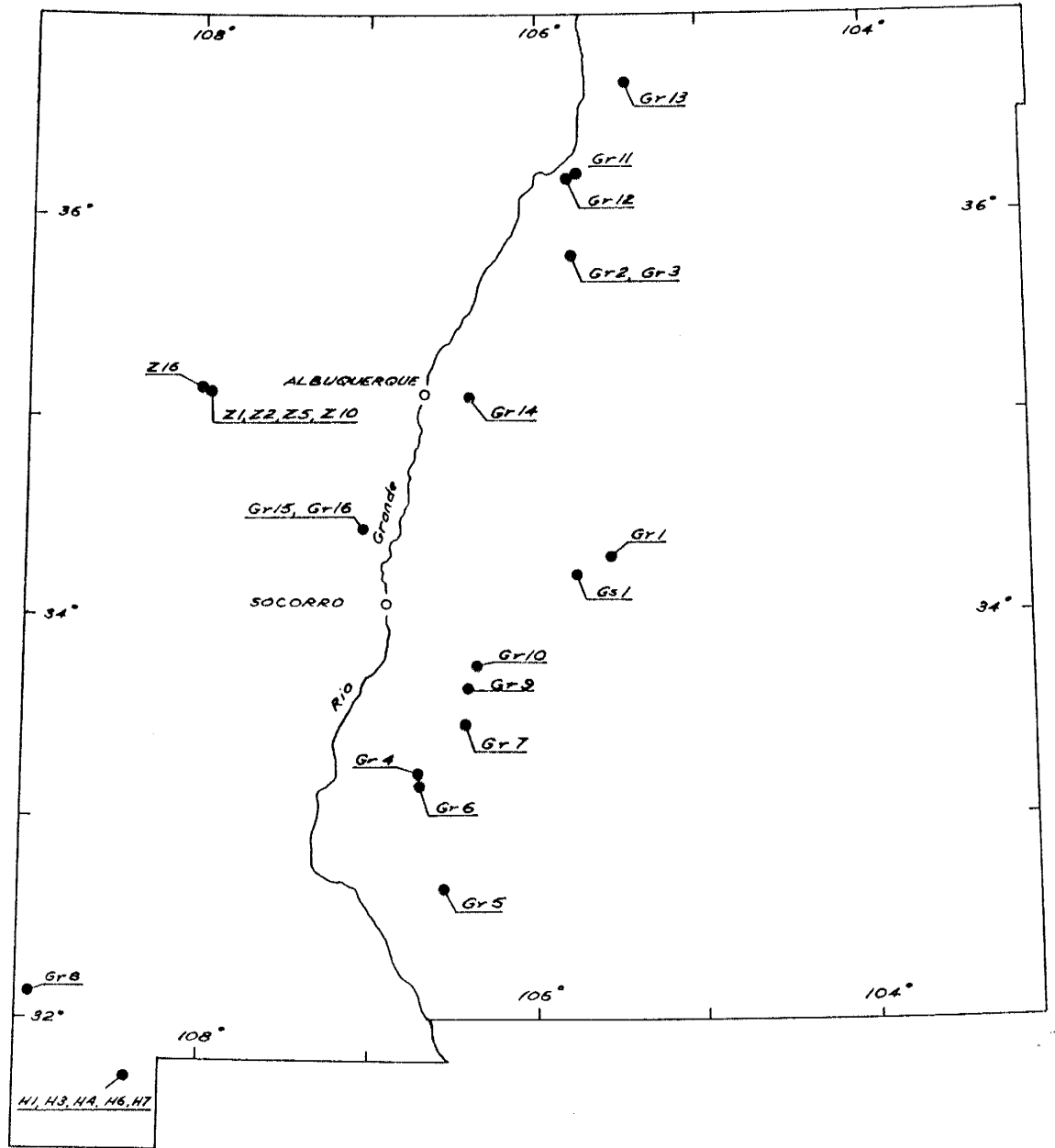


FIG. 7. NEW MEXICO GRANITES - SAMPLE LOCATION

Table V (Continued):

Sample	
H 2	Bliss Sandstone; hard, quartzitic, fine-grained. Overlying H1.
H 3	Precambrian, red, granite.
H 4	Precambrian, red, granite.
H 5	Bliss Sandstone; overlying H4.
H 6	Precambrian, red, granite.
H 7	Precambrian, red, granite.
H 8	Bliss Sandstone; feldspathic. Overlying H7.
H 9	Bliss Sandstone; feldspathic. NW of H8.

New Mexico Granites

Locations of granite samples, including those from the above areas, are shown in Figure 7 and described in Table VI. Although practically all of Precambrian age, these granites show much variety as to mineral composition.

Table VI: New Mexico Granites - Description

Sample	
Gr 1	Precambrian granite, Pedernal Mountain, Torrance County.
Gr 2	Precambrian, gneissic, biotite granite. Santa Fe ski basin, Santa Fe County.
Gr 3	Precambrian, biotite granite; pink feldspar.

Table VI (Continued):

Sample

- Santa Fe ski basin, Santa Fe County.
- Gr 4 Precambrian, mesocratic, porphyro-blastic, biotite-garnet gneiss. Rhodes canyon, San Andres mountains, Sierra County.
- Gr 5 Precambrian, biotite granite. San Andres Peak, San Andres mountains, Dona Ana County.
- Gr 6 Precambrian, porphyritic, muscovite granite. Cottonwood canyon, San Andres mountains, Sierra County.
- Gr 7 Precambrian, biotite granite. Tributary of Johnson Park canyon, northern San Andres Mountains, Sierra County.
- Gr 8 Precambrian granite. Granite Gap, Peloncillo mountains, Hidalgo County.
- Gr 9 Precambrian, fine-grained biotite granite; slightly gneissic. Central Oscura mountains, Socorro County.
- Gr10 Precambrian, biotite granite. Trail canyon, Oscura mountains, Socorro County.
- Gr11 Precambrian, gneissic granite (Embudo granite). East of Dixon, Taos County.
- Gr12 Gneissic granite (Embudo granite?). Apodaca, Taos County.
- Gr13 Tertiary, soda-granite. Flag Mountain stock,

Table VI (Continued):

Sample

- north side of Red River Canyon, Taos County.
- Gr14 Precambrian, biotite granite. Tijeras canyon, Bernalillo County.
- Gr15 Precambrian, pink, amphibole granite. Jeter Ranch, Ladron mountains, Socorro County.
- Gr16 Precambrian, leucocratic, biotite granite. Near Gr15, Ladron mountains, Socorro County.
- Z 1 Precambrian, fine-grained gneiss. Zuni mountains, Valencia County.
- Z 2 Precambrian granite, slightly gneissic. Zuni mountains, Valencia County.
- Z 5 Precambrian biotite gneiss. Zuni mountains, Valencia County.
- Z10 Precambrian, hornblende granite. Zuni mountains, Valencia County.
- Z16 Precambrian, red granite. McGaffey Lake, McKinley County.
- H 1 Precambrian, leucocratic granite. Hatchet Gap, Hidalgo County.
- H 3 Precambrian, red granite. Hatchet Gap, Hidalgo County.
- H 4 Precambrian, red granite. Hatchet Gap, Hidalgo County.

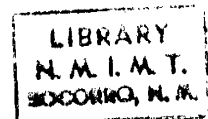


Table VI (Continued)

Sample

- | | |
|-----|--|
| H 6 | Precambrian, red granite. Hatchet Gap, Hidalgo County. |
| H 7 | Precambrian, red granite. Hatchet Gap, Hidalgo County. |
| Gsl | Precambrian granite. East of Red Cloud Campground, Gallinas mountains, Lincoln County. |

ANALYTICAL PROCEDURE

Introduction

Analytical techniques for the two elements, aluminum and gallium, should combine speed, accuracy and sensitivity, in the concentration range expected in the samples to be analysed. Available information shows that the classical chemical analysis for aluminum is a long and tedious process, and subject to many errors. ZrO_2 , Cr_2O_3 and V_2O_5 are almost always included in the values reported for Al_2O_3 in silicates (Fairbairn 1953).

Although emission spectrography is not commonly used for the determination of the major elements in rocks, the method readily lends itself to this kind of work, and satisfies all the requirements. Filby and Leininger (1960), in a review of the analysis of the major elements in U.S. Geological Survey Standard Granite G1 and Standard Diabase W1,* state that "...spectrographic methods appear adequately accurate and precise for the determination of Al_2O_3 in silicate materials." In a review of the rapidity and accuracy of the chemical and physical methods for determining aluminum in alumino-silicates, Voinovitch and

*These two standard rock crushes were prepared by the U. S. G. S. and distributed to laboratories for analysis. Analytical results and other details are given in U.S.G.S. Bull. 980, 1951, and U.S.G.S. Bull. 1113, 1960.

Debras (1957) find emission spectrography the most rapid and accurate method.

Gallium, as a trace constituent of rocks, is commonly determined spectrographically. Other methods, notably colorimetric and fluorimetric, are also in use, but these almost always require the total separation of any aluminum present, an obvious difficulty when dealing with rocks. One of the colorimetric methods investigated in detail is that developed by Sokolova (1962). This method has the advantage of great rapidity, but trial experiments clearly showed interference by aluminum. The rapidity of a method such as this is negated by the procedures required to remove all traces of aluminum.

Emission spectrographic analysis has been selected, therefore, for the determination of both aluminum and gallium.

All samples were burned on an ARL 1.5 meter grating spectrograph, with a ruling of 15,000 lines to the inch. Spectra were recorded on Kodak Spectrographic No. 1 film, and line densities (emulsion response) were determined microphotometrically on an ARL comparator - densitometer incorporating a master chart. The emission spectrograph is equipped with a simple arc - stand with manual adjustment of arc gap, and with a rotating sector between the stand and slit. The general procedure followed utilizes

internal standards as described by Ahrens (1955) and Ahrens and Taylor (1961). Strontium is used as the internal standard for aluminum, and indium for gallium.

General Sample Preparation

Samples are reduced in size on a steel plate with a steel hammer and the fragments thus obtained are crushed, with a minimum of grinding, in a cast iron mortar. Further reduction in size, to approximately 150 mesh, is carried out in a mechanical agate mortar.

The sample obtained in this way is fine enough to achieve homogeneity, and yet coarse enough for final grinding with standards, spectrographic carbon or diluent. If the sample is reduced to -200 mesh, difficulty is experienced in obtaining a good mix when other powders are added.

Final grinding for arcing, after the addition of standard and buffer material, is done by hand in a small agate mortar. The relative coarseness of the rock powder aids mixing in this process.

Mechanical mixing, using instruments such as the "Wig-L-Bug", tends to separate the fine powders. This is particularly noticeable when attempting to mix SrCO_3 with the rock powder in the preparation of samples for aluminum analysis.

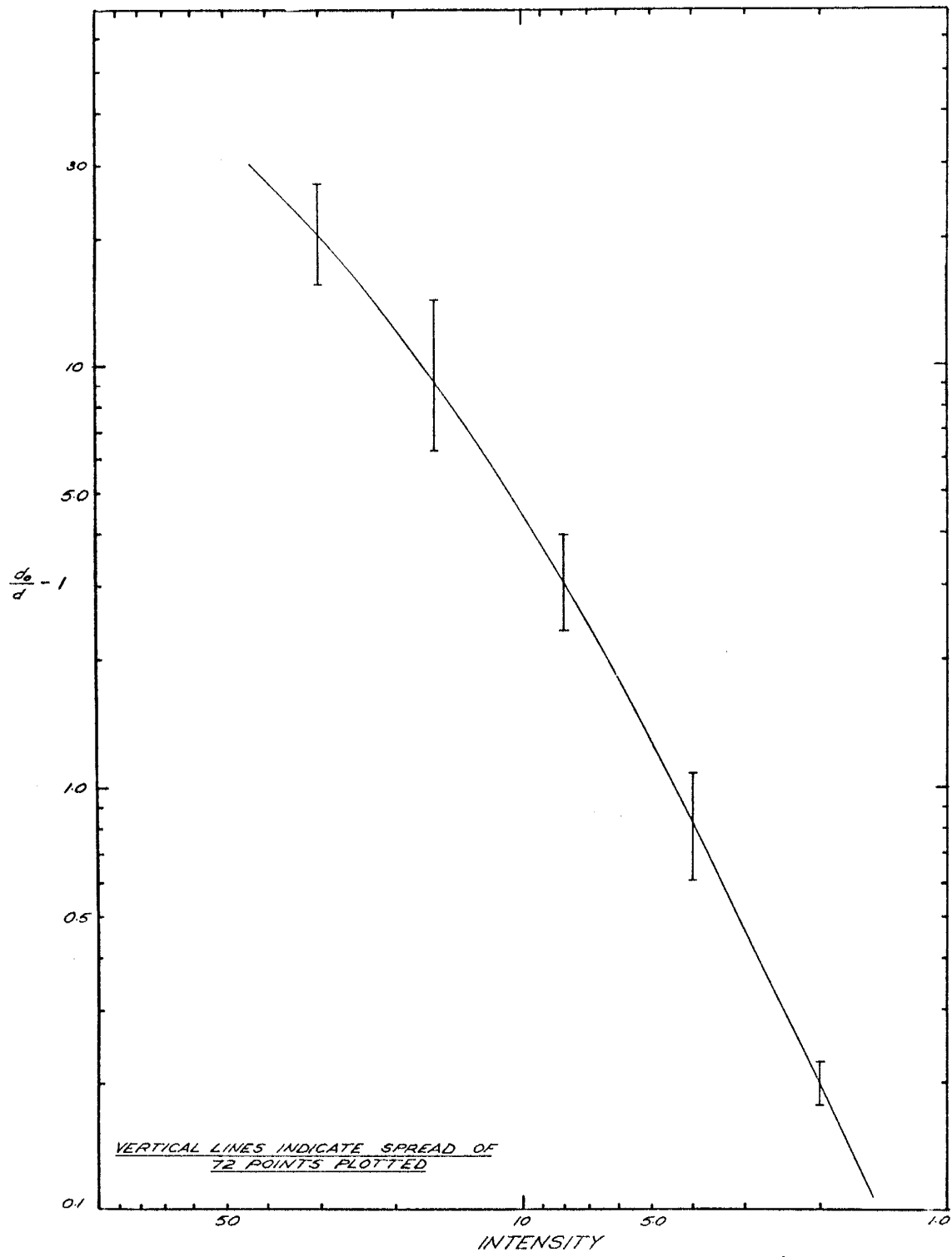


FIG. 8. FILM CALIBRATION CURVE FOR 3000 Å REGION

Finally, the carbon electrodes containing the mixture to be arced are heated at 110°C in an electric oven for at least four hours prior to arcing.

Film Calibration

The photographic emulsion was calibrated with iron lines for varying light response in the 3000 Å region using a step sector to obtain a graded series of intensities. The microphotometrically measured line density, in the form of the Seidel function $\left(\frac{d_0-d}{d}\right)^*$, is plotted against the relative intensity of each line as described by Ahrens and Taylor (1961, Chap. 11). This plot is shown as Figure 8. The intensity for any microphotometrically measured spectral line in the above-mentioned wavelength region is obtained from the plot for comparison with that of other lines.

Spectrographic Procedure

Aluminum:

The general method used for the spectrographic determination of aluminum is that of Kvalheim (1947) as modified by Dennen (1949). One part of sample (rock powder)

*Where d_0 is the galvanometer deflection for clear (unexposed) film, set at "100% transmission", and d is the measured galvanometer deflection, as percent transmission, for a particular spectral line.

is mixed with one part SrCO_3 and four parts spectrographic carbon. Although Dennen used 1/8" x 1mm (ID) x 4 mm (Depth) electrodes, it is found more convenient to use 1/8" x 2 mm x 1.5 mm electrodes (Ultra Carbon type 2509). Counter electrodes are of 1/8" diameter, sharpened to a point (Ultra Carbon type 1992, or National Carbon type 4036.)

Aluminum is a member of the involatile group of elements, and, hence, all arcing must be carried to completion. (The involatile elements, in emission spectrography, are defined as all those elements which "emit their maximum line intensity after the main phase of alkali metal distillation has subsided." Ahrens, 1955). Under the conditions used in this investigation, the sample is completely ignited within 50 seconds. The internal standard, too, must be comparatively involatile, and have a similar distillation rate and excitation properties to that of aluminum. Strontium not only satisfies these conditions, but, present in the form of SrCO_3 , forms an excellent flux in the arc that ensures a steady quiet burn.

The spectral lines used (analysis pair) are:

Al 2652.489

Sr 2931.830

Using these lines under the conditions described in Appendix A the range of concentrations that can be deter-

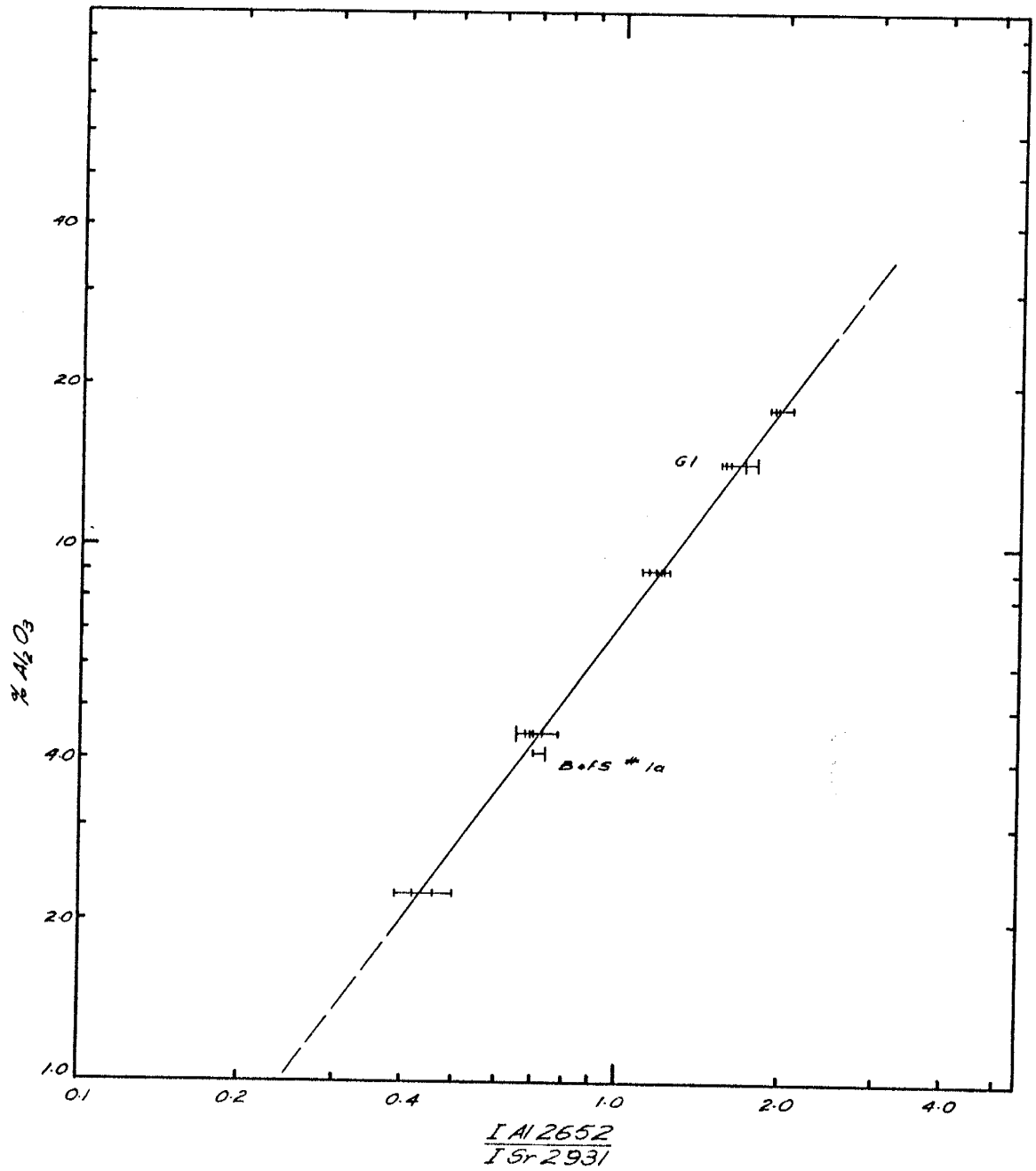


FIG. 9. WORKING CURVE FOR Al₂O₃

mined is from about 2% to about 25% Al_2O_3 . (If it is required to determine amounts less than 2%, it is a simple matter to construct a working curve utilizing Al 3082.155, all other conditions remaining the same.) The working curve is constructed by using National Bureau of Standard sample No. 70, "Feldspar",* with an Al_2O_3 content of 18.03%. This is diluted with crushed pure quartz crystal to give the following concentrations:

Sample	Quartz	% Al_2O_3
1 to 0	0	18.03
1 to 1	1	9.01
1 to 3	3	4.50
1 to 7	7	2.25

The curve obtained from these concentrations is tested with U.S.G.S. Standard Granite G1, and National Bureau of Standards sample No. 1a, "Argillaceous Limestone".* The Al_2O_3 contents of these samples are:

- G1 14.23% Al_2O_3 (Filby and Leininger, 1960)
- 1a 4.16% Al_2O_3 (N. B. S., 1931)

The results show the curve obtained in this manner is satisfactory. The final working curve, a plot of % Al_2O_3 versus line intensity ratio of the analysis pair, can be seen in Figure 9.

*Available from the N.B.S., Washington, D.C.

Attempts to plot U.S.G.S. Standard Diabase W1 on this curve give consistently high results. This working curve cannot, therefore, be used for low silica, high ferromagnesian rocks.

Replicate arcings of granite G1 are used to test the reproducibility of the method, as shown in Table VII. A relative deviation of 5.8% is obtained. This compares favorably with the results obtained by Ahrens (1955) with a relative deviation of 4.7%.

Complete details of the arcing procedure are given in Appendix A.

Gallium:

28076
Gallium is one of the volatile group of elements (although the least volatile of the group), and distills during the early part of the arc burn. The volatile elements are defined as those that completely volatilize before the total volatilization of the alkali metals (Ahrens, 1955).

Bell (1953) determines gallium by using Ga 4172.0%, the most sensitive gallium spectral line. This line falls within the interference range of the CN 4216 band spectrum and is usually completely masked. However, since the alkali metals suppress (CN) band emission and gallium is more volatile than the alkalis, Ga 4172 can be used if burning is limited to the period of alkali distillation. This method was examined and tested in the present investigation,

TABLE VII: Replicate determinations of Al₂O₃ for Standard Granite G1

Number	d		$\frac{d_o-d}{d}$		I		R	R ²
	Al 2652	Sr 2931	Al 2652	Sr 2931	Al 2652	Sr 2931		
1	27.2	52.0	2.62	0.92	7.53	4.23	1.78	3.168
2	44.0	65.3	1.27	0.53	5.00	3.20	1.56	2.434
3	34.6	60.0	1.89	0.67	6.18	3.61	1.71	2.924
4	43.5	70.8	1.30	0.41	5.03	2.81	1.79	3.204
5	40.4	61.5	1.47	0.63	5.40	3.50	1.54	2.372
6	39.2	64.5	1.55	0.55	5.55	3.26	1.70	2.890
7	38.5	60.8	1.60	0.64	5.65	3.52	1.60	2.560
							$\frac{I \text{ Al2652}}{I \text{ Sr2931}}$	
							11.68	19.550

$$\bar{m} = 1.67$$

$$\text{Standard Deviation} = \sqrt{\frac{\sum R^2}{n} - \frac{(\sum R)^2}{n^2}}$$

$$= \sqrt{\frac{19.55}{7} - \frac{136.42}{49}} = 0.10$$

$$\text{Relative Deviation} = \frac{\text{S.D.}}{\bar{m}} \times 100 = \frac{0.10}{1.67} \times 100 = 5.8\%$$

G1

but could not be used, due to the low dispersion* of the instrument employed which results in interference from Fe 4172.127.

The next most sensitive gallium line, Ga 4032.982, invariably has excessive interference from Mn 4033.073 in all rock, soil and mineral samples.

A line much less sensitive than those referred to above, but commonly used in spectrochemical analysis, is Ga 2943.637. This is the spectral line used for the determination of gallium in this investigation. Although the M.I.T. wavelength tables list the relative intensity of this line as "10" (compared to "2000" for Ga 4172 and "1000" for Ga 4032), Ahrens and Taylor (1961) assign the value of "100" as the line is sensitive enough for any trace analytical work.

In almost all gallium determinations, indium is used as the internal standard. It is volatile, has lines with excitation properties similar to, and near those of gallium, and has an extremely low concentration in silicate rocks, well below its detection limit (Ahrens, 1955). The analysis pair used is:

Ga 2943.637

In 3256.09

*Linear dispersion is defined as $d\lambda/dl$ where dl is the separation on the photographic plate of two neighboring lines differing in wavelength by $d\lambda$.

The indium is added to the rock powder as 5% K_2SO_4 containing 0.133% In_2O_3 . (The recommended amount of 1% K_2SO_4 containing 2% In_2O_3 , as given by Ahrens and Taylor, 1961, produces an indium line too intense to read under the conditions used. In_2O_3 from A. D. Mackay, Inc. New York).

Various attempts were made to establish a working curve for gallium. A synthetic sample, to approximate rock composition, was prepared as follows:

	%	
SiO_2	70	
Fe_2O_3	3	
Al_2O_3	10	
K_2SO_4	5	(includes In_2O_3)
Na_2CO_3	5	
$CaCO_3$	4	
MgO	3	

(SiO_2 and Al_2O_3 "Specpure" brand from Johnson, Mathey, London; all others "Baker Analysed" reagents from J. T. Baker Co., New Jersey). To this, varying amounts of gallium as Ga_2O_3 (A. D. Mackay, N. Y.) were added.

While a linear relationship is obtained for the gallium concentrations, reproducibility was poor. Furthermore, in testing the curve with standard rock samples with known gallium content, extremely low results were obtained.

Another attempt involved the dilution of U.S.G.S. Standard Granite G1, which contains 18 ppm gallium (Ahrens

and Fleischer, 1960) with quartz. Results were completely erratic.

Much of the trouble is due to SiO band spectra. Therefore, it was decided to remove much of the silica prior to arcing. This involved treatment of the rock crush with hydrofluoric acid and evaporation to remove the silica as silicon tetrafluoride. As both gallium and indium fluoride are involatile, there is no danger of loss of gallium or indium from the sample during the evaporation step.

A series of varying gallium concentrations is obtained by using U.S.G.S. Standard Granite G1. This is done in two ways: (a) by diluting G1 with quartz and keeping the amount of In_2O_3 added, fixed, and, (b) by varying the amount of In_2O_3 added to a fixed weight of G1. Both methods give corresponding results. The desilicified samples are mixed with spectrographic carbon in the ratio of 1:1. Electrodes $1/8'' \times 3\text{mm} \times 3\text{mm}$ are best suited for the arcing of these samples. No commercial electrodes with these dimensions are available, and $1/8'' \times 3\text{mm} \times 6.3\text{mm}$ electrodes (Ultra Carbon type 5440 or National Carbon type 3979) are turned down on a "Spec-Shaper" to the required dimensions. The curve obtained from the desilicified samples is tested with U.S.G.S. Standard Diabase W1 containing 16 ppm gallium (Ahrens and Fleischer, 1960), showing satisfactory results.

TABLE VIII: Replicate determinations of Ga for G1 diluted 1:1 with Quartz

Number	d		$\frac{d_0-d}{d}$		I		R	R ²	
	Ga 2943	In 5256	Ga 2943	In 5256	Ga 2943	In 5256	$\frac{I \text{ Ga} 2943}{I \text{ In} 5256}$		
1	73.5	27.5	0.36	2.64	2.63	7.45	0.35	0.123	
2	75.5	27.2	0.32	2.68	2.50	7.50	0.33	0.109	
3	85.0	30.5	0.18	2.28	1.90	6.82	0.28	0.078	
4	51.0	10.0	0.96	9.00	4.32	16.00	0.27	0.073	
5	89.2	55.0	0.12	0.82	1.57	4.00	0.39	0.152	
6	87.0	42.6	0.15	1.35	1.74	5.11	0.34	0.116	
7	81.5	35.2	0.23	1.84	2.14	6.07	0.35	0.123	
8	79.8	37.8	0.25	1.64	2.22	5.76	0.39	0.152	
							2.70	0.926	
							$\bar{m} = 0.34$		

$$\text{Standard Deviation} = \sqrt{\frac{\sum R^2}{n} - \frac{(\sum R)^2}{n^2}}$$

$$= \sqrt{\frac{0.926}{8} - \frac{7.290}{64}} = \underline{.014}$$

$$\text{Relative Deviation} = \frac{\text{S.D.}}{\bar{m}} \times 100 = \frac{0.014}{0.34} \times 100 = \underline{4.1\%}$$

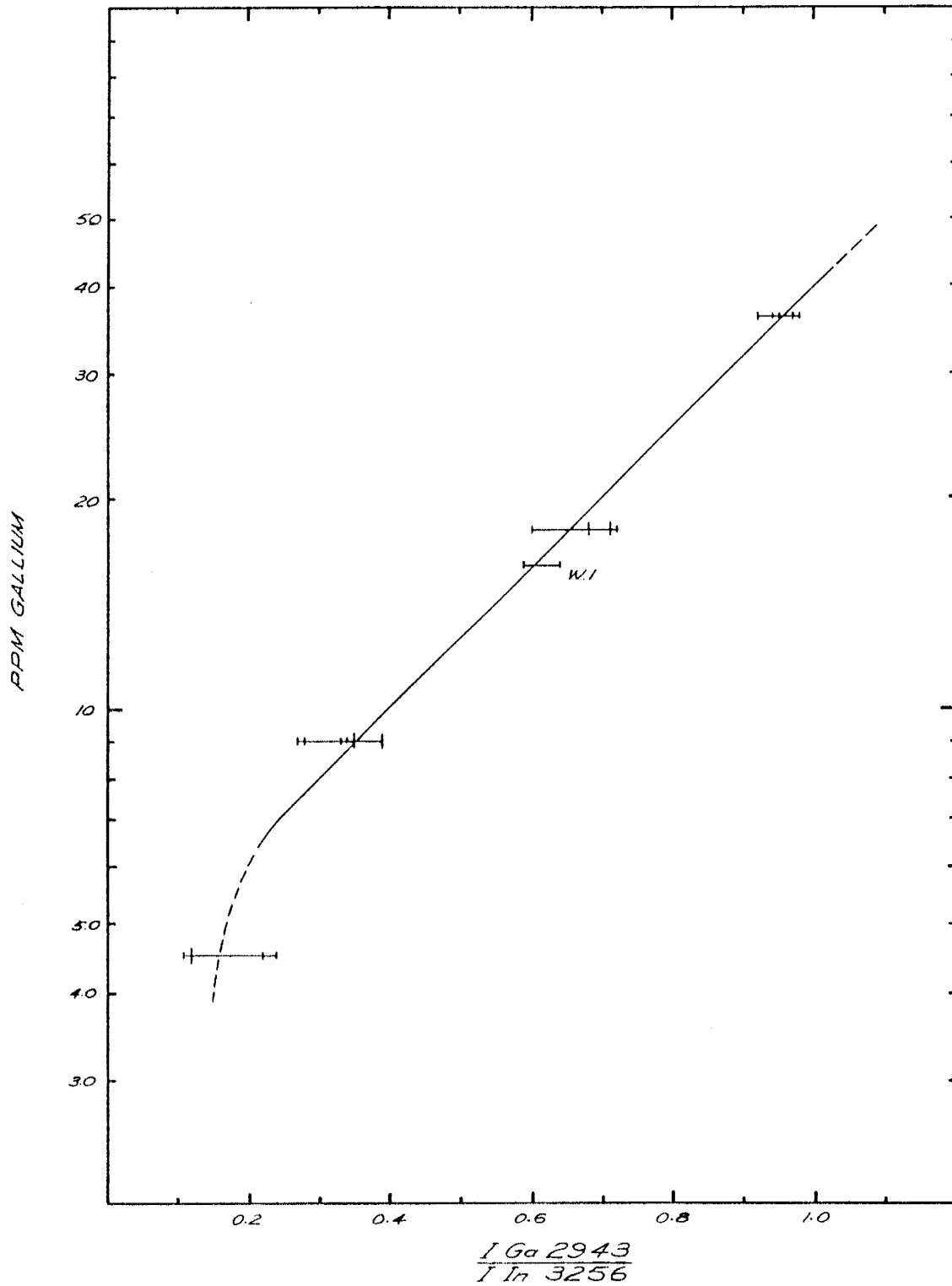


FIG. 10. WORKING CURVE FOR GALLIUM

The final working curve for gallium is shown in Figure 10.

Replicate arcings of G1, diluted 1:1 with quartz and containing 9 ppm gallium, show a relative deviation of 4.1% (Table VIII).

Complete arcing details are given in Appendix B.

RESULTS

Gallium Content and the Ga/Al Ratio in Sedimentary and Source Rocks

Tables IX, X, and XI show the gallium content and Ga.1000/Al ratios for rocks from the Zuni, Gallinas, and Hatchet Gap areas respectively.

Zuni Mountains Area:

The results from this area, the largest covered, show that the gallium content generally varies sympathetically with the aluminum content in both crystalline and younger, overlying, derived rocks.

There is little difference, with the exception of sample Z7, among the Ga.1000/Al ratios of the various granitic or meta-rhyolitic rocks. The average gallium content is 13 ppm with a Ga.1000/Al ratio of 0.15. The corresponding figures for the overlying sedimentary rocks are 8 ppm and 0.17. If only the samples taken from the basal arkose are considered, that is, ignoring samples 9b, 9c, and 9d, a Ga.1000/Al ratio of 0.18 is obtained. This slight increase in the arkose of the gallium content relative to that of aluminum over that of the parent source rock is very close to the precision of the analyses and more sampling is necessary to determine its significance.

The high value for the Ga.1000/Al ratio in sample Z7 may indicate some sort of sedimentary content, or par-

Table IX: Zuni Mountains Samples - Aluminum and Gallium
content and Ga.1000/Al ratios

Sample	$\frac{I \text{ Al}^{2652}}{I \text{ Sr}^{2931}}$	%Al ₂ O ₃	%Al	$\frac{I \text{ Ga}^{2943}}{I \text{ In}^{3256}}$	ppm Ga	Ga.1000/Al
Z 1	2.03	18.7	9.91	0.51	13	0.13
Z 2	1.85	16.5	8.74	0.48	12	0.14
Z 3	0.91	6.2	3.29	0.22	6.5	0.20
Z 4	1.69	14.6	7.74	0.46	11.5	0.15
Z 5	1.92	17.3	9.17	0.53	13.5	0.15
Z 7	1.65	14.1	7.47	0.63	17	0.23
Z 8	1.48	12.2	6.47	0.35	9	0.14
Z9a	1.00	7.1	3.76	0.385	10	0.26
Z9b	1.68	14.5	7.68	0.415	10	0.13
Z9c	0.97	6.8	3.60	0.12	5	0.14
Z9d	1.03	7.4	3.92	0.22	6.5	0.16
Z10	1.81	16.0	8.48	0.445	11	0.13
Z11	1.42	11.4	6.04	0.30	8	0.13
Z12	1.76	15.4	8.16	0.48	12	0.15
Z13	1.47	12.0	6.36	0.56	14.5	0.23
Z15	1.44	11.7	6.20	0.37	9	0.14
Z16	1.86	16.6	8.80	0.59	15.5	0.18

tial sedimentary origin, for the "metarhyolite". Hydrothermal fluids, the presence of which is shown by nearby fluorite mineralization, may, however, have affected the original Ga/Al ratio. Sample Z13 is from what appears to be a sandstone inclusion in this type of rock, and has a Ga.1000/Al ratio of 0.23.

The reversion of the Ga.1000/Al ratio in stratigraphically higher sedimentary layers to the value obtained for the crystalline rocks, indicates that any change in this ratio only occurs in the first derived rocks. Of the four localities where basal arkoses were investigated in this area, three show an increase in the Ga.1000/Al value over the immediately overlain crystalline rocks, and the fourth shows no change. Hydrothermal alteration after deposition appears unlikely as a cause for this increase since the underlying rocks would be expected to show a similar change.

Gallinas Area:

The area sampled in the Gallinas Mountains, though small, shows similar values for the Ga.1000/Al ratios as those obtained in the Zuni Mountains. The granitic basement contains 12 ppm gallium with a Ga.1000/Al ratio of 0.15, while the overlying sedimentary rock contains 7.5 ppm and has a Ga.1000/Al ratio of 0.17.

Hatchet Gap Area:

The Ga.1000/Al data from the basement granite support the field observation that there are, in fact, two

Table X: Gallinas Samples - Aluminum and Gallium Content,
and Ga.1000/Al ratios

Sample	$\frac{I \text{ Al2652}}{I \text{ Sr2931}}$	%Al ₂ O ₃	%Al	$\frac{I \text{ Ga2943}}{I \text{ In3256}}$	ppm Ga	Ga.1000/Al
Gs1	1.73	15.0	7.95	0.48	12	0.15
Gs2	1.05	7.6	4.03	0.28	7.5	0.19
Gs3	1.13	8.4	4.45	0.28	7.5	0.17
Gs4	1.28	10.0	5.30	0.27	7.5	0.14

Table XI: Hatchet Gap Samples - Aluminum and Gallium
content, and Ga.1000/Al ratios

Sample	$\frac{I \text{ Al2652}}{I \text{ Sr2931}}$	%Al ₂ O ₃	%Al	$\frac{I \text{ Ga2943}}{I \text{ In3256}}$	ppm Ga	Ga.1000/Al
H1	1.76	15.4	8.16	0.65	18	0.22
H2	xx	xx	xx	N.D.		
H3	1.67	14.3	7.58	0.835	27	0.36
H4	1.64	14.0	7.42	0.815	26	0.35
H5	0.48	2.6	1.37	N.D.		
H6	1.52	12.5	6.62	0.67	18.5	0.28
H7	1.73	15.0	7.95	0.795	25	0.31
H8	1.16	8.6	4.56	0.345	9	0.20
H9	1.04	7.5	3.97	0.275	7.5	0.19

xx Less than 2%

N.D.. Not detected.

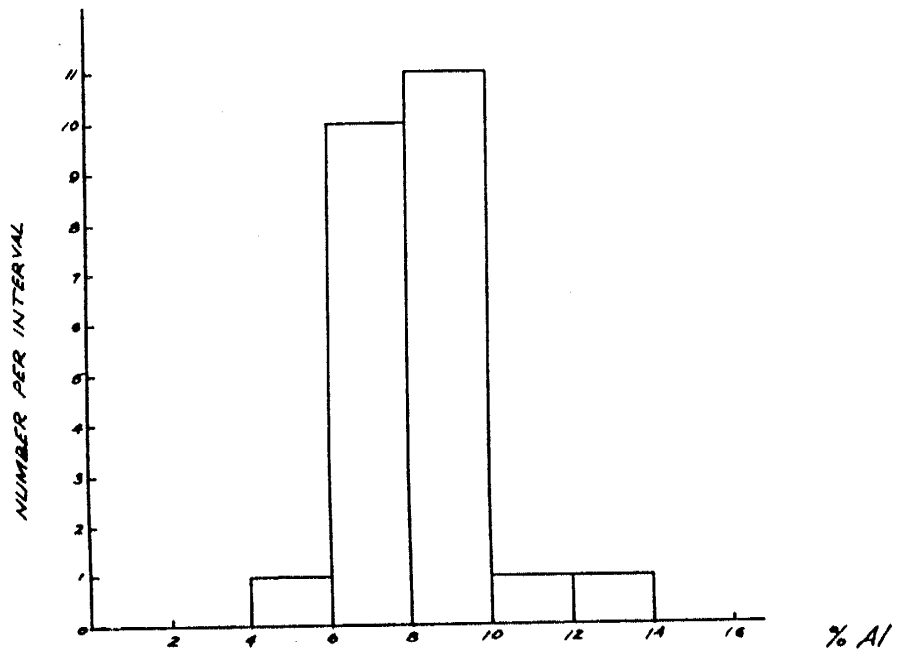


FIG. 12. FREQUENCY DISTRIBUTION FOR ALUMINUM IN NEW MEXICO GRANITES

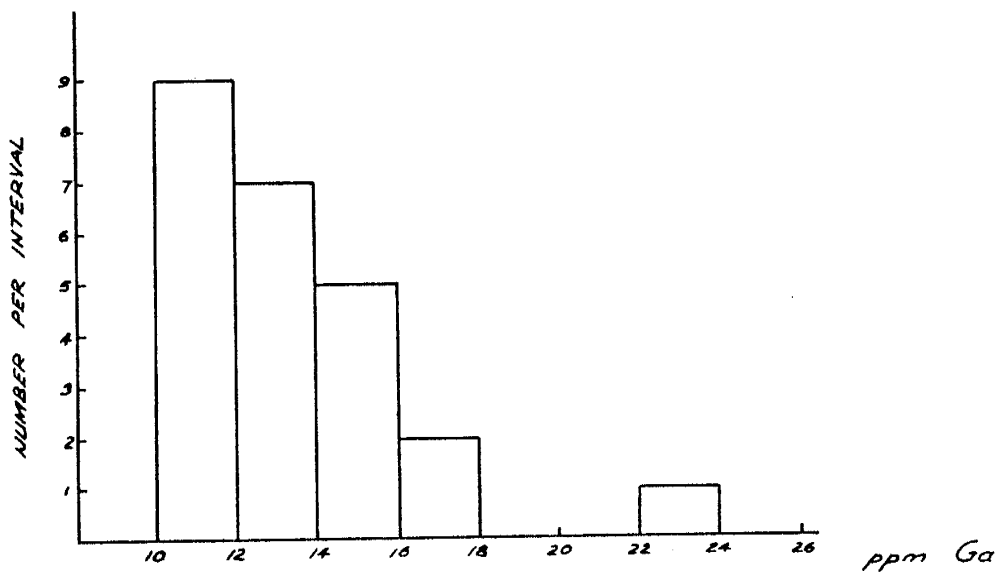


FIG. 11. FREQUENCY DISTRIBUTION FOR GALLIUM IN NEW MEXICO GRANITES

granites in the area sampled. Sample H1, characteristically different from the other granite samples, has a gallium content of 18 ppm, and a Ga.1000/Al ratio of 0.22, as compared to the average values for the rest of 24 ppm and 0.32.

The figures show little relationship between the overlying sandstone, with a Ga.1000/Al ratio of 0.20, and the basement granites. A method for decreasing the Ga/Al ratio in the sedimentary rocks cannot easily be postulated, and one must conclude that the source rocks are not the underlying granitic masses.

The Gallium Content and the Ga.1000/Al
Ratios in New Mexico Granites

A total of twenty-four granite samples from the State of New Mexico, whose locations are shown in Figure 7, were analysed for aluminum and gallium. The samples are described in Table VI, and results are given in Table XII.

The gallium content of the granites is remarkable for its uniformity, the concentration for 22 samples varying from 11 ppm to 16 ppm, with one sample containing 18 ppm and one 24 ppm. This, of course, agrees with the results for Canadian granites (Ahrens, 1954), as shown in Figure 2. The frequency distribution plot for gallium in the New Mexico granites, as shown in Figure 11, differs from previous work in showing definite positive skewness (as op-

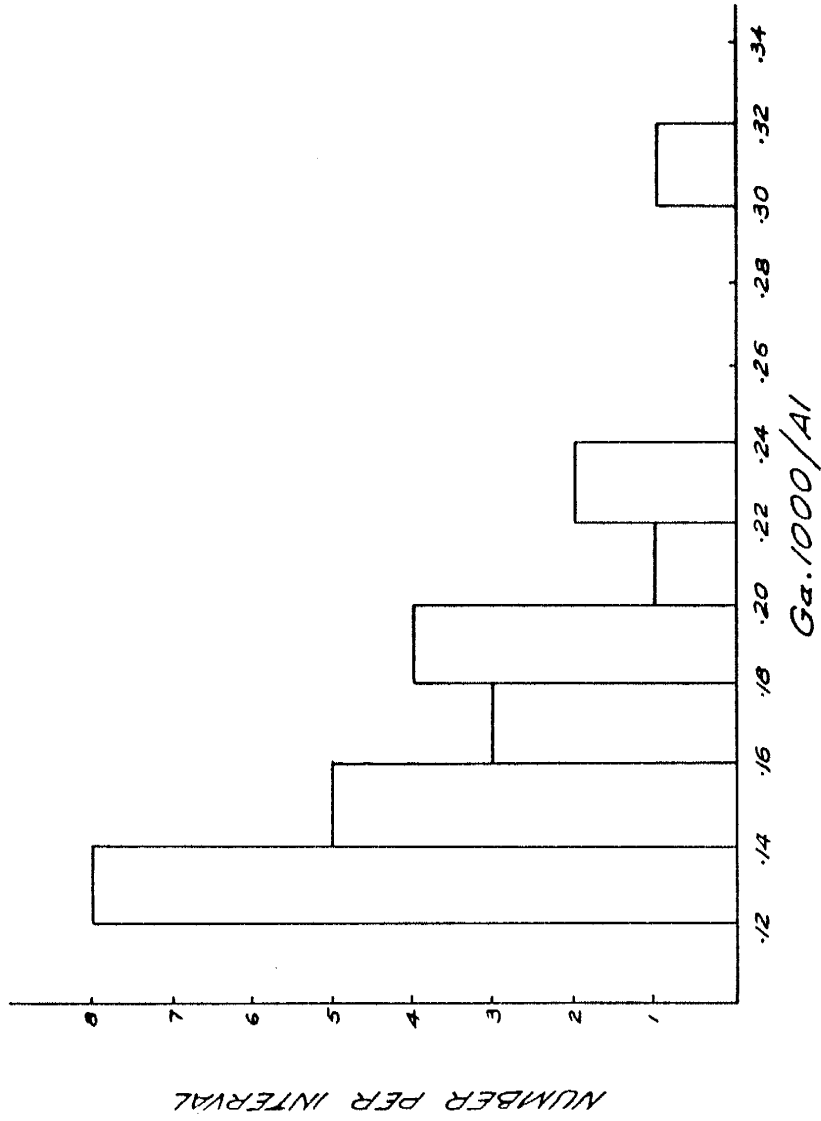


FIG. 13. FREQUENCY DISTRIBUTION FOR Ga.1000/AI
IN NEW MEXICO GRANITES

posed to the normal distribution shown by Ahrens, (1954). This skewness is further emphasized by the frequency distribution plot for the aluminum (Figure 12), which shows normal distribution.

The Ga.1000/Al ratios for twenty - three samples varies from 0.13 to 0.23, with one sample at 0.32. This frequency distribution plot is also positively skewed (Figure 13).

It appears that there is some mechanism for the control of the gallium content in the production of granite, or granitic magma, that operates independently of the aluminum concentration. Iron (III) may have some influence due to its ionic size (0.67 \AA). The fact that gallium is slightly chalcophilic may be a factor, but such an effect, judging from the literature, is believed to be slight. Rooke (1964) suggests that sodium may also have a slight influence on the gallium concentration.

A factor that may explain the skewness in the frequency distribution plots is the possibility that the granites may have been formed by two completely different processes, that is "igneous" and "metasomatic". The granites examined by Ahrens (1954) appear to be of unquestionable igneous origin. If, however, some granites of sedimentary origin with different Ga/Al ratios are included in such a frequency distribution plot, skewness may well result. Before any definite conclusions are drawn, however, many more granites should be investigated.

Samples H3, H4, H6, and H7 from the Hatchet Gap area, show an average gallium content of 24 ppm and a Ga.1000/Al ratio of 0.32 for this granite. These values are exceptionally high when compared to the other granites, and may indicate a different and quite unique origin for this particular rock. If this granite is sedimentary in origin, the figures indicate extreme fractionation of gallium and aluminum in the original sedimentary process. Such fractionation could occur in moderately acidic or alkaline waters.

The Ga.1000/Al ratio may possibly be used for correlation purposes in granites. Sample Gr12, tentatively identified as Embudo granite, has a Ga.1000/Al value of 0.18, while the Embudo granite, Gr11, has a value of 0.16. These values fall within the precision of the analysis. Compared to this are the two granites, Gr15 and Gr16, sampled close together in the Ladron mountains, with Ga.1000/Al values of 0.19 and 0.13 respectively. As noted in Table VI, these granites are also mineralogically different. Both have the same gallium content of 12 ppm.

CONCLUSIONS AND RECOMMENDATIONS

Results obtained in the Zuni and Gallinas areas suggest that some fractionation of gallium and aluminum may occur during the formation of arkosic rocks from a pre-existing igneous source. If such fractionation is generally true, the Bliss Sandstone in the Hatchet Gap area has not been formed from the immediately underlying granite.

The frequency distribution plots of the gallium and aluminum contents of the granites from New Mexico suggest that some mechanism other than aluminum content, such as different origin, variation in mineral composition, or association with other ions, may determine the distribution of gallium.

It is recommended that as many granites as possible be investigated in the manner described in order to obtain sufficient data for more precise statistical conclusions. It is further recommended that the gallium content in granites be compared to that of other ions such as iron (III) and sodium so that the variation of gallium with other major ions in granitic rocks will be better defined. A complete petrographic study of the granites here analysed will be of value.

Chemically, there exists a need for more accurate and reliable data on the solubilities of gallium and aluminum under varying conditions of pH.

APPENDIX A

Spectrographic Analysis of Aluminum

Electrodes: Lower, 1/8" x 2mm (ID) x 1.5mm (depth)

Upper, 1/8" solid, sharpened.

Amount of sample: Lower electrode filled, tamped in firmly.

Arc gap: 6 mm

Rotating sector setting: 6 %

Slit: 50 microns

Current: 7 amps

Voltage: Approximately 40 volts

Period of preheat: 5 seconds deadshort

Period of burn: 50 seconds

Film: Kodak Spectrographic Number 1

Developer: Kodak D19, 4 and 1/2 minutes

Quick-stop: 1.8% acetic acid solution, 15 seconds

Fixer: Hypo, 5 minutes

Wash: 15 minutes in running tap water, final rinse in
distilled water

APPENDIX B

Spectrographic Analysis of Gallium

Electrodes: Lower, 1/8" x 3mm (ID). x 3mm (depth)

Upper, 1/8" solid, sharpened

Amount of sample: Lower electrode filled, tamped in firmly

Arc gap: 6 mm

Rotating sector setting: 30 to 40%

Slit: 50 microns

Current: 7 amps

Voltage: Approximately 40 volts

Period of preheat: None

Period of burn: To end of alkali volatilization plus 5
seconds. (Completion of alkali vola-
tization indicated by sudden drop in
arc gap current)

Film and developing: As for aluminum

REFERENCES

- Ahrens, L. H. 1952, The use of ionization potentials. Part 1. Ionic radii of the elements: *Geochim. et Cosmochim. Acta*, v. 2, p.155-169
- Ahrens, L. H., 1954, The lognormal distribution of the elements (2): *Geochim. et Cosmochim. Acta*, v. 6, p.121-131
- Ahrens, L. H., 1955, Quantitative Spectrochemical Analysis of Silicates: Pergamon Press Ltd., London, 119p
- Ahrens, L. H., and Fleischer, M., 1960, Report on trace constituents in granite G.1 and diabase W.1: in *U. S. Geol. Survey Bull.* 1113, 126p
- Ahrens, L. H., and Taylor, S. R., 1961, Spectrochemical Analysis: Addison-Wesley Publishing Co., Reading, Mass. 454p
- Bell, C. K., 1953, The geochemistry of gallium: unpublished dissertation PhD., M.I. T., Cambridge, Mass.
- Burton, J. D., Culkin, F., and Riley, J. P., 1959, The abundances of gallium and germanium in terrestrial materials; *Geochim. et Cosmochim. Acta*, v. 16, p.151-180
- Dennen, W. H., 1949, Spectrographic investigation of major element variations across igneous contacts: un-

published dissertation Ph.D., M. I. T., Cambridge, Mass.

Fairbairn, H. W., 1953, Precision and accuracy of chemical analysis of silicate rocks: *Geochim. et Cosmochim. Acta*, v. 4, p143-156

Filby, R. H., and Leininger, R. K., 1960, Spectrographic determination of the major constituents of granite G.1 and diabase W.1; in U. S. Geol. Survey Bull. 1113, 126p

Kvalheim, A., 1947, Spectrochemical determination of the major constituents of minerals and rocks: *Journal of the Optical Society of America*, v. 37, p. 585-592

Lasky, S. G., 1947, Geology and ore deposits of the Little Hatchet Mountains: U. S. Geol. Survey Professional Paper 208, 101p

Latimer, W. M., 1952, The oxidation states of the elements and their potentials in aqueous solutions, 2nd ed.: Prentice Hall, Inc., Englewood Cliffs, N. J., 392p

National Bureau of Standards, 1931, Certificates of analysis of standard samples: U. S. Govt. printing office, Washington, D. C.

Nockolds, S. R., and Mitchell, R. L., 1948, The geochemistry of some Caledonian plutonic rocks: a study

in the relationship between major and trace elements of igneous rocks and their minerals: Trans. of the Royal Society of Edinburgh, v. 61, p.533-575

Perhac, R. M., 1960, Geology and mineral deposits of the Gallinas Mountains, New Mexico: unpublished dissertation PhD., University of Michigan, Ann Arbor, Mich.

Rooke, Joan M., 1964, Element distribution in some acid igneous rocks of Africa: Geochim. et Cosmochim. Acta, v. 28, p.1187-1197

Smith, Clay T., and others, Mount Sedgwick 15 min. quadrangle, unpublished.

Sokolova, L. D., 1962, Colorimetric determination of trace amounts of gallium with crystal violet: Materialy 4-oi (Chetvertoi) Nauchn. Konf. Aspirantov, Sb 1962, Rostov University, Rostov-on-Don, U. S. S. R., p.130-133

Taylor, S. R., 1964, Abundance of chemical elements in the continental crust; a new table: Geochim. et Cosmochim. Acta, v. 28, p.1273-1285

Vinogradov, A. P., 1962, Average contents of chemical elements in the principal types of igneous rocks of the Earth's crust: Geochemistry (translation) number 7, p.641-664

Vainovitch, I. A., and Debras, J., 1957, Sur la précision et la rapidité de certains dosages chimiques et physiques de l'alumine dans les silico-alumin-eaux: Chimie Analytique, v. 39, p.418-428

Zeller, R. R., 1958, in Guidebook of the Hatchet Mountains and the Cook's Range-Florida Mountains areas: 11th field conference, Roswell Geological Soc., Roswell, N. M.

This thesis is accepted on behalf of the faculty of the
Institute by the following committee:

Edward C. Bugh

Frank E. Kottlowicki

Lawrence R. Hathaway

Clay T. Smith

Date: March 19, 1965

