AN INVESTIGATION OF SOME GERMANIUM OCCURRENCES IN SOUTHWESTERN NEW MEXICO

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Master of Science
in Geology

by
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ABSTRACT

Germanium occurrences in coal and base-metal ores of Southwestern New Mexico were investigated. Carthage coal fines contain 4 parts per million germanium which is uniformly distributed throughout the various constituents of the coal. Ashing of the coal fines concentrates the germanium in the ash to the extent of 35 parts per million. The vitrain fraction of the coal, having a low ash content of 3.36 percent, indicates a concentration of 122 parts per million germanium in the ash.

Forty-three base-metal ore samples were investigated for possible germanium content. Although fifteen samples contain detectable amounts of germanium, only three samples contain germanium in a concentration greater than 10 parts per million. The three samples were obtained from the Tres Hermanas, Hillsboro, and Iron Mountain #2 Districts and contain 47, 71, and 88 parts per million germanium, respectively.

The zinc silicate mineral, willemite, is the predominant mineral in these three samples, and is found to be the principal host for germanium.

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INTRODUCTION

Germanium has attained importance only in recent years although it has been known for many years and considerable study has been made of this element and its various compounds. It has properties somewhere between that of a true metal and a nonmetal and is usually considered a metalloid. Materials such as germanium belong to a class of materials known as semiconductors and have become of major importance in electronic devices. The United States began commercial production of germanium scarcely a decade ago.

The major use of germanium is in manufacturing transistors, diodes, and power rectifiers. Other uses for germanium are small in comparison to those mentioned above. Several potential uses of germanium do exist, however. According to Fisher (1960), glass, in which all or part of the silicon dioxide has been replaced by germanium dioxide, displays an unusually high index of refraction and is useful for wide-angle camera lenses and microscope objectives. Glass containing magnesium germanate has the property of transmitting infrared radiation over broad regions of the spectrum and is used in infrared spectroscopes and other infrared optical instruments. Germanium-magnesium phosphors have been used in fluorescent lights. Germanium has been used for imparting increased hardness and strength to copper, aluminum, and magnesium and improves their rolling properties. Germanium-gold alloys have been experimented with as dental alloys.

Germanium requirements in the United States at the present time are met by imported concentrates, importation of germanium metal and by recovery of germanium from domestic zinc smelter flue dusts. The above sources are not sufficiently large to supply adequately the current and future demands for this metal. This is especially true in the event of restrictions on imports due to a national emergency. These unreliable sources have also been a major factor in curtailing usage of this important metal. Any new sources of germanium in the United States, therefore, would be of considerable economic and strategic importance.

Previous Work

Stadnichenko, Murata, Zubovic, and Hufschmidt (1953) investigated the concentration of germanium in the ash of American coals. Among the samples analyzed were two samples from the Carthage coalfield in Socorro County, New Mexico. The results of their analyses showed a germanium content of approximately 10 parts per million in the ash for both samples. Early in 1962, a U. S. Bureau of Mines engineer found germanium in a sample of coal from a stockpile of coal fines in the SE¼ Sec. 10, T. 5S., R. 2E., Socorro County, New Mexico.

Kaiser, Herring, and Rabbitt (1954) report a germanium content of 80 parts per million in a copper-gold-silver concentrate from the Banner mill near Lordsburg, Hidalgo County, New Mexico. The ore from which this concentrate was obtained came from the Bonney and Anita #1 mines in the Lordsburg District.

An additional report of germanium occurrences in ore deposits in New Mexico, although encountered too late for consideration in the current investigation, should be mentioned. Warner, Holser, Wilmarth, and Cameron (1959), in their report of the association of beryllium with other elements, mentioned germanium occurrences in one sample from the Central District in Grant County and in several samples from the Victorio Mountains in Luna County. The analyses indicated an average germanium content of approximately 10 parts per million.

Purpose of Investigation

Since coal and coal fly ash as well as sulfide ore deposits are potential sources of germanium, the purpose of the present investigation was to examine certain coal and ore deposits, especially base-metal ores, in Southwestern New Mexico for their germanium content. Germanium in coal has been shown to occur in certain hydrocarbon constituents (Stadnichenko, 1953) and such values might be economically recovered after physical separation of the germanium-bearing constituent. The germanium contained in sulfide deposits is currently recovered as a by-product of the smelting operation. Identification of possible geological occurrences or likely mineral associations might enlarge domestic resources of germanium. Moreover, a favorable occurrence of germanium in such base-metal ores might reactivate the depressed base-metal mining industry in New Mexico.

Acknowledgements

Special recognition must be given to Mr. Abner D. Hahn of the U. S. Bureau of Mines for his initial suggestion to investigate germanium-bearing mineral deposits in New Mexico. It was through his efforts that a fellowship was set up for this purpose as a cooperative agreement between the U. S. Bureau of Mines and the New Mexico Institute of Mining and Technology. As the first recipient of the fellowship, the author gratefully acknowledges the financial assistance of the U. S. Bureau of Mines which made this investigation possible.

A deep feeling of gratitude and appreciation is extended to Dr. Clay T. Smith and Dr. Roshan B. Bhappu who served as co-advisors during the preparation of this thesis.

The author also acknowledges valuable help received from several members of the Institute staff. Special mention is made of: Dr. Dexter H. Reynolds, for his aid in the development of suitable analytical techniques; Dr. Antonius J. Budding and Mr. Donald Stephenson for their assistance in x-ray analysis; and Mr. George B. Griswold for his assistance in locating certain mineral properties.

Lastly, the author wishes to thank Dr. Gerald U. Greene and Mr. Donald Fingado for their assistance in locating claims and securing samples.

ANALYTICAL METHODS

Spectrographic

Spectrographic methods have been extensively used in the determination of germanium in the past. The general procedure consists of volatilizing samples in a D.C. arc and comparing the intensity of spectral lines with known standards.

In the current investigation a modification of the procedure used by the American Zinc Company of Illinois, Monsanto, Illinois, was utilized in order to increase the accuracy of quantitative determination. This modification entails the use of an internal standard and comparison of the line intensity of homologous pairs. A more detailed description of the above procedures can be found in Appendix I.

Spectrophotometric-Phenylfluorone Color

Carbon Tetrachloride Extraction Isolation

Luke and Campbell (1956) developed an improved spectrophotometric phenylfluorone method for determination of microgram quantities of germanium. Interference from other metals is eliminated by isolating germanium with a carbon tetrachloride extraction previous to the photometric determination. For the purpose of the present investigation, slight modifications of their procedure have been made as outlined in Appendix II.

Distillation Method

The procedure used here has been adapted from the method employed by the American Zinc Company of Illinois, Monsanto, Illinois. The procedure consists of a peroxide fusion followed by suitable oxidation and chlorination to form germanium tetrachloride ($GeCl_4$). This latter compound is then distilled and the color developed by adding phenylfluorone to the distillate. A spectrophotometer is used to measure optical densities. A more detailed outline of the procedure is given in Appendix III.

GERMANIUM IN CARTHAGE COAL

Extensive studies have been made by many investigators on the germanium content of coal. The following broad generalizations were made by Fisher (1960):

(1) Coals with a high vitrain (shiny coal) content are much richer in germanium than coal with a low vitrain content.

(2) Low-ash coals are richer in germanium than coals with a high-ash content.

(3) Germanium is believed to be associated with the organic matter and not the mineral matter in the coal.

(4) Germanium is usually concentrated in the top or bottom few inches of coal beds.

Samples and Location

Samples of coal fines were obtained from the A. B. Baca Coal Mine stockpile located in the SE¼ Sec. 10, T. 5S., R. 2E., Socorro County, New Mexico. The coal fines in this stockpile came from the Carthage coal bed, a part of the Mesaverde formation of Upper Cretaceous age.

Screen Analysis and Spectrographic Analysis

Several sacks of the fine coal, having a total weight of about 200 pounds, were combined to form a bulk sample. A screen analysis of a representative fraction cut from the bulk sample is given in Table I.

TABLE I - Screen analysis of stockpiled Carthage fine coal

Mesh (Tyler)	Grams Retained	Percent Retained	Percent Passing
10	212	42.7	57.3
20	133	26.8	30.5
35	76	15.3	15.2
48	24	4.8	10.4
65	19	3.8	6.6
100	14	2.8	3.8
Minus 100	19	3.8	
Total	497	100.0	

Each of the screen fractions listed in Table I was analyzed for germanium content by the spectrographic method.

The results of the preliminary spectrographic analysis with known germanium standards indicated that the lower limit of sensitivity for germanium was about 10 parts per million using the technique described in Appendix I. Since germanium lines could not be detected for the screen fractions tested, it was assumed that germanium content of the fractions analyzed was less than 10 parts per million.

The above results were confirmed by chemical analysis of germanium on the same screen fractions by the analytical laboratories of the U. S. Bureau of Mines, Salt Lake City, Utah. The results of the chemical analyses as shown in Table II confirm the assumption that the fractions contained less than 10 parts per million germanium.

TABLE II - Germanium content of sized fine coal fractions

Sample Identification	Mesh size (Tyler)	Germanium (ppm)*
HWS - 1	Head sample	4
HWS - 2	plus 10	2
HWS - 3	10 to 20	4
HWS - 4	20 to 35	4
HWS - 5	35 to 48	2
HWS - 6	minus 48	1

* Results from U. S. Bureau of Mines Laboratories, Salt Lake City, Utah

Froth Flotation Separation

Since it was thought possible that germanium might be concentrated in one of the constituents of the coal an effort was made to separate the germanium enriched fraction of the coal by froth flotation. This technique has been recommended by Gaudin (1957) for selective separation of different constituents of coal. For froth flotation testing the bulk sample of fine coal was devided into two fractions by screening on 10-mesh. The plus 10-mesh fraction was discarded while the minus 10-mesh was subjected to froth flotation.

Eight laboratory flotation tests were conducted using a Fagergren laboratory machine. Each sample was processed as follows:

(1) a 500 gram charge of coal was placed in the cell,

(2) 2,200 milliliters of water were added, which produced a pulp containing 18.5 percent solids,

(3) methyl isobutyl carbinol was added and the cell contents were conditioned,

(4) auxiliary reagents were added and the pulp further conditioned,

TABLE III - Results of flotation tests on minus 10-mesh Carthage coal

Test No.	Reagents	Amounts (lb. ton)	Conditioning time (min.)	Products	Germanium (ppm)
1	MIBC#	0.12	1.5	Conc. #1-1	*
	Kerosene	0.36	1.5	Conc. #1-2	*
	MIBC Kerosene	0.12 0.36 **	1.5	Conc. #1-3	*
				Tailing #1	*
2	MIBC Kerosene	0.12 0.36	1.5	Conc. #2-1	*
				Tailing #2	*
3	Same as Test #2			Conc. #3-1	*
				Tailing #3	*
4	Same as Test #2			Conc. #4-1	*
				Tailing #4	*
5	MIBC	0.12	1.5	Conc. #5-1	*
	NaOCl##	0.125	4.5		
	Kerosene	0.36	1.5		
				Tailing #5	*
6	MIBC	0.12	1.5	Conc. #6-1	*
	NaCN### Kerosene	0.50 0.36	6.5		
				Tailing #6	*
7	MIBC	0.06	1.5	Conc. #7-1	*
	MIBC	0.06	1.5	Conc. #7-2	*
	MIBC	0.06	1.5	Conc. #7-3	*
	Pine Oil	0.06	1.5	Conc. #7-4	*
				Tailing #7	*
8	MIBC Potassium Permanganate	0.12 0.40	5.0	No Product	---
	Kerosene	0.12	3.0	Conc. #8-1	*
	Kerosene	0.06	3.0	Conc. #8-2	*
				Heavy Tailing #8	*
				Light Tailing #8	*

\# Methyl isobutyl carbinol
\## Sodium hypochlorite
\### Sodium cyanide
* Less than 10 parts per million
** Added together

(5) air was then introduced to the working cell and the flotation removed.

Results of the flotation tests are given in Table III. Each flotation product was analyzed spectrographically for germanium content.

During the course of investigating flotation procedure for selective separation of coal constituents, a suggestion was made by Hahn (personal communication) to employ selective flotation techniques of "starvation" additions of collectors and frothers, and of depressants such as potassium permanganate.

In Test #7 the "starvation" reagent technique was used on the minus 10-mesh Carthage coal. The reagents MIBC and pine oil were stage added to obtain selectivity. In Test #8 potassium permanganate solution was used as a depressant for the vitrain and gangue fractions while floating the dull variety of coal. The vitrain fraction was then separated from the tailings by gravity concentration.

Heavy Liquid Separation

Gravity concentration was also investigated in an effort to separate possible germanium rich constituents of the Carthage coal. Moore (1940) states that the specific gravity of coal ranges from 1.30 for most lignites to approximately 1.70 for anthracite. Based on this fact, a series of heavy liquid separation tests were made. A diluted tetrabromoethane solution with a specific gravity of 2.0 was selected and used to separate the coal fractions from any siliceous or shaly fractions having a specific gravity greater than 2.0. The sink fraction was found to contain three products, a calcareous, a siliceous, and a shaly fraction. The float fraction, having a specific gravity of less than 2.0, contained two distinct constituents- a shiny coal and a dull coal. Efforts were made to separate these two varieties of coal at a specific gravity of 1.4 obtained by diluting tetrabromoethane with acetone. No apparent separation was obtained at a specific gravity of 1.4.

The fractions obtained from this series of gravity concentration tests were analyzed spectrographically for germanium content. No germanium lines were detected for any of the above fractions, indicating less than 10 ppm of germanium in the fractions.

In another series of tests, four distinct fractions from minus 10-mesh Carthage coal were hand separated with tweezers under a binocular microscope. The four fractions were: siliceous minerals, sulfide minerals, shiny coal, and dull coal. Each of these fractions was analyzed spectrographically and found to contain less than 10 parts per million germanium.

Based on the results of the preceding flotation, heavy liquid, and hand separation tests, it was concluded that germanium was not concentrated to an extent greater than 10 ppm in any one fraction or fractions of the Carthage coal.

Concentration by Ashing

Ashing of coal samples would presumably drive off the volatile constituents and concentrate the germanium in the ash. The dangers of losing, by volatilization, large proportions of germanium during the ashing of a coal have been discussed by Stadnichenko (1953) and

Corey (1959). From those references it was ascertained that a temperature of 600° F for ashing would be suitable for the current investigation.

The samples of Carthage coal were ashed using the following procedure. A 10 gram sample of minus 10-mesh coal was weighed and placed in an uncovered porcelain crucible for ashing. The crucible was placed in an electric furnace for 12 hours at a temperature of about 600° F, removed from the furnace, cooled, and weighed. Percent ash was calculated by use of the formula:

$$\frac{\text{Weight of Ash}}{\text{Weight of Sample}} \times 100 = \text{Percent Ash}$$

The results of ashing and spectrographic analyses on two different samples of the minus 10-mesh Carthage coal were as follows:

Sample No.	Percent Ash	Germanium in Ash (ppm)	Germanium in Sample (ppm)
1	15.84	33	5.2
2	14.90	36	5.3

These results are in fairly good agreement with the 4 parts per million germanium reported by the analytical laboratory of the U. S. Bureau of Mines, Salt Lake City, Utah.

The preceding ashing-spectrographic analysis technique was also used on the products of flotation Test #7 and Test #8. The results of these analyses are given in Table IV and Table V.

TABLE IV - Results of Ashing and Spectrographic Analysis on Test #7 Products

Product	Weight (gm)	Weight (percent)	Ash (percent)	Germanium in Ash (ppm)	Germanium in Product (ppm)
Conc. #7-1	12.0	5.4	8.38	60	5.0
Conc. #7-2	24.2	10.8	9.11	59	5.3
Conc. #7-3	12.5	5.7	15.03	40	6.0
Conc. #7-4	20.3	9.2	9.89	60	5.9
Tailing #7	152.2	68.9	14.35	40	5.7
Composite	221.2	100.0			5.6

TABLE V - Results of Ashing and Spectrographic Analysis on Test #8 Products

Product	Weight (gm)	Weight (percent)	Ash (percent)	Germanium in Ash (ppm)	Germanium in Product (ppm)
Conc. #8-1	33.7	15.5	9.37	57	5.3
Conc. #8-2	12.5	5.8	12.44	43	5.3
Light Tailing #8	147.0	67.9	11.53	47	5.4
Heavy Tailing #8	23.5	10.8	66.46	Undetectable	5.4*
Composite	216.7	100.0			5.3

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* Calculated value from metallurgical balance.

Germanium lines were not detectable in the heavy tailing product. This was as expected since a high ash content in the heavy tailing would not upgrade the product enough for germanium lines to be detectable on the spectrograph.

In order to obtain cleaner separation between the constituents of Carthage coal, samples of shiny coal (vitrain fraction) and dull coal were hand separated by the aid of a binocular microscope from the minus 10-mesh fraction. A one gram sample of each variety was ashed and found to contain 3.36 percent ash and 13.60 percent ash, respectively. Each ash was analyzed spectrographically and was found to contain 122 ppm germanium for the shiny coal and 25 ppm germanium for the dull coal. Conversion of the germanium content to the original samples resulted in 4.1 ppm germanium and 3.4 ppm germanium, respectively. These results again substantiate the previous indication of the lack of differential concentration of germanium in the various coal constituents.

In addition to the shiny and dull coal fractions, a sample of all other extraneous material associated with the coal was ashed in like manner and found to contain 69.64 percent ash. This ash was analyzed spectrographically but germanium lines were not discernable indicating a germanium content of less than 10 ppm. This result is in agreement with previous tests. The high ash content (greater than 60 percent) would not produce an upgraded product having a germanium content large enough to exceed a value of 10 parts per million, the lower limit of detection by the spectrographic technique used.

The above test results are in accord with the previous investigation by Stadnichenko (1953). The reported results were 12.56 percent ash and 10 parts per million germanium content in the ash for Stadnichenko sample #1 and 9.65 percent ash and 12 parts per million germanium content in the ash for Stadnichenko sample #2. Conversion of ash weights and parts per million germanium back to the original samples gives a result of 1.3 and 1.2 parts per million germanium, respectively.

GERMANIUM IN BASE-METAL ORES

According to Fisher (1960), germanium does not occur in the native state and its abundance in the earth's crust is 6.7 parts per million. Several germanium minerals are found, chiefly in South-West Africa, Germany, and Bolivia. The more important germanium minerals are:

(1) Germanite - $7CuS \cdot FeS \cdot GeS_2$ - containing 5 percent germanium

(2) Argyrodite - $4Ag_2S \cdot GeS_2$ - reported to contain between 5 and 7 percent germanium

(3) Renierite - $(Cu,Fe)_3(Fe,Ge,Zn,Sn)(S,As)_4$ - containing between 6.37 and 7.80 percent germanium

None of the above minerals have been found in the United States.

The most common occurrence of germanium is as diadochic atoms or ions within the molecular structure of other minerals. It occurs most abundantly in Sphalerite (ZnS) in quantities ranging from traces to tenths of one percent. Germanium has also been said to occur in cinnabar, pyrargyrite, calamine, pyrites, euxenite, cassiterite, and in tantalum and columbium ores. The amounts recorded for these minerals are small, usually about 10 parts per million or less.

Samples and Location

Samples for analysis were obtained from the Southwestern part of New Mexico. Copper-lead-zinc ores have been mined in Socorro, Sierra, Grant, Luna, and Hidalgo Counties since the latter part of the 19th Century. Samples of ore material or dump rock were obtained from currently operating mines as well as from mines which are now shut down. Several samples were collected from prospect pits and a few samples were taken from rock outcrops.

Forty-three samples in all were collected and analyzed spectrographically for germanium content. The locations of these samples are given in Table VII. The sample numbers given in Table VII are used in Figures 1 through 13 as a guide to the location of the samples.

Spectrographic Analysis of Ore Samples

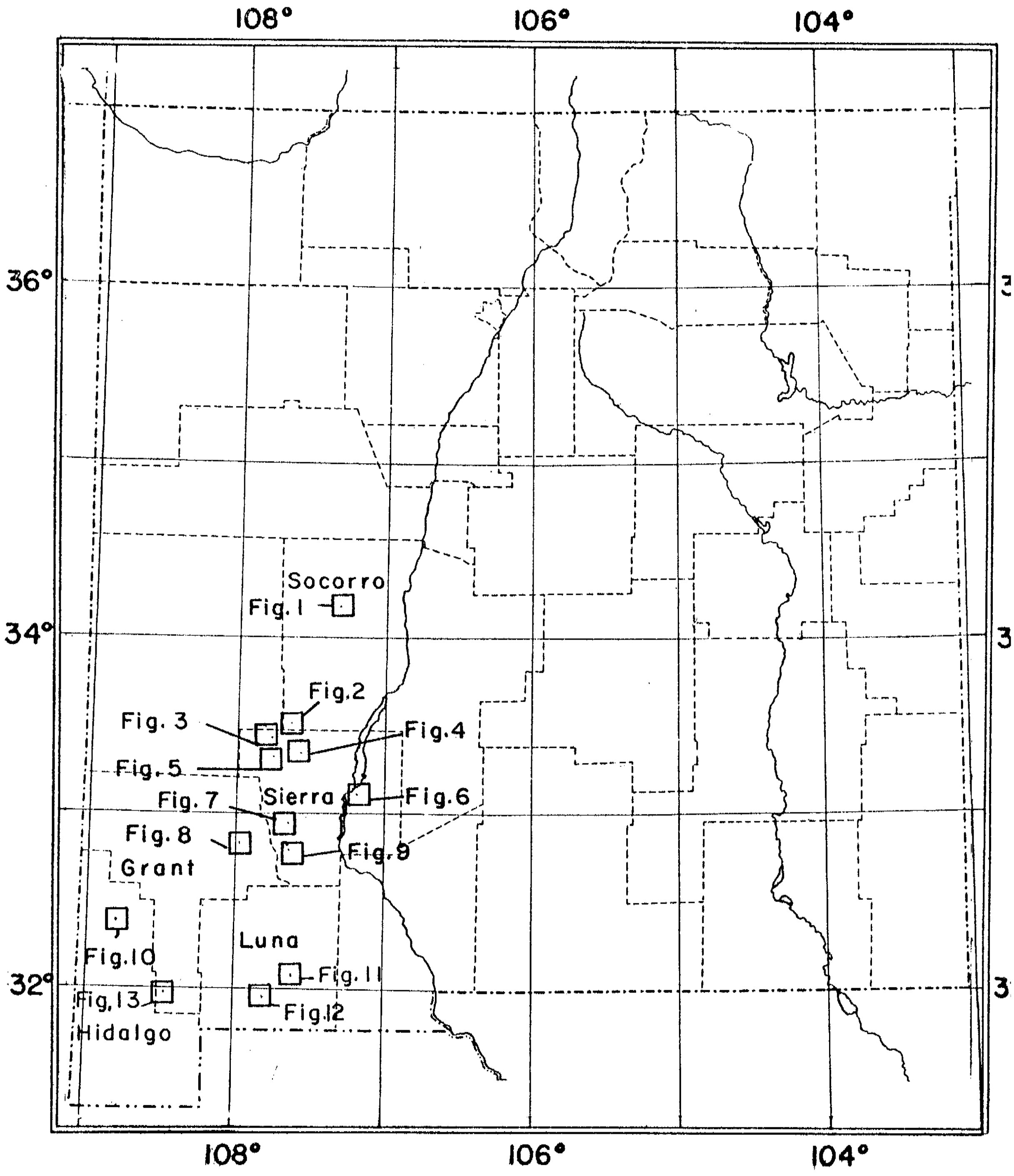
Each sample was prepared for spectrographic analysis as described in Appendix I. In addition to germanium, several other elements present in the ore samples were analyzed qualitatively. The results of these analyses are given in Table VIII.

Germanium content is less than 10 parts per million for all samples tested with the exception of the samples from Petroglyph (Sample #19), Tres Hermanas (Sample #40), and Iron Mountain Mine (Sample #43). In these samples the germanium content ranges from 35 to 73 parts per million.

In regard to the presence of other metallic values in the ore samples investigated, Table VI gives the number of reported occurrences of each metal in the total number of samples analyzed.

TABLE VI - Number of reported occurrences of other metals

No of Samples	Ge	Mo	Co	Ni	Ag	Cu	Pb	Ti	Mn	Be	Cr	Li	V
43	16	31	2	15	29	20	32	42	13	15	13	3	30



INDEX MAP OF NEW MEXICO SHOWING LOCATIONS OF SAMPLES AND FIGURES 1 THROUGH 13

6	5	4	3	2	1
7	8	9	10	11	12
18	17	16	15	14	13
19	20	21	22	23	24
30	29	28	27	26	25
31	32	33	34	35	36

KEY TOWNSHIP

Scale $\frac{1}{126720}$ or 1 Inch = 2 Miles

Explanation of Figures 1 Through 13

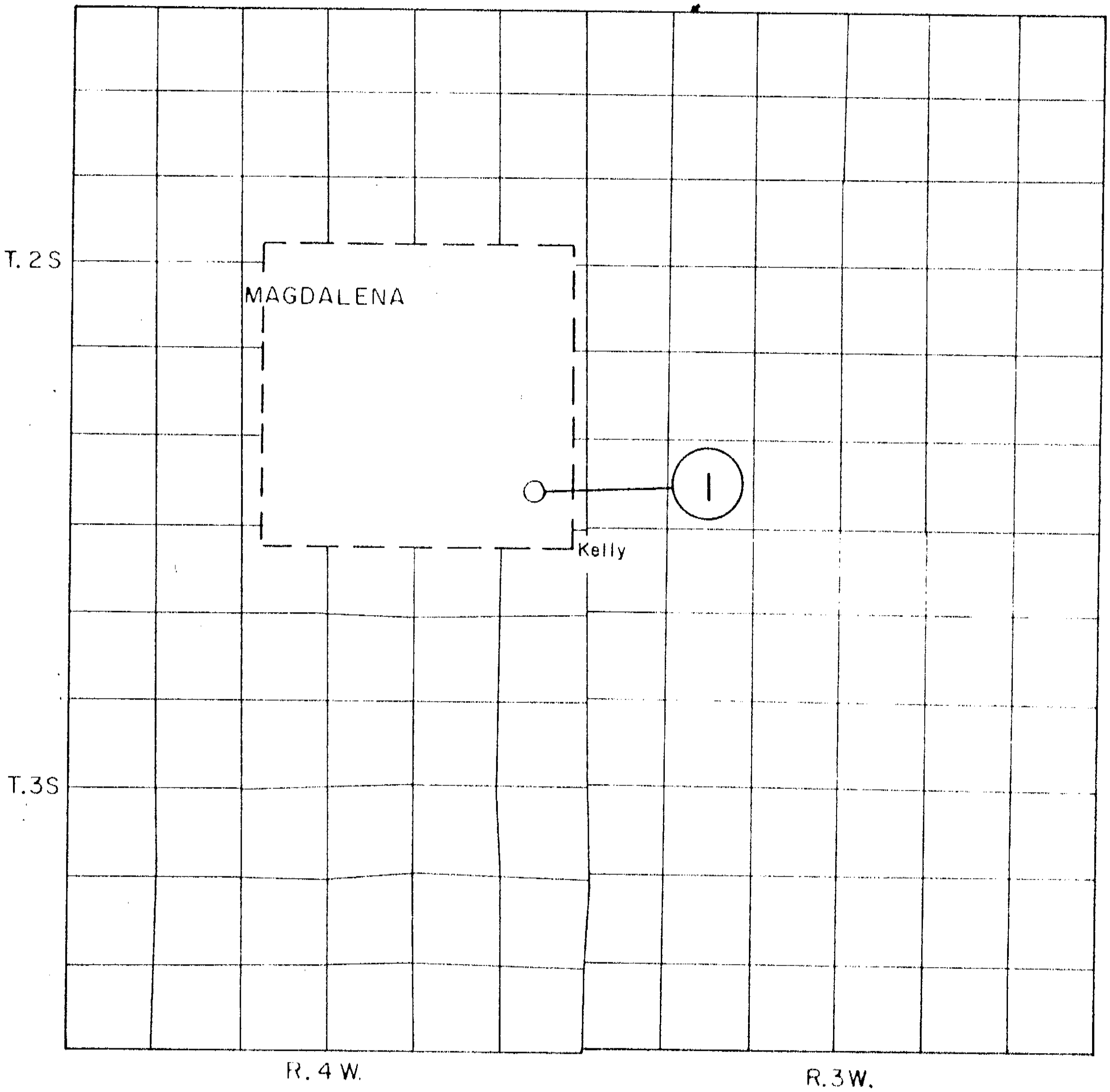


Figure 1 - Sample Location Map - Magdalena Area

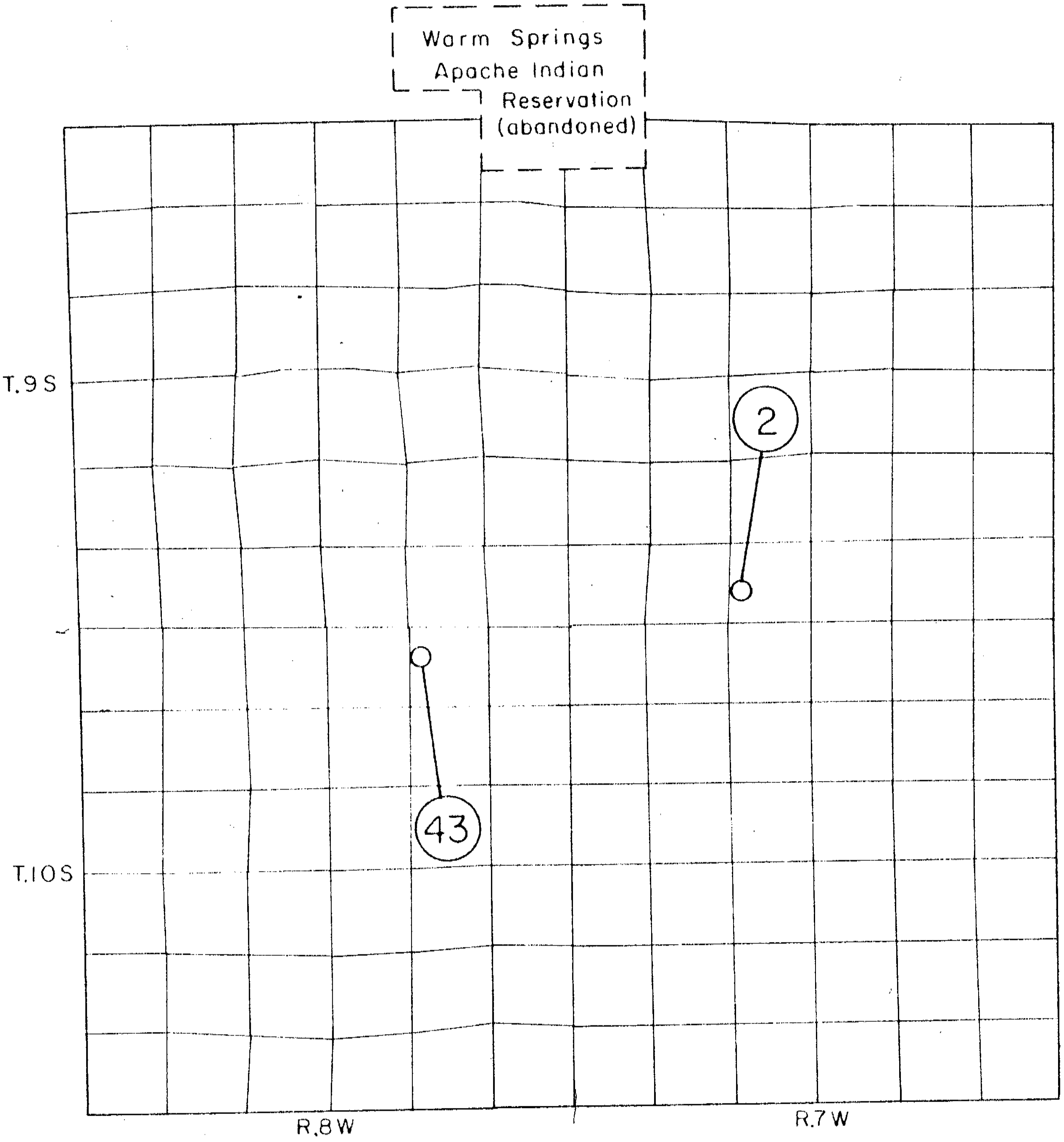


Figure 2 – Sample Location Map – Monticello Area

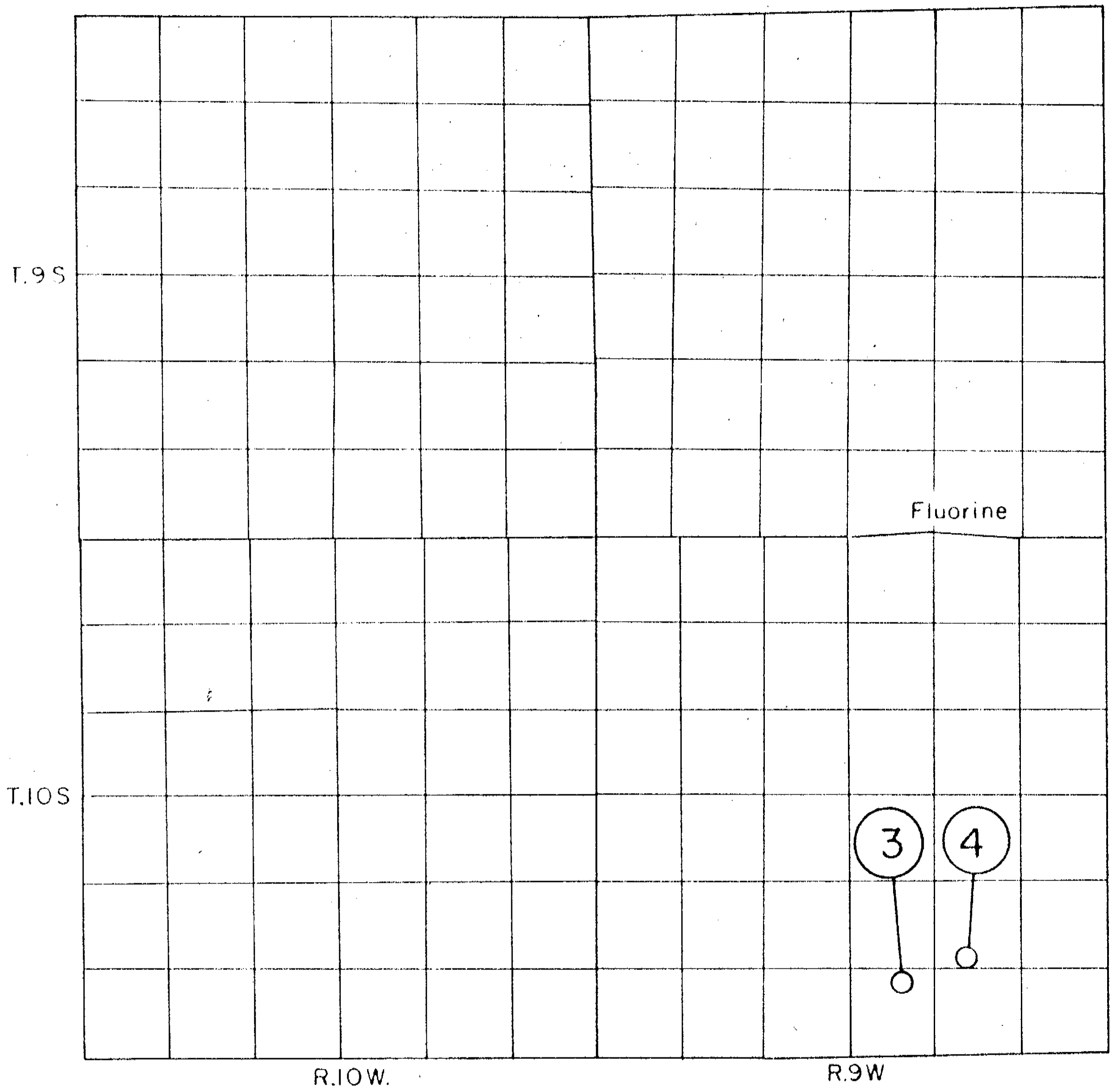


Figure 3 - Sample Location Map - Apache Mining District

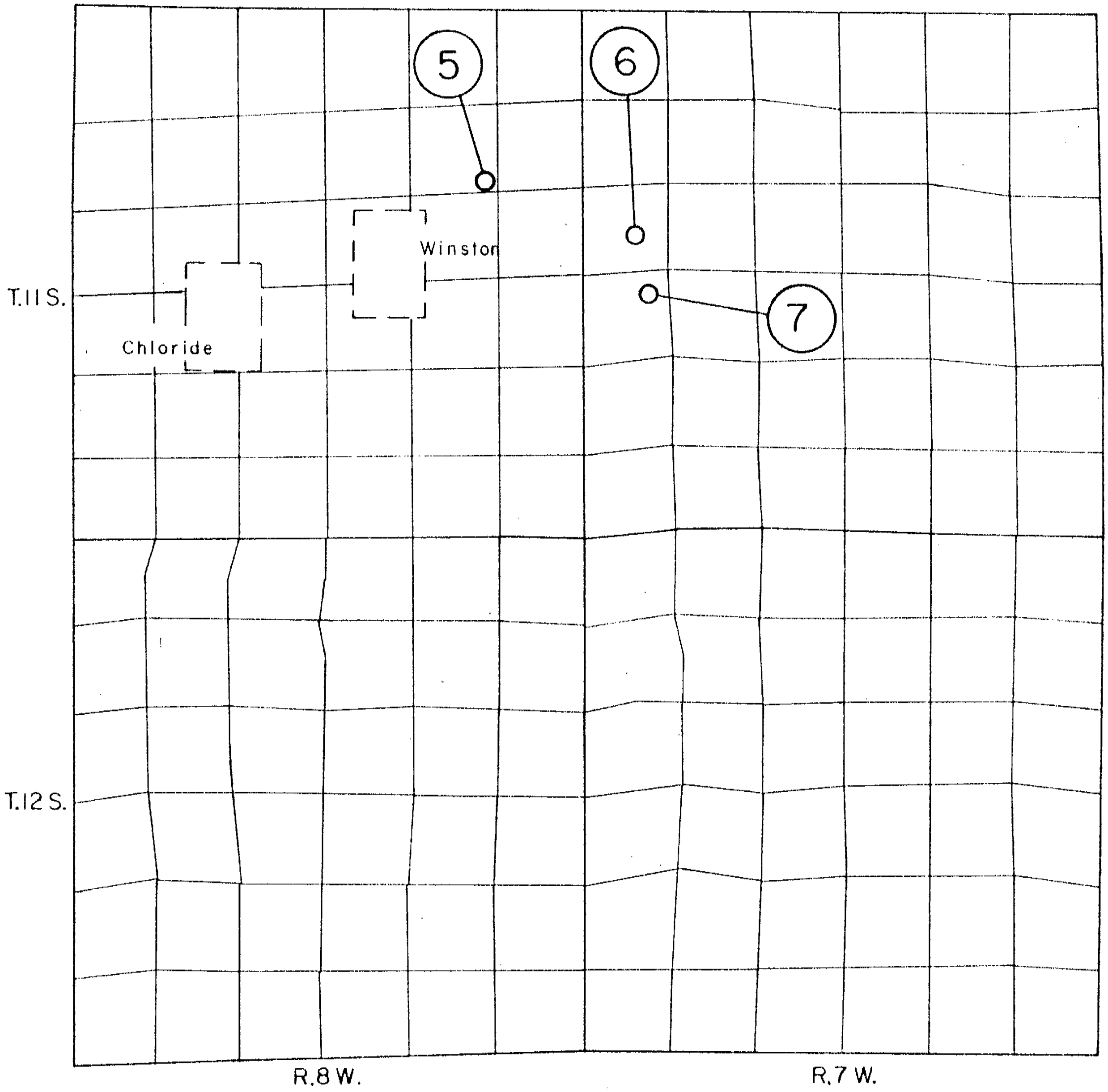


Figure 4 - Sample Location Map - Winston Area

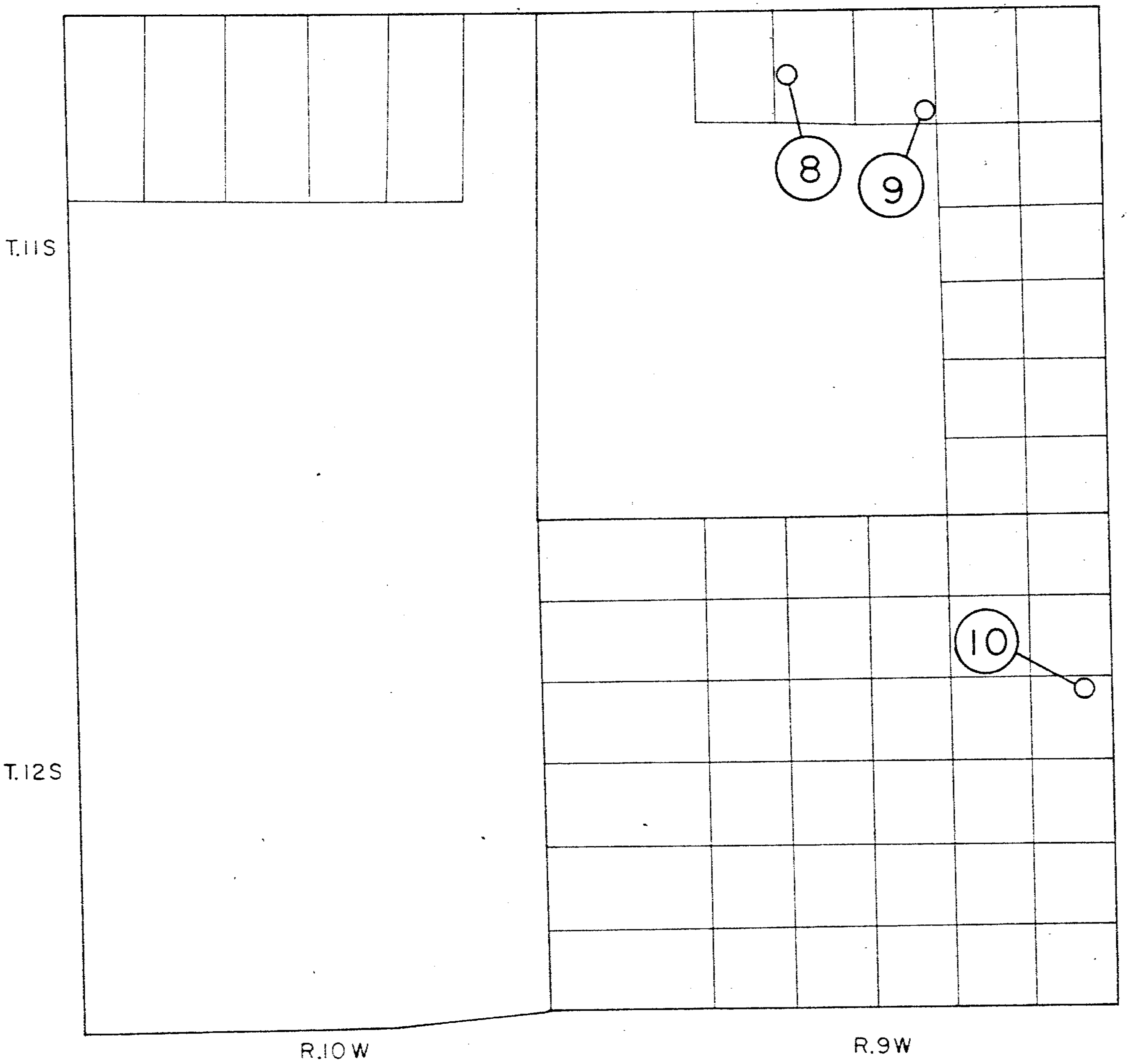


Figure 5 - Sample Location Map - Apache Mining District

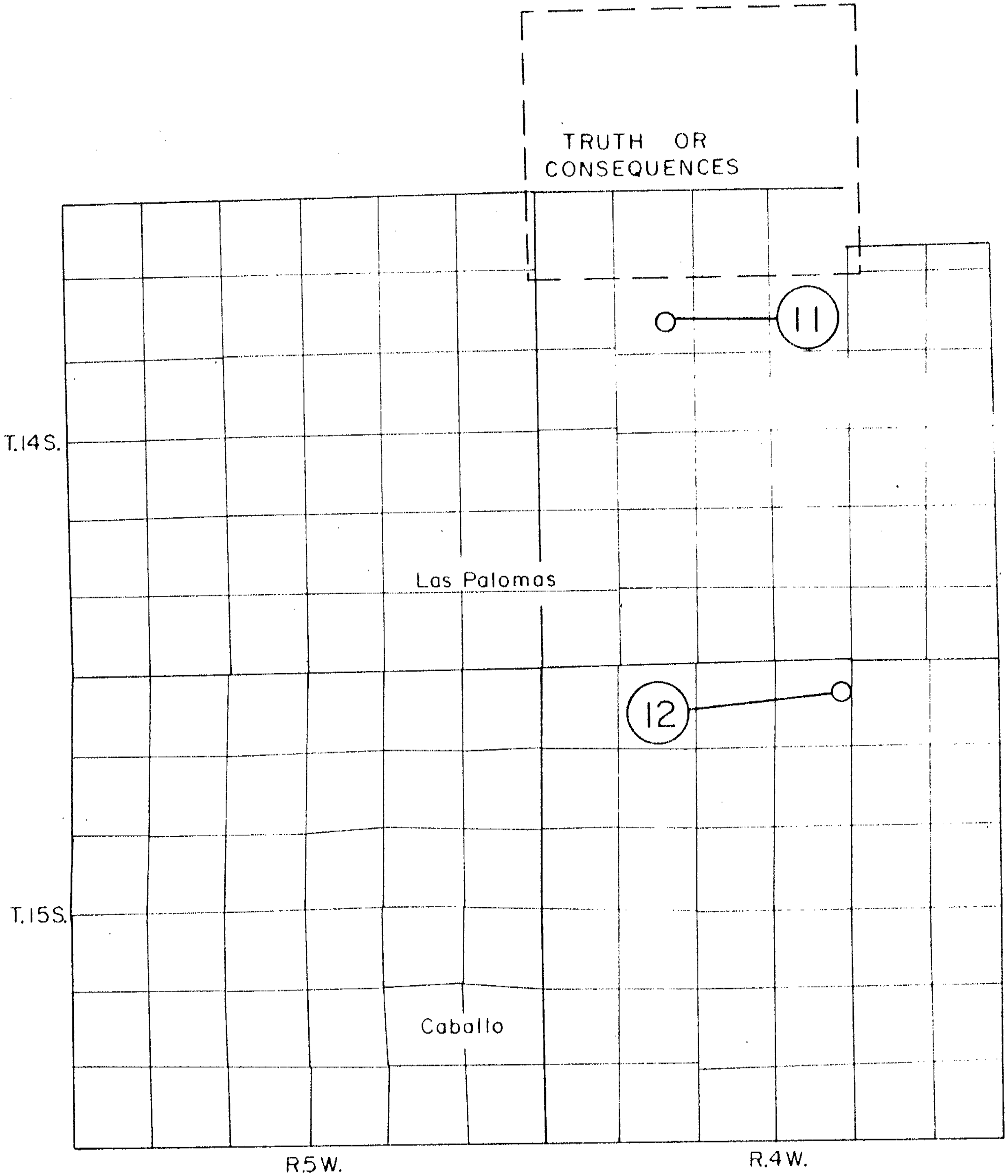


Figure 6 - Sample Location Map - Palomas Gap Area

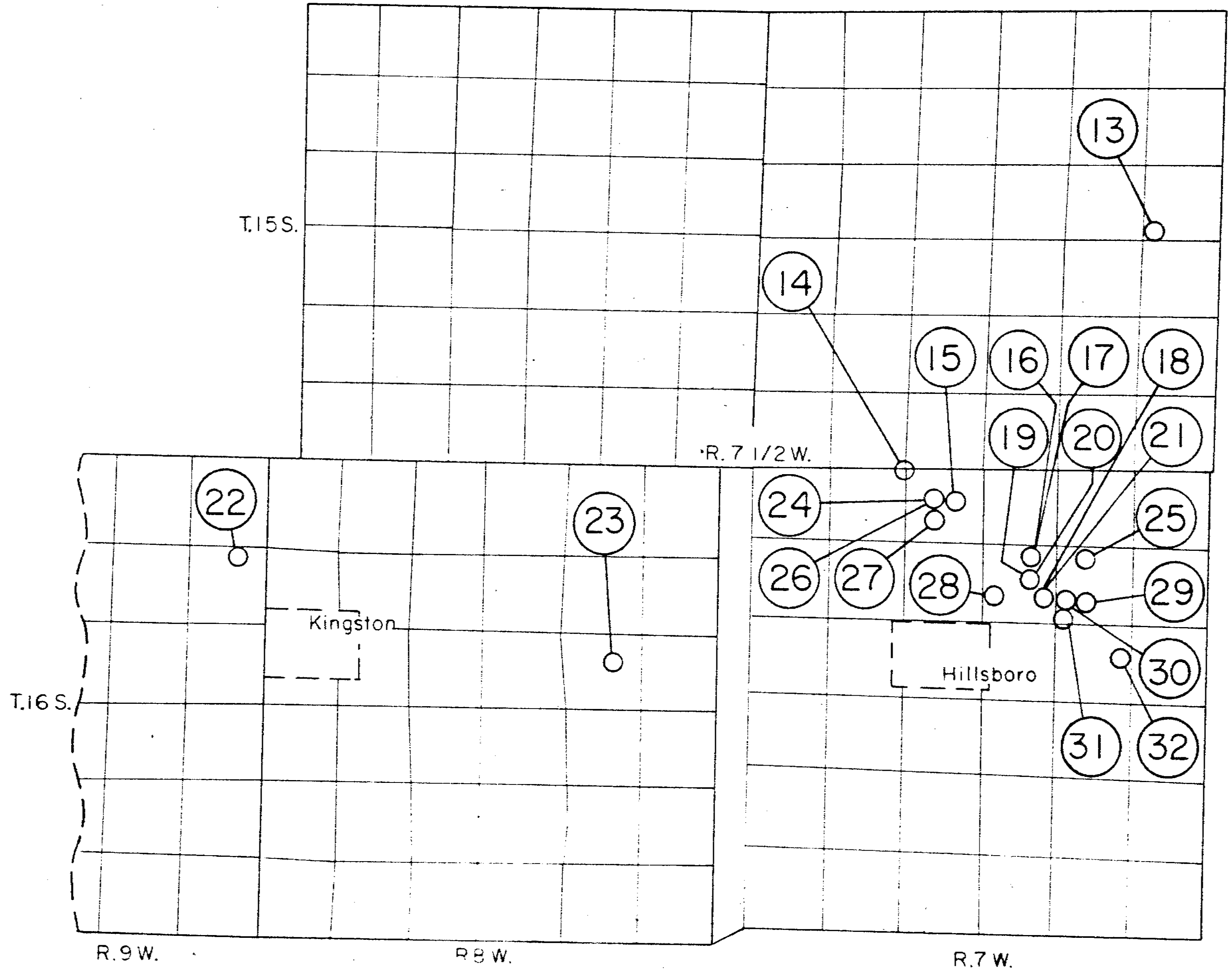


Figure 7 - Sample Location Map - Hillsboro Area

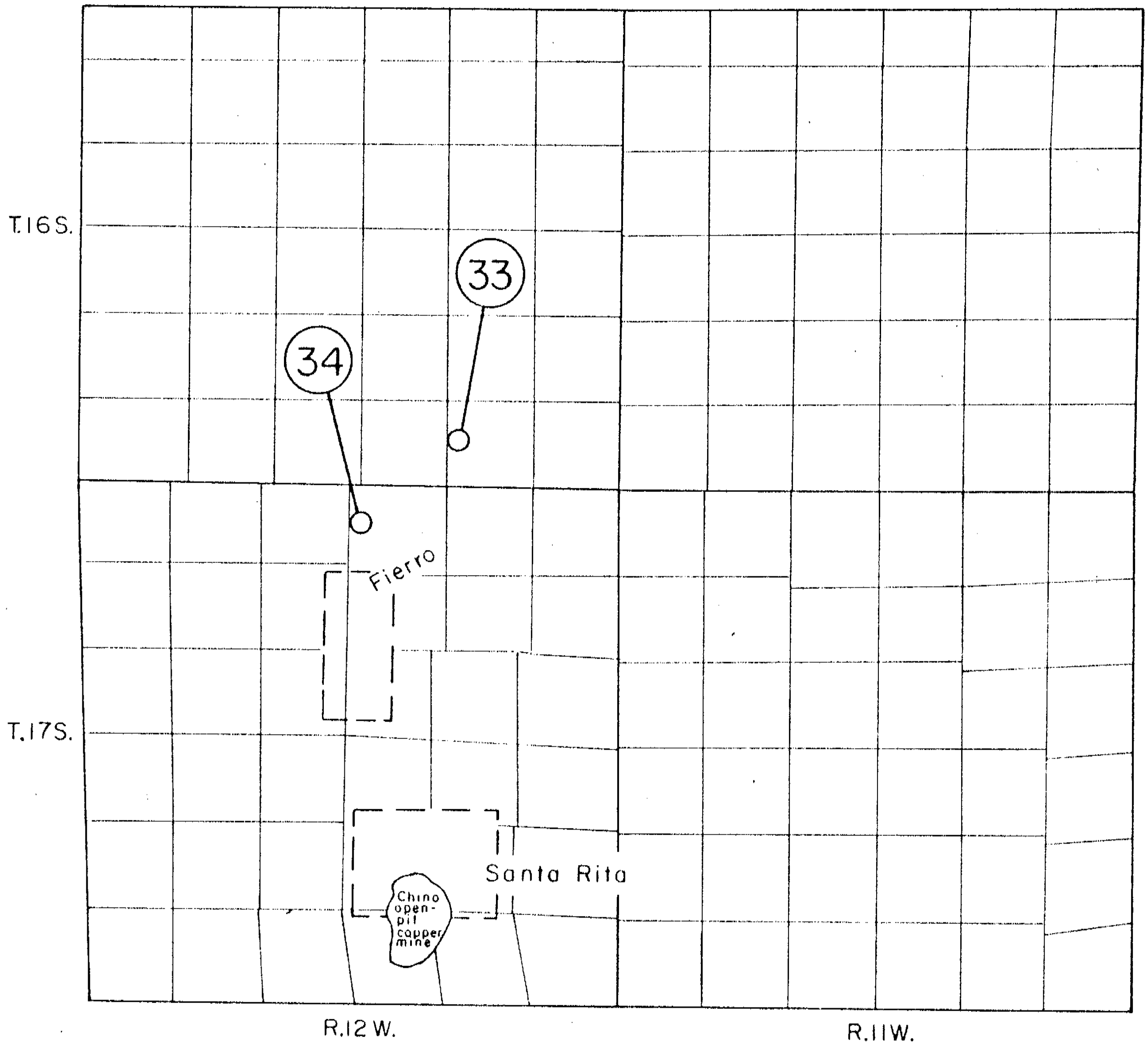


Figure 8 — Sample Location Map - Fierro Area

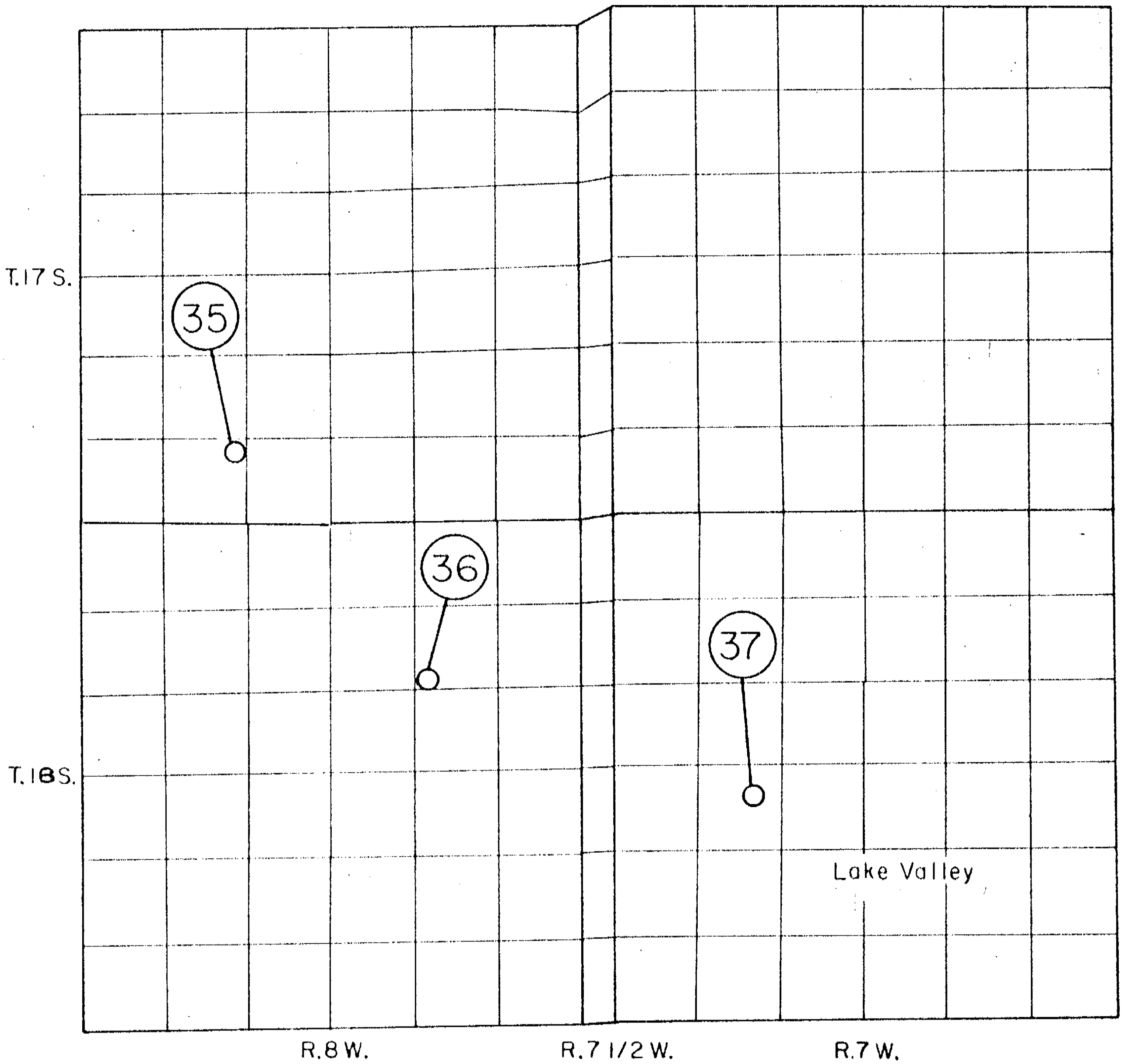


Figure 9 – Sample Location Map – Lake Valley Area

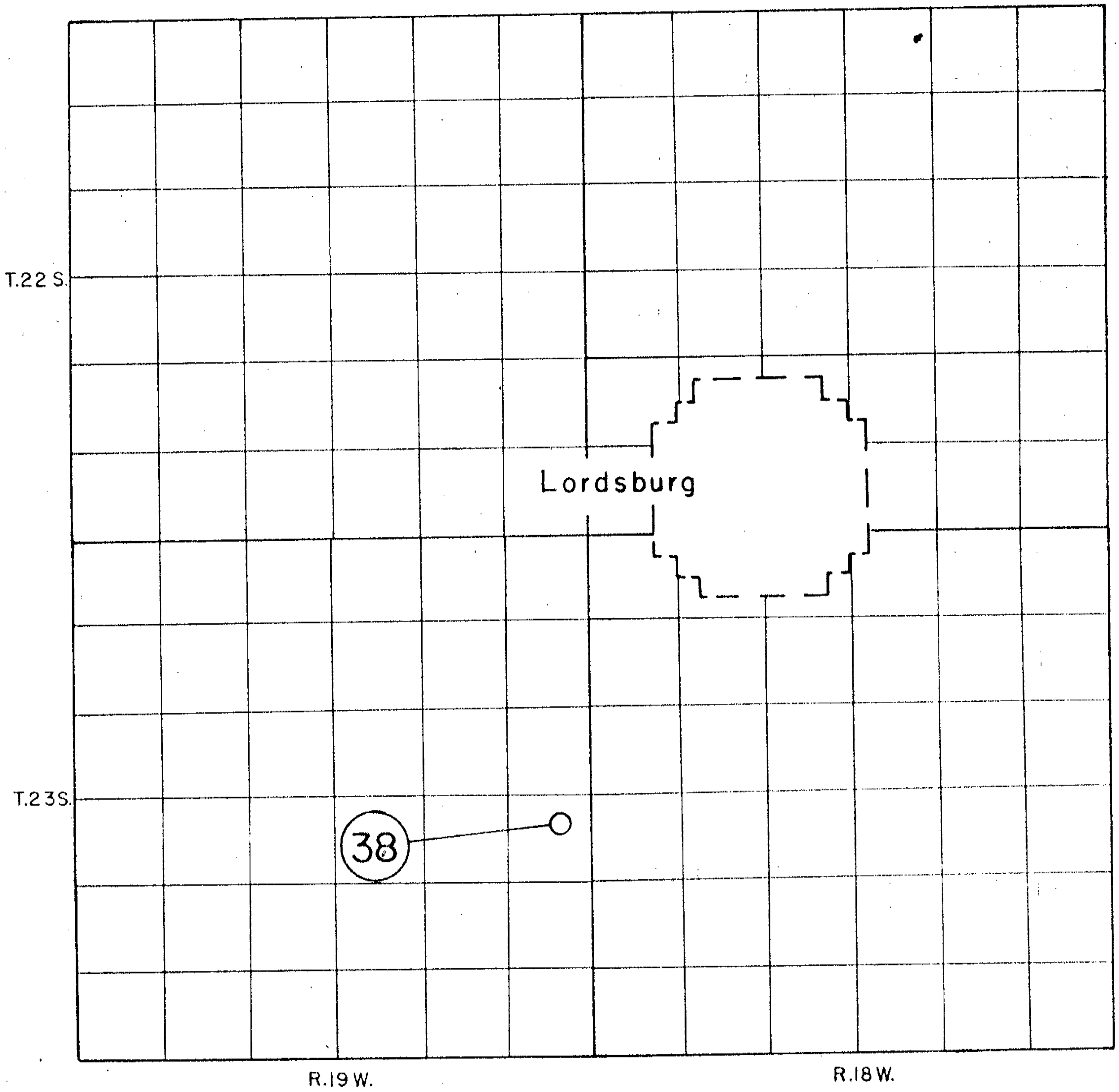


Figure 10 — Sample Location Map - Lordsburg Area

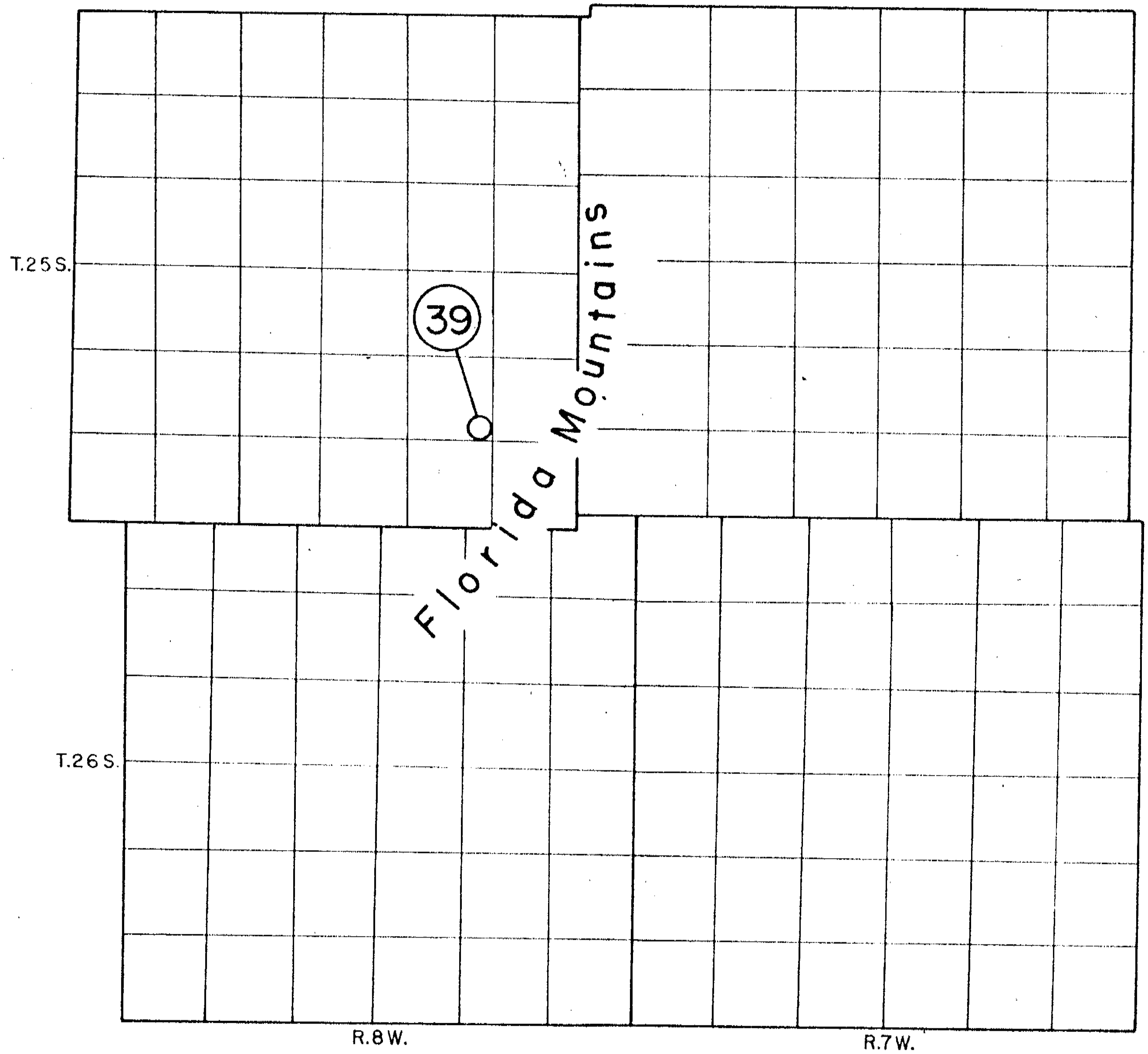


Figure II — Sample Location Map – Florida Mountains Area

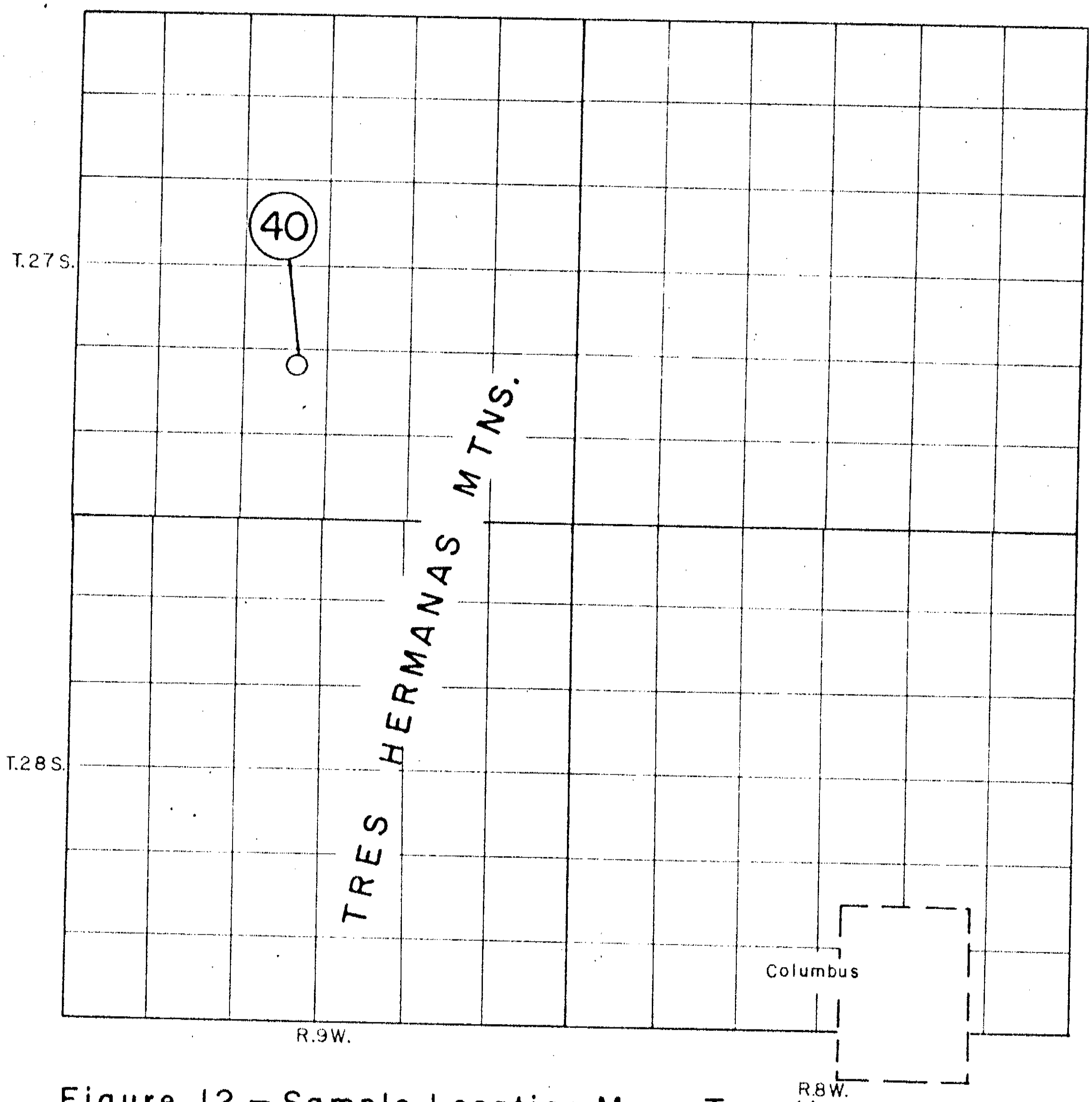


Figure 12 – Sample Location Map – Tres Hermanas Area

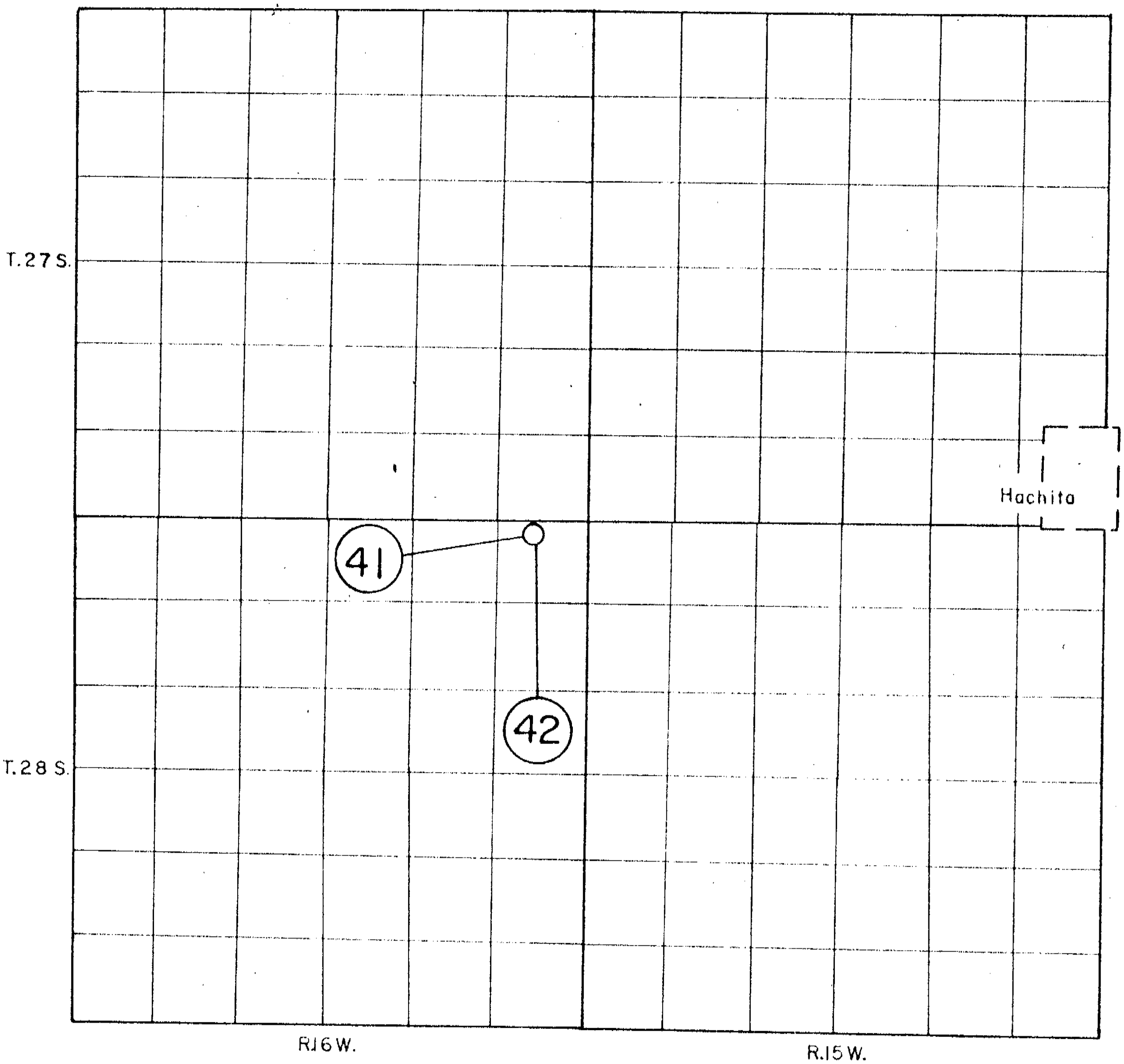


Figure 13 - Sample Location Map - Hachita Area

TABLE VII - Location of samples from Socorro, Sierra, Hidalgo, Grant, and Luna Counties

Sample No.	Name of Sample		Location		
			Section	Township	Range
1	ASR - Magdalena	NE¼ SW¼	36	2S	4W
2	Monticello Canyon	NW¼ SW¼	33	9S	7W
3	Nord Hausen	NW¼ NE¼	34	10S	9W
4	Bear Creek	SE¼ SW¼	26	10S	9W
5	Iron Ore Float (Cuchillo Mtns)	SW¼	11	11S	8W
6	Prospector's Delight	NW¼ SE¼	18	11S	7W
7	Prospector's Delight (Contact)	NE¼	19	11S	7W
8	Big Bear	NW¼ SW¼	4	11S	9W
9	Black Hawk	SE¼ SE¼	3	11S	9W
10	Apache Min. Dist. Bald Eagle Mine	NW¼ NE¼	13	12S	9W
11	Hanson Manganese	NW¼ SE¼	8	14S	4W
12	Palomas Gap Caballo Mtns.	SE¼ NE¼	3	15S	4W
13	Barite Hill	SW¼ SW¼	13	15S	7W
14	Warm Springs, Magnetite	Intersection of Sec. 32, 33, T. 15S., R. 7W., and Sec. 4, 5, T. 16S., R. 7W			
15	Bigelow	SW¼ NE¼	4	16S	7W
16	North Petroglyph Cut	NW¼ NE¼	10	16S	7W
17	North Petroglyph #1	NW¼ NE¼	10	16S	7W
18	Tripod Fence West	NE¼ SE¼	10	16S	7W

TABLE VII (Continued)

Sample				Location	
No.	Name of Sample		Section	Township	Range
19	Petroglyph	SW¼ NE¼	10	16S	7W
20	Mohawk	SW¼ NE¼	10	16S	7W
21	Garnet	NE¼ SE¼	10	16S	7W
22	Kingston - Iron King Mine	NW¼ NE¼	12	16S	9W
23	Middle Percha Float	SW¼ NE¼	14	16S	8W
24	Kalispell #2	SE¼ NW¼	4	16S	7W
25	Chet-Mar, South End	NE¼ NW¼	11	16S	7W
26	Ferguson Mine	SE¼ NW¼	4	16S	7W
27	Kalispell #1	NE¼ SW¼	4	16S	7W
28	Ojala	NW¼ SW¼	10	16S	7W
29	Tyrell Shaft	NE¼ SW¼	11	16S	7W
30	Tripod Ridge	NW¼ SW¼	11	16S	7W
31	Tripod Mine	SW¼ SW¼	11	16S	7W
32	Little Jewel, North	SE¼ NE¼	14	16S	7W
33	Shingle Canyon	SW¼ NW¼	35	16S	12W
34	Emma K Mine	SW¼ NW¼	3	17S	12W
35	Berenda Canyon, Bliss	NE¼	32	17S	8W
36	Berenda Canyon, Copper	SW¼ SW¼	11	16S	8W
37	Lake Valley Quartz	SW¼ NE¼	20	18S	7W
38	Henry Clay Mine	SW¼ NE¼	24	23S	19W

TABLE VII (Continued)

Sample No.	Name of Sample		Location		
			Section	Township	Range
39	Ramsey	SE¼	26	25S	8W
40	Tres Hermanas	NW¼ NE¼	28	27S	9W
41	Hornet Mine (Old)	NE¼ NW¼	1	28S	16W
42	Hornet Mine (New)	NE¼ NW¼	1	28S	16W
43	Iron Mountain Mine	SW¼ NW¼	2	10S	8W

TABLE VIII - Results of spectrographic analyses[#]

Sample No.	Name of Sample	Strong	Medium	Weak
1	ASR - Magdalena	Ca Fe Ni	Si Mg	Al Pb Mo Ti K Ge[*]
2	Monticello Canyon	Ca Fe Si Mg	Al Mo	Ti Cr V Ge[*]
3	Nord Hausen	Ca Si Mg Fe Ag Pb Cu Ti Mn	Al V	Mo Be
4	Bear Creek	Ca Al Si Mg Cu Ti Mn	Fe V	Pb Mo Be Ag Cr
5	Iron Ore Float (Cuchillo Mtns.)	Ca Si Mg Fe Ti	Al Mo Ni Cr	Pb Be V Ge[*]
6	Prospector's Delight	Ca Fe Mg Cu Ti Pb	Al Si Ag	Mo V Ge[*]
7	Prospector's Delight (Contact)	Ca Cu Mn	Al Fe Si Mg Pb Ag Ti	V
8	Big Bear	Ca Si Mg Be Cu Ag	Al Fe Pb Mn	Mo Ti V
9	Black Hawk	Si Cu Ag	Ca Fe Mg	Al Ti
10	Apache Min. Dist. Bald Eagle Mine	Ca Fe Mg Cu Pb	Al Si Mo Ag	Ti
11	Hanson Manganese	Ca Fe Mg Mn	Al Si Mo Ti	Ag V
12	Palomas Gap-Caballo Mtns.	Fe Si Mg Cu	Ca Al	Mo
13	Barite Hill	Ca Fe Si Mg	Al Pb Mo Ag	Ti
14	Warm Springs, Magnetite	Ca Fe Mg Ti	Al	Ag Pb Li Cr Be Mo V Ge[*]

TABLE VIII (Continued)

Sample No.	Name of Sample	Strong	Medium	Weak
15	Bigelow	Ca Si Mg Fe Cu	Al Pb Mo Ag	Sn Be Cr Ti Ni Ge*
16	North Petroglyph Cut	Ca Fe Mg	Al Si Ti	V
17	North Petroglyph #1	Ca Al Fe Mg	Si Ti	Pb Be Cr Ni V K
18	Tripod Fence West	Ca Al Fe Si Mg Ti		Pb Ni V Ga*
19	Petroglyph	Ge Si Mg Pb Be V	Ca Al Fe Mo Ag Ti	Sn Sb Cd Ni Cr
20	Mohawk	Al Ca Ti	Fe Si Mg	
21	Garnet	Ca Fe	Al Si Mg Ti	Pb Li V
22	Kingston - Iron King Mine	Ca Fe Mg Pb Cu Mn	Al Si Mo Ag	Ti
23	Middle Percha Float	Ca Fe Mg Mn	Al Pb Ag	Mo Ti
24	Kalispell #2	Ca Al Si Mg Fe	Pb Mn Cr Ni Ti	V
25	Chet-Mar South End	Ca Si Mg Cu Mn	Al Fe Ti	Pb Mo Be Ag Cr V
26	Ferguson Mine	Ca Al Si Mg Fe Cu	Pb Ag Ti	Be Cd Ni Cr V
27	Kalispell #1	Si Mg Fe	Ti Ca Al	Mo Zr Ni V
28	Ojala	Ca Al Si Mg Ti Mn	Fe Pb Cu V	Mo Be Ag
29	Tyrell Shaft	Ca Al Si Mg Fe Mo	Pb Be Ag Ti V	Sn Sb Ni Ge*
30	Tripod Ridge	Fe Si	Ca Mg Cu Ag Ti	Al

TABLE VIII (Continued)

Sample No.	Name of Sample	Strong	Medium	Weak
31	Tripod Mine	Ca Si Mn	Al Mg Pb Mo Ti V	Fe Be Ag
32	Little Jewel North	Ca Al Si Mg Fe Ti V	Be	Mo Cr Ge*
33	Shingle Canyon	Fe Si	Ca Al Mg Ti Pb	Mo Ag Ni Ge*
34	Emma K Mine	Al Fe Si Mg Ti	Ca Cu	Mo V
35	Berenda Canyon, Bliss	Fe Si	Ca Mg Ti	Al Mo V Ge*
36	Berenda Canyon, Copper	Fe Si Mg Cu Ti	Ca Al	Pb Ag V
37	Lake Valley Quartz	Ca Si	Al Mg Pb Cu	Fe Mo Ag Ti V
38	Henry Clay Mine	Ca Fe Si	Al Mg Pb Cu Ti	Mo Ag Ni Ge*
39	Ramsey	Fe Si Cu	Ca Mg Ti Ag	Al Pb Li Bi Mo V
40	Tres Hermanas	Ca Si Fe Mg Ba Mn Ge	Al Pb Ti	Mo Cu Cd Ag Ni Cr V
41	Hornet Mine (old)	Ca Fe Mg	Al Si Pb	Ag Ti
42	Hornet Mine (new)	Si Fe Al Ti Ca	Ag Pb Mg	Mo Co Ni V Ge*
43	Iron Mountain Mine	Ge Ca Al Fe Ba Mn Si Mg	Pb Ag Ti	Mo Sn Co V Ni Cd Cr

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* Less than 10 parts per million

\# Zinc and Bismuth added as a buffer and therefore not reported

TABLE IX - Results of spectrographic analysis of hand picked specimen grains from Petroglyph ore

Specimen	Elemental content measured in relative concentrations* Strong	Medium	Weak	Germanium content in parts per million (Quantitative)
Orange-red hexagonal crystals	Ca Si Mg Fe Pb Ge	Al Cu V Ag Ti	Mo Cd Ni Mn Cr	71
Red-black fragments	Si Ge	Al Cu Ti Ca Pb Fe Mg Mo Ag	Cd V Ni Mn Cr	64
Reddish-brown spheroids	Ca Si Mg Pb Ge	Al Cu Ti Mn Fe	Mo Ag V Co Ni Cr	49
Wulfenite	Ca Pb Mo	Si Mg V	Al Fe Ag Ti Cr	Undetectable
Cerrusite	Ca Si Mg Pb Ag	Al Fe Mo Cu Ti Mn	Sn Cd Co Cr	Undetectable
Sphalerite	Si	Ca Pb Mg Fe Cd Mn	Al Mo V Cu Ag Ti Ni Ge	Less than 10
Galena	Pb Ag	Ca Si Mg Cu	Al Sb Mo Sn Cd Ti V	Undetectable
Quartz	Si			Undetectable

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* Zinc and Bismuth added as a buffer and therefore not reported

by the powder x-ray diffraction method as outlined by Azaroff and Buerger (1958). The same powder pictures were obtained for all three specimens showing them to be the same mineral. Thirty-five lines were measured for d-spacing values. Comparison of these calculated values with similar values recorded for willemite, indicate that the three specimens are different crystal forms of willemite. This was confirmed by visual comparison of the patterns with a pattern of a known specimen of willemite. The calculated d-spacing values for the unknown mineral and those for willemite are shown in Table X.

It has been stated earlier that the most common occurrence of germanium is in the crystal structure of other minerals. Sphalerite has been the most commonly recognized host for the germanium association. However, in the Petroglyph ore where the mineralization includes both sulfide and oxide or silicate minerals, germanium is concentrated to the extent of 71 parts per million in the silicate mineral of zinc and less than 10 parts per million in the sulfide mineral of zinc.

Papish (1929) reported the presence of germanium in certain specimens of the following silicate minerals: Topaz, leucite, pollucite, lepidolite, muscovite, phlogopite, biotite, fuchsite, orthoclase, microcline, albite, oligoclase, andesine, labradorite, bytownite, anorthite, tourmaline, andalusite, kyanite, sillimanite, spodumene, kunzite, hiddenite, diopside, augite, actinolite, tremolite and cordierite. The germanium content of these minerals was very low, in the range of traces only.

TABLE X - d-spacing values for unknowns and willemite

Unknown mineral			Willemite	
d-spacing	Intensity I/I_0	(hkl)	d-spacing	Intensity I/I
6.95	25	110	6.98	22
5.058	5			
4.337	3	012	4.35	4
4.0331	50	300	4.026	33
3.5841	5			
3.4820	95	220	3.486	81
3.2499	5	122	3.264	4
3.1486	5	131	3.153	7
2.8271	95	113	2.834	97
2.6255	100	140	2.634	100
2.5293	3	042	2.533	2
2.4779	3			
2.3178	75	223	2.318	47
2.2139	5	241	2.215	1
2.1435	7	502	2.144	4
2.0759	5	214	2.074	1
2.0102	25	600	2.013	7
1.9332	25	250	1.9332	2
1.8567	75	333	1.8592	36
1.7226	5	125	1.7235	3
1.6874	20	603	1.6882	7
1.6417	20	523	1.6404	7

TABLE X (continued)

Unknown mineral			Willemite	
d-spacing	Intensity I/I_o	(hkl)	d-spacing	Intensity I/I_o
1.5983	25	710	1.5986	10
1.5508	25	006	1.5516	11
1.5194	15	630	1.5203	9
1.4207	75	713	1.4205	30
1.3933	10			
1.3647	40			
1.3376	40			
1.2508	7			
1.2284	10			
1.2114	15			
1.1606	15			
1.1460	10			
1.1137	15			

Plus 20 lines to 1.0056, not printed on card.

Donnay and Nowacki (1954) have reported the unit cell dimensions for willemite from Franklin, New Jersey as follows: c = 9.34 Å ± 0.01, a = 13.94 Å ± 0.01, c/a = 0.67000. Using the d-spacing values determined for the willemite from the Petroglyph sample, the following values for the unit cell dimensions have been calculated: c = 9.32 Å, a = 13.93 Å, c/a = 0.6691. It will be noted that there is no apparent distortion in the unit cell dimensions for the willemite from the Petroglyph sample. This result is as expected since calculations based on the highest Ge content (71 ppm) indicate that there is but 1 unit of Ge for every 5000 units of Zn_2SiO_4.

It has not been determined whether germanium substitutes for zinc in the plus two oxidation state or for silicon in the plus four oxidation state in the crystal structures of willemite. Ahrens (1950) reports the ionic radius of Ge^{+4} to be 0.53 Å and that of Si^{+4} to be 0.42 Å. Goldschmidt (1954) reported 0.44 Å for Ge^{+4} and 0.39 Å for Si^{+4}. Ahrens (1950) reports the ionic radius of Ge^{+2} to be 0.73 Å and a value of 0.74 Å for Zn^{+2}. Goldschmidt also stated that the most prominent feature of the geochemistry of germanium in the upper lithosphere is its substitution for silicon in silicates.

It must be noted, however, that some germanium (less than 10 parts per million) has entered the crystal structure of the sphalerite obtained from the same fault zone. In this respect it is interesting to note that the atomic radii of Zn and Ge are 1.33 Å and 1.22 Å, respectively.

The identification of the mineral willemite by the powder camera method was verified by microscopic tests. Willemite is a zinc silicate mineral having a chemical formula of Zn_2SiO_4. According to Hurlbut (1956) willemite crystallizes in hexagonal prisms with rhombohedral terminations although it is usually massive to granular and is rarely found in crystals. Most of the willemite known in the United States is found at Franklin, New Jersey. Franklin willemite fluoresces in ultraviolet light.

Northrop (1959) has reported willemite in New Mexico in Grant County in the Central District, in Luna County in the Tres Hermanas District, in Sierra County in the Hillsboro and Iron Mountain No. 2 Districts, and in Socorro County in the Iron Mountain No. 2, Magdalena, and Socorro Peak Districts.

Germanium in Tres Hermanas Samples

Samples from Tres Hermanas were obtained from dumps adjacent to the Comfort shaft in the Mahoney Mining District, south of Deming, New Mexico in the NW¼ of the NE¼ of Sec. 28, T. 27S., R. 9W. The samples were collected under ultraviolet light. As was found out later, not all of the willemite contained in the ore samples fluoresces under the ultraviolet lamp.

The ores samples were crushed and screened. The minus 35 plus 48-mesh size contain nearly completely liberated mineral fragments and this size was used to separate willemite from other minerals. The willemite fragments and a head sample from the ore prior to separation were analyzed spectrographically for germanium content. The results of these analyses are given in Table XI.

TABLE XI - Results of spectrographic analysis on hand-picked willemite and a head sample from the Tres Hermanas locality

Sample	3039.1 Ge A	2898.0 Bi A	3039.1 Ge/ 2898.0 Bi Intensity Ratio	Germanium (ppm)
Willemite	19.0	26.6	0.714	47
Head sample	27.0	29.4	0.918	35

A 5 gm sample of the head sample was subjected to heavy liquid separation using tetrabromoethane having a specific gravity of 2.94. A light and a heavy fraction were obtained. The light fraction was 23.89 percent of the total amount, while the heavy fraction was 76.11 percent. All of the heavy fraction consisted predominantly of willemite in one form or another. This was confirmed by x-ray diffraction patterns. Each of the fractions obtained in the heavy liquid separation was analyzed spectrographically for germanium content. The heavy fraction contained 47 ppm germanium, while germanium lines were not discernable for the light fraction. As a check on the spectrographic analysis results, one need only to make the following calculation.

The heavy fraction was almost entirely willemite. This fraction represents 76.11 percent of the head sample. Multiplying 76.11 percent by 47 parts per million germanium contained in the willemite, one obtains a value of 35.8 parts per million contained in the head sample. This value checks very closely with the reported value of 35 parts per million germanium by spectrographic analysis.

Germanium in Iron Mountain Sample

A sample from the Iron Mountain Mine was obtained from the walls and ceiling of the old mine workings in the SW ¼ of the NW¼ of Sec. 2,

T. 10S., R. 8W., Sierra County, New Mexico. The samples were collected by assistance of an ultraviolet lamp.

The ore samples were crushed and screened. The minus 35 plus 48-mesh size was used to separate willemite from other minerals. The willemite fragments and a head sample from the ore prior to separation were analyzed spectrographically for germanium content. The results of these analyses are given in Table XII.

TABLE XII - Results of spectrographic analysis on hand-picked willemite and a head sample from Iron Mountain Mine locality.

Sample	3039.1 Ge A	2898.0 Bi A	3039.1 Ge/ 2898.0 Bi Intensity Ratio	Germanium (ppm)
Willemite	4.3	14.0	0.307	88
Head sample	8.8	21.3	0.413	73

SUMMARY AND CONCLUSIONS

An estimate of germanium resources in the United States is not available. The major domestic source of germanium has been the Tri-State zinc district of Missouri-Kansas-Oklahoma where germanium is recovered as a by-product of zinc production. In such ores, germanium occurs within the crystal structure of sphalerite (ZnS) in quantities ranging from traces to tenths of one percent. An additional tremendous, but as yet untapped, source of germanium exists in coal deposits. Coal ash with a germanium content of 10 parts per million is considered low, whereas a content of about 1000 parts per million is high. Coal containing from 50 to 100 parts per million germanium in the ash may be considered a possible source of the element, while coal ash containing 500 to 1000 parts per million is a likely source.

The current investigation concerns the occurrence of germanium in Southwestern New Mexico. The two primary host materials investigated were coal samples from the Carthage coalfield in Socorro County and base-metal ores from Socorro, Sierra, Luna, and Grant Counties, New Mexico.

Germanium is contained in reject Carthage coal fines to the extent of 4 parts per million. Ashing of the Carthage coal fines drives off the volatile constituents and concentrates the germanium in the ash to the extent of approximately 35 parts per million. Certain hydrocarbon constituents of Carthage coal have a lower ash content and thereby exhibit a germanium content as high as 122 parts per million in the ash. The germanium contained in Carthage coal, nevertheless, is equally distributed throughout the constituents. From the results of this investigation it would seem that ashing of reject coal fines from Carthage coal might provide a potential source of germanium.

In regard to the concentration of germanium in the base-metal ore samples investigated it was ascertained that the average concentration of germanium was less than 10 parts per million. However, in three ore samples from different localities, namely the Tres Hermanas, Petroglyph, and Iron Mountain Mine samples, the concentration of germanium was found to be 35, 55, and 73 parts per million, respectively.

A detailed study of the concentration of germanium in the mineral constituents in these three ore samples revealed that germanium was primarily contained in the zinc silicate mineral, willemite. These findings differ from the previous observations that germanium is contained in the zinc sulfide mineral, sphalerite. Germanium in the willemite from the Petroglyph sample amounted to 71 parts per million, while the germanium in the sphalerite from the same sample amounted to less than 10 parts per million. Explanation of this preferential concentration of germanium in willemite will probably be found in oxidation conditions surrounding deposition of Ge in the rock, since oxidizing conditions could favor co-precipitation of Ge^{+4} with Si^{+4}.

Previous to the present investigation there were but three reported occurrences of germanium in New Mexico. On the basis of the current study the number of occurrences has been increased to eighteen. The major contribution of this research is the establishment of the fact that in the rocks studied germanium is concentrated in willemite, a zinc silicate mineral, rather than the zinc sulfide mineral. Because of this fact, it appears that future geochemical prospecting should be directed towards the examination of the occurrence of willemite as a guide to potential germanium resources.

RECOMMENDATIONS FOR FURTHER STUDY

Although the scope and purpose of this investigation have been satisfied, several important points encountered during the course of investigation need further study.

(1) Samples should be obtained from other coal deposits in New Mexico. The Public Service Company of New Mexico might supply samples from their extensive drilling program near Farmington.

(2) A search should be made for the localization of any germanium concentrations within coal beds (the top or bottom few inches) coupled with the examination of material immediately above or below coal beds.

(3) In the case of the occurrences of germanium in willemite one needs to answer the question, does germanium substitute for zinc in the plus two oxidation state or for silicon in the plus four state.

(4) If germanium substitutes for silicon in willemite, other silicate minerals should be examined for possible germanium content.

(5) Since willemite has been shown to contain appreciable amounts of germanium, known base-metal deposits should be re-examined for the presence of willemite.

(6) The genetic relationship of willemite and sphalerite in the samples might have a strong bearing on the concentration of germanium in one or the other of these minerals and therefore this relationship should be studied.

APPENDIX I

A 1.5 meter ARL-Dietert emission spectrograph with a replica diffraction grating with 15,000 lines to the inch was used for all samples. The samples were pulverized to approximately 200 mesh in an agate mortar. A representative split of the pulverized material was used for analysis. Spectrographic carbon was used as a dilutent in all samples tested. An internal standard buffer compound was also used. The buffer contained a mixture of (bismuth oxycarbonate) $(BiO)_2CO_3$ and ZnO (zinc oxide). The bismuth content of the buffer was 342.6 ppm. In each test 20 mg of the buffer was combined with 40 mg of spectrographic carbon and 20 mg of unknown sample.

In all burns sample electrodes were 0.25 inch graphite rods having a coaxial cavity of 0.068 inch depth and 0.187 inch diameter. Counter electrodes used in the tests were 0.125 inch graphite electrodes. The samples were not preheated. The arc was maintained until all the sample was volatilized. A sector wheel setting of 33 percent transmission with a 50 micron slit was used. All tests were run at a current of 12 amp. Arc gap was maintained at 6 mm throughout the burn.

The exposed spectrographic films were developed by immersing the film in Kodak D-19 developer for 3 minutes, next in 1.8 percent acetic acid for 15 seconds, in Kodak fixer solution for 5 minutes, and in water for 15 minutes. After drying, the films were read by comparison with a master chart on an ARL-Dietert Comparator-Densitometer. Densitometer readings were recorded for the Bi 2898.0 Å line and the Ge

3039.1 Å line for each sample tested. A standardization curve was prepared by plotting the Ge 3039.1 Å/ Bi 2898.0 Å intensity ratio versus ppm germanium. The germanium content in ppm for all unknowns was read from the standardization curve shown in Figure 14.

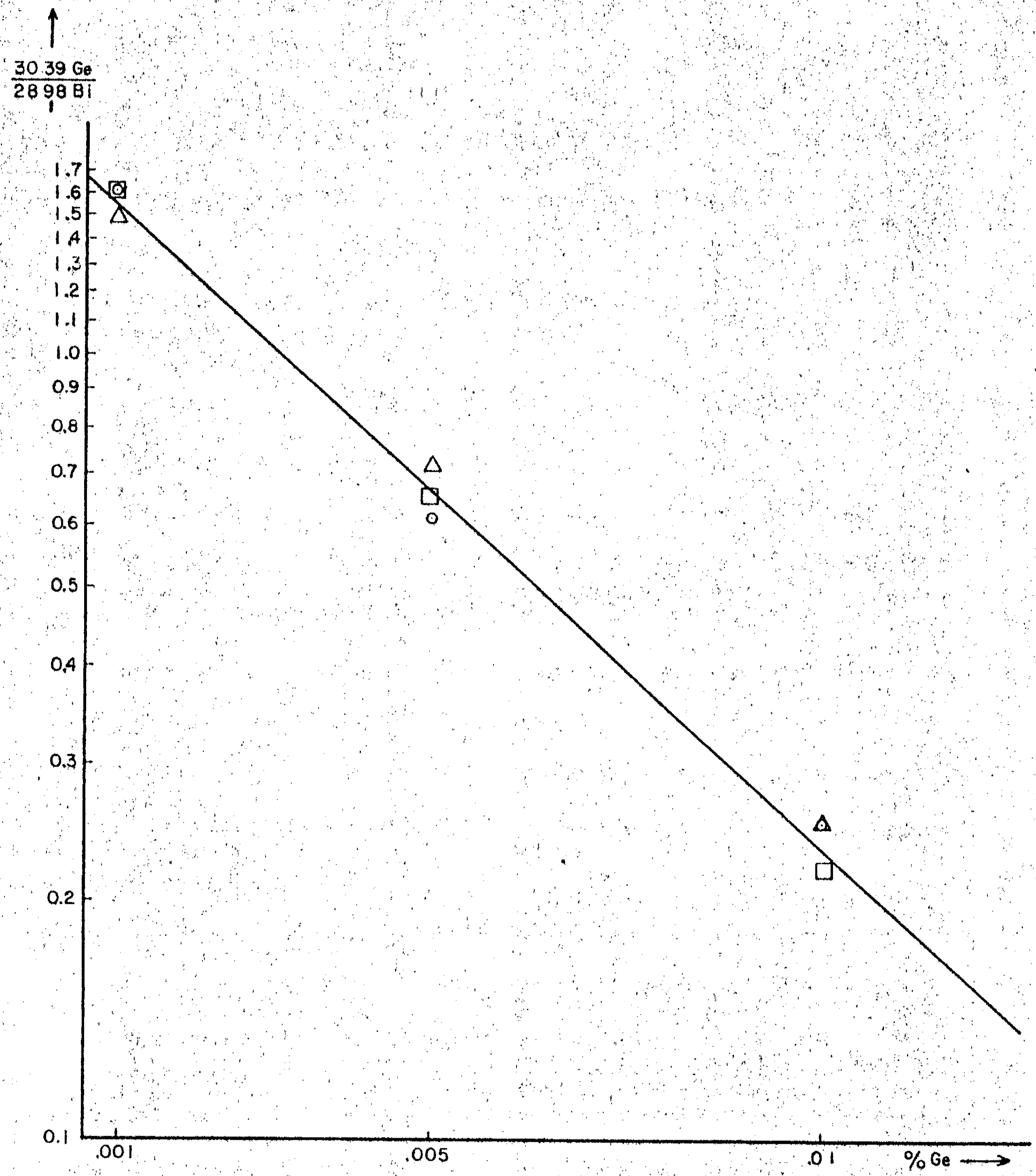

Figure 14 – Standardization Curve (Semi-Logarithmic)
Ratio of Line Intensities vs. % Ge

APPENDIX II

SPECTROPHOTOMETRIC PHENYLFLUORONE COLOR

The following procedure is modified from the procedure as outlined by Luke and Campbell (1956).

Carbon Tetrachloride Extraction Isolation

Reagents:

1. NaOH (5 percent) - Dissolve 5 gm NaOH pellets in 100 ml of water and place in a polyethylene bottle.
2. HCl (9N) - Dilute 385 ml concentrated HCl to 500 ml with water.
3. Buffer solution pH 5 - Dissolve 900 gm (2 lb.) NaAc . 3 H_2O in 700 ml of water. Filter through #40 filter paper and transfer to a 2 liter volumetric flask containing 480 ml glacial acetic acid. Cool, dilute to mark on flask and mix.
4. Gum arabic solution - dissolve 0.5 gm in 50 ml hot water by stirring. Filter with suction (platinum cone) through #42 filter paper. Prepare fresh each day.
5. Phenylfluorone solution - weigh 0.050 gm phenylfluorone into 100 ml beaker. Add 50 ml methanol and 1 ml concentrated HCl. Stir to solution. Transfer to 500 ml volumetric flask with methanol. Dilute to mark with methanol and mix. Keep solution in flask and store in refrigerator. Solution should be stable 1 month or more.
6. Standard germanium solution - weigh 0.1441 gm GeO_2 (germanium dioxide) and transfer to 1 liter volumetric flask. Add 3 ml of 5 percent NaOH, stir with plastic rod to solution. Dilute with 75 ml H_2O and neutralize dropwise with 10 percent H_2SO_4 using

Congo Red paper, then add 3 or 4 drops in excess. Dilute to mark with water. One ml of solution contains 0.1 mg germanium.

7. Germanium working solution - transfer 50 ml standard solution to a 500 ml volumetric flask, dilute to mark with water and mix. One ml of solution contains 0.01 mg germanium.

8. EDTA (disodium ethylenediaminetetraacetate) solution (10 percent) - Dissolve 10 gm EDTA in water and dilute to total volume of 100 ml.

Dissolution of sample:

One gram samples are used for concentrations less than 40 ppm germanium. Smaller samples are used for concentrations greater than 40 ppm germanium.

1. Wet samples with concentrated HNO_3, add 5 ml $HClO_4$ and 5 ml concentrated H_2SO_4. Heat slowly to fumes and fume to pasty mass, not dry.

2. Add 2 ml H_2SO_4 and 0.1 gm $N_2H_4 \cdot H_2SO_4$ (hydrazine sulphate) and again evaporate to pasty mass. Cool.

3. Add 1 ml H_2O and evaporate just barely to SO_3 fumes. Cool, add 6 ml H_2O by buret and pour into 60 ml separatory funnel. Rinse flask with 19 ml of 9N HCl by buret in small portions, and add to separatory funnel. Make the final rinse with 2-3 ml 9N HCl. Cool.

4. Add 20 ml CCl_4, stopper and shake vigorously for 1 minute. Allow layers to separate and drain lower layer (CCl_4) into 50 ml conical flasks used for digestion of sample. Add 2 ml CCl_4, shake for 10 seconds and allow layers to separate. Draw off CCl_4 layer into flask. Discard aqueous layer. Rinse separatory funnel with 9N HCl and discard.

5. Transfer CCl_4 solution from conical flasks back to separatory funnel with 2-3 ml 9N HCl to rinse flask. Stopper and shake for 10 seconds and allow layers to separate. Draw off CCl_4 layer into a dry 60 ml separatory funnel, rinse first funnel with 1 ml CCl_4, shake for 10 seconds, allow to separate and draw off CCl_4 layer into second funnel.
6. To second funnel add exactly 12 ml H_2O by buret. Stopper and shake vigorously for 1 minute. Allow layers to separate, draw off and discard CCl_4 layer. Filter aqueous layer through dry #40 filter paper into a 50 ml conical flask.
7. Pipet 10 ml of filtrate into a 50 ml volumetric flask. Add 1.5 ml 1/1 H_2SO_4 and mix by swirling. Add 10 ml pH 5 buffer solution and mix by swirling. Add 1 ml gum arabic solution and mix by swirling. Add 2 ml 10 percent EDTA and mix by swirling. Add 10 ml phenylfluorone solution and mix by swirling. Allow to stand for 5 minutes, dilute to mark with 1/9 HCl and mix.
8. Read absorption at 510 mμ versus distilled H_2O within 10 minutes after dilution to volume.

Calibration Curve

1. Transfer 0, 0.5, 1.0, 2.0, 3.0, and 4.0 ml of working standard solution (0.01 mg Ge/ml) to 50 ml conical flask.
2. Add H_2O to give a total volume of 7 ml by buret.
3. Transfer to 60 ml separatory funnels, using 19 ml 9N HCl (by buret) in 3-4 ml portions to rinse flask.
4. Proceed as for unknowns from Step #4 of procedure for dissolution of sample.

Notes:

1. If Ti and Fe are present, omit fuming with hydrazine sulfate. Instead, add 5 drops $HClO_4$ and fume until residue is just wet with H_2SO_4. The method is not very satisfactory (low results) if more than a trace of Sb is present along with Ti and Fe. EDTA added during color forming step reduces, but does not eliminate interference by Sb.
2. If Cr is present in sample, several additions of H_2O and evaporations to SO_3 fumes may be necessary to dissolve basic Cr^{III} sulfate formed in dissolution step.
3. Reagent blanks are carried in 50 ml conical flasks along with samples.

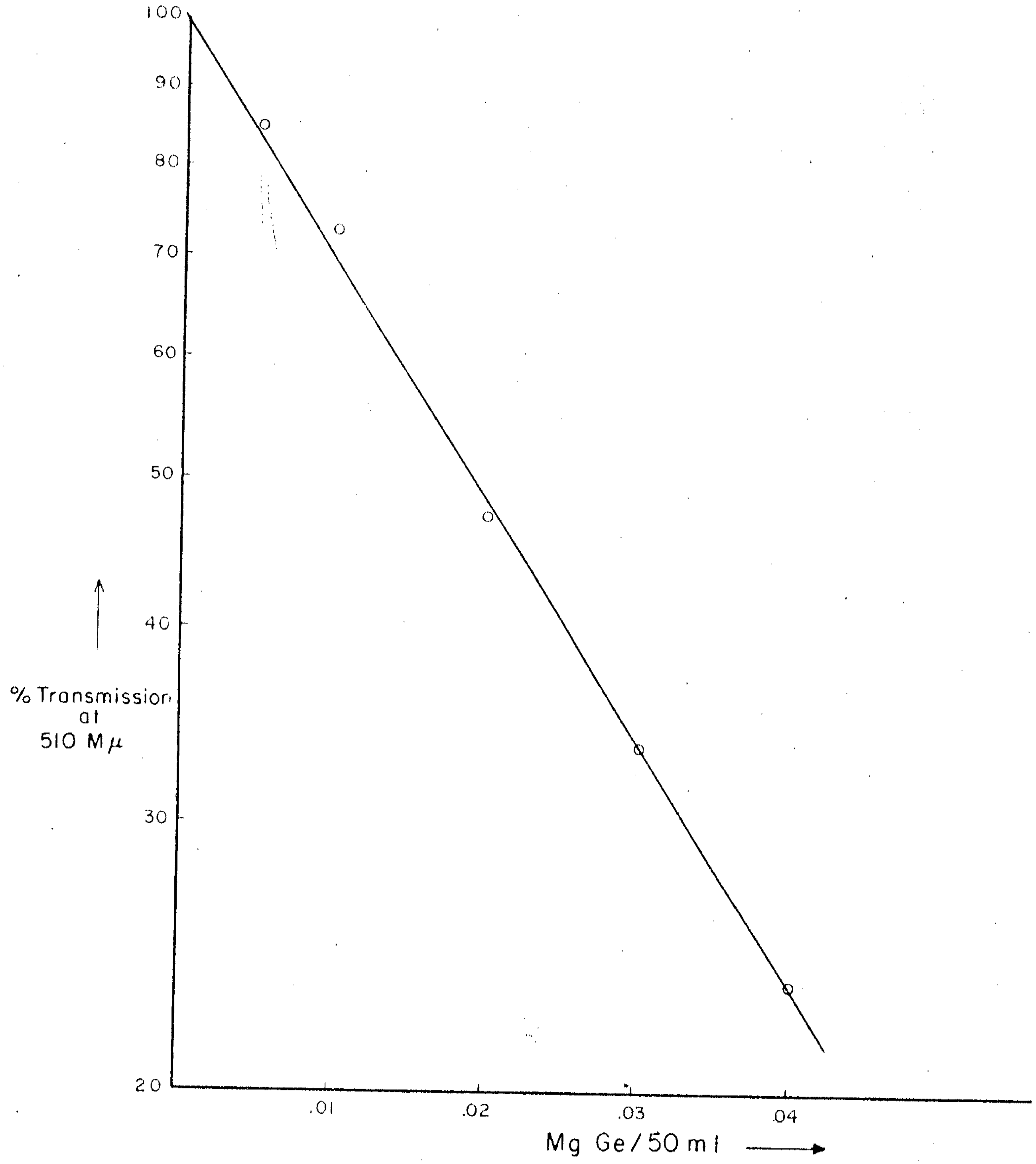

Figure 15 - Standardization Curve (Semi-Logarithmic)

Phenylfluorone Color - Carbon Tetrachloride Extraction Isolation

APPENDIX III

SPECTROPHOTOMETRIC PHENYLFLUORONE COLOR

The following procedure is modified from the procedure as used by The American Zinc Company of Illinois, Monsanto, Illinois.

Distillation

Reagents:

1. Distilled water.
2. Gum arabic solution - Dissolve 1 gm gum arabic in 100 ml of hot water and allow to cool. Prepare fresh each day.
3. Hydrazine sulphate solution - saturated - Prepare a saturated solution of hydrazine sulphate in hot water and cool.
4. Dilute hydrochloric acid (1:4) - Dilute 200 ml of concentrated HCl to 1 liter with water.
5. Phenolphthalein indicator - Dissolve 1 gram of phenolphthalein in 50 ml of alcohol and dilute to 100 ml with water.
6. Cellosolve (2 ethoxyethanol) - Use Eastman Kodak reagent No. 1697.
7. H_2SO_4-H_3PO_4 solution - Add 50 ml concentrated H_2SO_4 and 50 ml H_3PO_4 (85 percent) to 200 ml of water. Cool and dilute to 500 ml.
8. HBF_4 solution - Add 5 ml of 48 percent hydrofluoric acid to 45 ml of saturated boric acid solution. Mix and dilute to 500 ml.
9. Hydroxylamine hydrochloride reagent - Use crystals.
10. Potassium permanganate reagent - Use crystals.
11. Phenylfluorone solution - Transfer 0.150 gm of phenylfluorone to a 200 ml volumetric flask. Add 60-80 ml of cellosolve and 10 ml of 1:1 H_2SO_4, swirl to hasten dissolution, then dilute to 200 ml with cellosolve and mix.

Apparatus

Distillation Unit - This consists of a 500 ml Erlenmeyer flask, a thistle tube, and a water cooled condenser. Connection between the flask and condenser is made with glass tubing and rubber stoppers. The end of the thistle tube extends below the liquid level of the flask. The discharge end of the condenser extends into a 150 ml beaker containing approximately 0.5 gm hydroxylamine hydrochloride and sufficient water to cover the condenser tip. During distillation this beaker is kept in a vessel containing cold water.

Spectrophotometer - Beckman "Spectronic 20."

Preparation of Standards

Use high purity grade oxide. Heat approximately 2 gm GeO_2 at 600° F for two hours and then cool in a desiccator. Weigh 0.7204 gm GeO_2, equivalent to 0.5 gm Ge, into a platinum crucible. Add 2 gm potassium carbonate and 3 gm of sodium carbonate and mix thoroughly. Fuse at low temperature until a quiet fusion is obtained and cool. Dissolve the cake in about 100 ml of water, neutralize with sulfuric acid and dilute to 500 ml. Make dilutions of this solution until the final dilution gives a solution containing 0.01 mg or 10 gammas of Ge per ml. Store all standard solutions in polyethylene containers.

Procedure for Calibration Graph

By means of a semi-microburette, transfer 0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 ml portions of the standard Ge solution to 100 ml volumetric flasks. To each flask add 5 pellets of NaOH and sufficient water to make a total volume of 20 ml. Swirl to dissolve the NaOH and cool to room temperature.

Add two drops of phenophthalein indicator and neutralize by dropwise addition of 1:1 hydrochloric acid. Add 5 ml H_2SO_4-H_3PO_4 solution, 5 ml HBF_4 solution, 2 ml hydrazine sulfate solution 5 ml gum arabic solution, 5 ml cellosolve, and 2 ml phenylfluorone solution. Mix well after each addition. Allow to stand for 75 minutes, then dilute to 100 ml with 20 percent HCl and mix.

Read absorption at 507 $m\mu$ in a 1 cm absorption cell. Prepare a graph plotting optical density against mg Ge in the standards.

Procedure for Solution of Sample and Distillation

1. Weigh a sample of suitable size to contain 0.4 to 2.4 mg of Ge.
2. Transfer to a 20 ml nickel crucible.
3. Add 4 to 5 gm of sodium peroxide and mix thoroughly.
4. Add 10 to 12 pellets of NaOH and fuse to a moderate temperature until a quiet fusion is obtained.
5. Cool.
6. Transfer the crucible and fusion to a 150 ml beaker, cover with a watch glass, and then slowly add 50 ml of water. CAUTION: The reaction will be vigorous.
7. When action has subsided, and not more than a very small amount of fusion remain in the crucible, rinse the cover glass and the crucible and transfer the solution to a narrow mouthed 500 ml Erlenmeyer flask. Reserve the crucible for a future step in the procedure.

8. Add an "anti-bump" granule and approximately 0.4 gm of potassium permanganate to the flask. Wash down the sides of the flask. The total volume should be held between 80-85 ml.
9. Assemble the distilling apparatus.
10. Fill the nickel crucible, reserved above, with concentrated HCl.
11. Let stand for about 2 minutes and pour the acid through the thistle tube into the flask. Add an additional 100 ml of concentrated HCl to the flask through the thistle tube.
12. Start the distillation and distill until the final volume of distillate is about 100 ml.
13. Remove the source of heat, disconnect the apparatus and wash down the condenser. The distillate contains the germanium.

Color Development

Transfer a 10 ml aliquot of the distillate to a 100 ml volumetric flask. Add 2 drops of phenolphthalein indicator and neutralize the solution by dropwise addition of 20 percent NaOH solution. Then just neutralize with careful addition of 1:1 HCl. A blank is carried along from this point containing about the same amounts of NaOH and HCl and a similar initial volume.

To each flask make the following additions, mixing between each addition: 5 ml H_2SO_4-H_3PO_4 solution; 5 ml HBF_4 solution; 2 ml hydrazine sulfate solution; 5 ml gum arabic solution; 5 ml cellosolve; and 2 ml phenylfluorone solution. Allow to stand 75 minutes, and then dilute to 100 ml with 20 percent HCl and mix.

Determine the optical density as in preparing the calibration graph. Using the values obtained, read from the calibration graph the mg of Ge contained in the aliquot.

Calculations

$$\frac{100}{\text{Original sample (gms)}} \times \frac{\text{ml of distillate}}{\text{ml of aliquot}} \times \text{Gms Ge in aliquot} = \%\ \text{Ge}$$

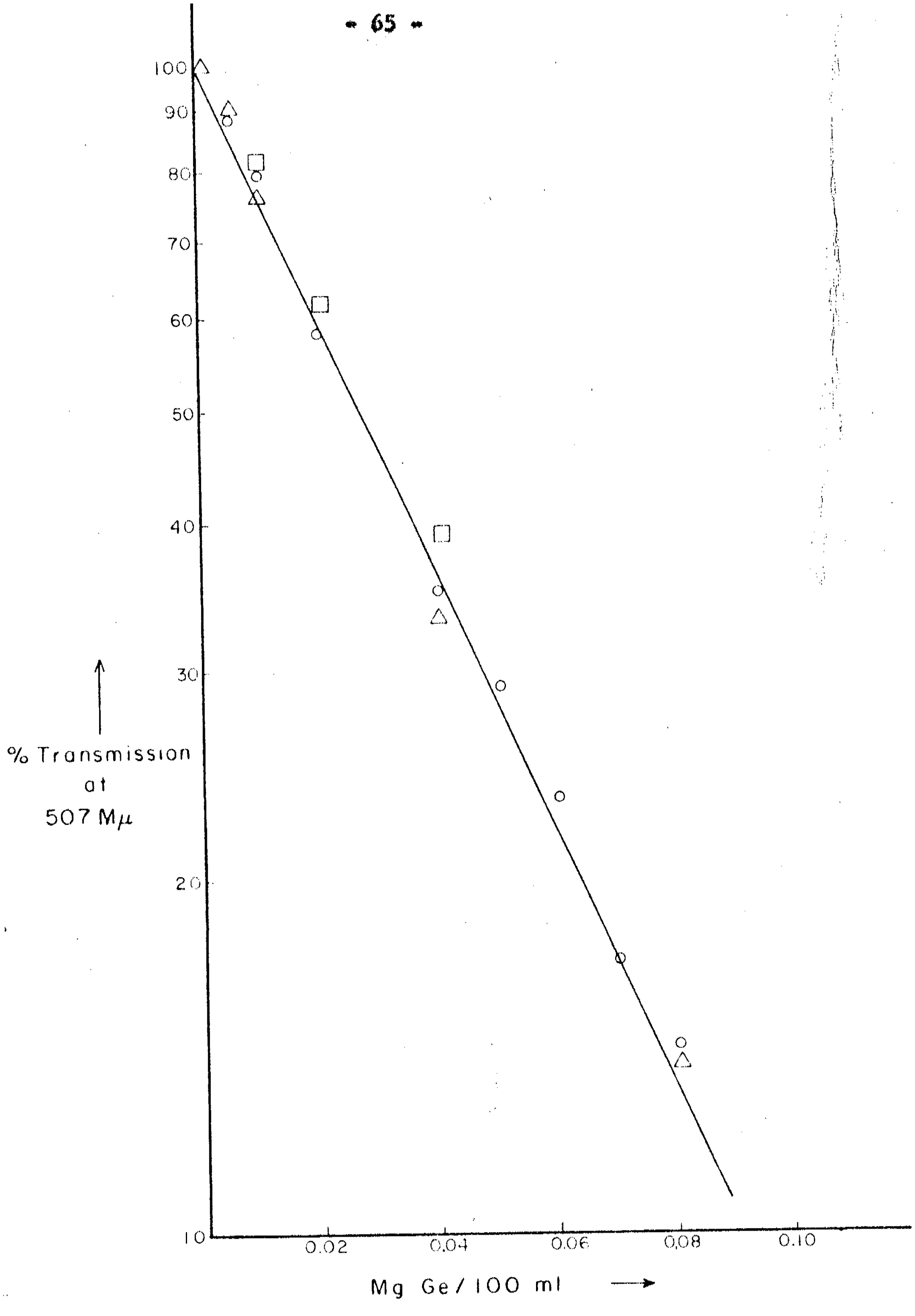

Figure 16 - Standardization Curve (semi-Logarithmic)

Phenylfluorone Color - Distillation

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