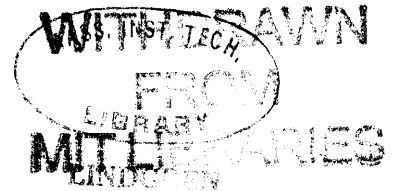ABUNDANCE AND DISTRIBUTION OF CERTAIN

ELEMENTS IN SPHENE

by

EDWIN ROBERT ROSE

SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF

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Signature of Author ....
        Department of Geology and Geophysics, August 22, 1959

Certified by ...   ...
                                     Thesis Supervisor

Accepted by ....
        Chairman, Departmental Committee on Graduate Students

ABSTRACT

ABUNDANCE AND DISTRIBUTION OF CERTAIN ELEMENTS IN SPHENE

by Edwin Robert Rose

Submitted to the Department of Geology and Geophysics
August 24, 1959 in partial fulfillment of the requirements
for the degree of Master of Science

The trace element content of accessory sphene from granitic rocks was investigated to determine if genetic similarity between igneous rocks can be detected by such means. This study also supplies considerable data on the trace element contents of sphenes.

Analyses were made using a grating spectrograph on a Wadsworth mounting. Quantitative determinations were made for iron, chromium, zirconium, neodymium, lanthanum, cerium, samarium, gadolinium, scandium, vanadium, yttrium and tungsten in twenty-three samples from northeastern North America. Semi-quantitative estimates were made for aluminum and strontium whenever present.

A standard was prepared from one of the sphene samples. This standard was then used as a "measuring stick" in the determinations of the analysis elements in the remaining twenty-two samples. The original concentrations of the analysis elements in the standard was determined by use of the addition procedure. In connection with the addition plots, use was made of a ratio of the intensity of each analysis element to either calcium or titanium; usually calcium. This ratioing of intensities improved the addition plots in most cases, making it easier to determine the original concentrations of the analysis elements in the standard. It is estimated that the error involved in some of the determinations may vary from about ten percent to perhaps as much as twenty percent. Different elements will have different errors.

It was found that lanthanum, cerium and neodymium were geochemically coherent as were samarium and gadolinium. Cerium and lanthanum showed an inverse relationship to yttrium. Samples highest in chromium seemed to be lowest in iron. Chromium, scandium and tungsten concentrations were low in all samples. Iron was always present in high concentrations, averaging about 20,000 ppm. The remainder of the analysis elements with an occasional exception were present in quantities less than one percent (10,000 ppm). Manganese, yttrium, and neodymium values generally fell in a range from 3500 to 6000 ppm. Gadolinium, samarium, lanthanum, cerium, zirconium and vanadium values lie for the most part between 1000 and 3500 ppm.

Eleven of the thirteen samples from New England showed significant similarity to one another. This group, containing most of the New England samples, is distinctly different from the rest of the samples. Similarity between three samples from Ontario is noted. Analyses of two samples from Quebec also show a distinct relationship to each other.

The results seem to indicate that trace element content of sphene can be useful in determining the fact of genetic relationships between igneous rocks.

Thesis Supervisor: William H. Dennen
Associate Professor of Geology

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the entire thesis investigation.

INTRODUCTION

Purpose

The purpose of this thesis is to investigate the possibility that the trace element distributions and variation in sphene might be used as a means of establishing or recognizing genetic similarity or dissimilarity between granitic rocks. To date little trace element analysis of sphene has been done and thus little is known concerning the trace element content of sphene. This investigation will furnish considerable data on the abundance and distribution of certain trace elements in this mineral.

The usefulness of trace element distribution as a possible means to group and separate igneous rocks of similar and different histories is based on the assumption that elements present in trace quantities do not effect the cooling of the magma. It is important that one choose elements accepted into the sphene structure that have vering concentrations in different magmas and that this variation of original concentration be reflected by the relative proportions of the same elements in the sphenes.

Sphene was chosen as the analysis mineral for this investigation for two main reasons. First, considering its formula $CaTi(SiO_4)O$, and the previous work done (to be covered later), it appeared that the mineral would furnish ample opportunity for substitution of trace elements in its structure. This is quite important since in an investigation of this type it is desirable to have detectable amounts of several trace elements present in order to establish some understanding of the significance of the results. It is impractical to attempt to make determinations of trace elements in a mineral which admits non-formulary constituents only in quantities below the detection limits of the method used. It is also useless to investigate a mineral which is, so to speak, a trash bin for

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a great number of elements which enter its structure without any selection, and in a great variety of concentrations.

A second reason for choosing sphene as the analysis mineral was the availability of over twenty sphene samples separated from granitic rocks. These samples were from rocks used in a program of radioactive age studies in the M.I.T. Department of Geology and Geophysics. In connection with this program, granitic rocks from northeastern North America were collected, crushed, and certain minerals of which sphene was one, were separated (Hurley and Fairbairn, 1957). Of course, the fundamental consideration behind this availability of sphene, is the widespread occurrence of sphene as an accessory mineral in granitic rocks.

Previous Work

Review of the literature showed that little work has been done on the trace element constituents and their quantities in sphenes.

Fersman (1926) reports analysis of a sphene from a nephelite syenite. This analysis shows 1700 ppm of cerium and yttrium oxides and about 1200 ppm of iron oxides both ferrous and ferric. Also reported are trace quantities of magnesium, sodium and potassium. Another article by Fersman (1937), though not seen by the author is supposed to include some data on sphenes. Bray (1942), states "sphenes are notable for their high rare-earth content, as well as high aluminum, iron, manganese, chromium and vanadium." The work which Bray did on the sphenes was qualitative and thus one cannot estimate what "high" means. Bray himself points out that this is a relative term for each element and what is high for one element may be low for another.

In a study of four sphenes, one of which was the rare-earth-rich

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variety, keilhauite, Prince (1938) reports from about one to not quite four percent iron oxide. In each of the "normal" sphenes he also found about six percent aluminum oxide and several hundredths of a percent of manganese oxide was reported in two of the samples. In the keilhauite variety, Prince reports 3.58 percent (35,800 ppm) for the total of cerium and yttrium oxides, about six percent ferric oxide and over seven percent of aluminum oxide.

Sahama (1946) reports quantative analyses of six sphenes, three from nephelite syenites on the Kola Peninsula, one from a limestone, one from a gabbro, both of these from Finland and the sixth specimen from the Urals. For the rare-earth group of elements he has values reported for lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium, erbium, ytterbium and yttrium oxides. Values for these oxides range from a trace to about 1200 ppm, with neodymium, lanthanum, cerium and yttrium running in quantities several times larger than the concentrations of 100 to 200 ppm for the other rare-earth oxides. Other elements determined in oxide form by Sahama include: tantalum, vanadium, aluminum, iron, chromium, magnesium, zirconium, strontium, barium, manganese and niobium. Niobium oxide values vary from 300 ppm to over 15,000 ppm. Tantalum oxide values are 300 ppm or less. The values for vanadium oxide are of the order of about 800 ppm. Ferrous iron oxide values lie in the neighborhood of 2,000 ppm, zirconium oxide values average about 600 ppm, strontium varies highly, from 40 to 4,400 ppm, while barium oxide varies from 50 to 500 ppm. Niobium, tantalum, vanadium, iron, zirconium, strontium and barium were found in all six samples. Values for aluminum oxide are reported for only three of the samples and vary from 500 to about 4400 ppm. Chromium oxide values are reported for two samples with an average value of 150 ppm.

Other elements reported are magnesium, manganese, sodium and potassium. Of all these elements only vanadium, chromium and zirconium were analysed for by spectrochemical techniques.

Sahama (1946) also included an analysis of another supposed sphene. This supposed sphene contains about 9600 ppm of yttrium oxide, 1900 ppm of cerium oxide. These values are considerable larger than those for any of the other specimens, and this sphene is likewise much higher in tantalum and iron than any of the other analyses. The total iron oxide value is reported as 26,000 ppm. According to Sahama sphene can be used as an indicator of the bulk composition of the rare-earth elements in rocks.

In their book, Geochemistry, Rankama and Sahama mention reports of europium in sphene up to 340 ppm and that it may contain up to several percent of columbium oxide. They feel that the yttrium rare-earths are characteristic of granites, while the cerium rare-earths usually seem to be enriched in nepheline syenites. It is also pointed out that sphene is one of the main seats of radio-activity in igneous rocks.

Columbium is reported in quantities from 1,000 to 10,000 ppm in sphenes analysed by Jaffe (1947). Jaffe investigated sixteen sphene samples using spectrographic methods. He found iron, aluminum, and fluorine in all samples and columbium in about half.

Goldschmidt (1954) notes a sphene variety containing about ten percent tin dioxide. He also mentions that the calcium in sphene is frequently re-placed in part by yttrium, the rare-earths, uranium and thorium and that one to two percent niobium is found in some sphenes replacing the titanium.

In twenty-four sphene samples, sixteen of which were also used by the author, Hurley and Fairbairn (1957) determined uranium and thorium

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concentrations. The average thorium concentration was 540 ppm and the uranium content averaged near 300 ppm. The minerals zircon, apatite and epidote from some of the same rock samples were also analysed for uranium and thorium. It was found that the sphenes contained more uranium and thorium than apatite and epidote, but less uranium and thorium than zircon.

Molybdenum concentrations ranging from 34 to 400 ppm have been reported by Rabinovich and associates (1958). Of the minerals they analysed, sphenes had the largest molybdenum content. The highest values were from sphenes obtained from areas near molybdenum mines. The method of analysis was spectrographic.

Selection of Analysis Elements and Lines

It is necessary in choosing analysis elements to pick elements which might be expected to be present at least fairly commonly in detectable quantities in sphenes. The selection of analysis elements in this work was done using three primary guides. One was the consideration of which trace elements were of suitable size to substitute for one of the major elements. The second guide was information available from previous work. This guide however, was only a rough general guide. The third guide was the qualitative analysis of sphene 3085, the standard. This was the most important step in deciding on the analysis elements. It was noticed in the study of the previous work that while the widespread occurrence of rare-earths in sphenes was noted in most cases, only in the case of Sahama (1946) was there any major breakdown into the individual elements.

On examination of the spectra of sphene 3085 numerous rare-earth lines were identified. These included lines of neodymium, lanthanum, cerium, gadolinium, samarium, ytterbium, erbium and praseodymium. The rare-earth elements chosen for analysis were neodymium, lanthanum, cerium, gadolinium and samarium. The other rare-earths were not chosen as analysis elements because of the great difficulty in recognizing the individual lines of the different elements, due to near coincidence, primarily with other rare-earth lines. These other rare-earth lines were also of very low intensity and thus were assumed to be much more likely to be present only in quantities near the sensivity limits of the procedure. It should be noted here that in the case of gadolinium and samarium, it was still quite difficult to distinguish between the lines of the two elements, since in the region used they are very close together. In order to furnish some measure of a check on the correct choice of lines, two lines for samarium and

gadolinium were chosen (see Table 1).

Other elements found to be present in sphene 3085 and chosen as analysis elements were chromium, iron, manganese, molybdenum, scandium, vanadium, yttrium, tungsten and zirconium.

Table 1 lists all lines that were measured for use in constructing the addition plots, their rated intensities as tabulated in the M.I.T. Wavelength Tables, and the wavelength and intensities of significant lines that interfere with the particular analysis line. All lines picked were the most sensitive lines of each element, which also had the minimum of interference from other lines. Also considered in cases where interference of some sort seemed unavoidable, was what element was conflicting with the analysis line. No analysis line was chosen that had a conflict with one of the major elements calcium, titanium or silicon. Every attempt was also made not to use analysis lines which conflicted with a line of another analysis element. In cases where this was not entirely possible, the analysis line was picked whose conflicting line had the lowest intensity rating. The only elements where it was impossible to avoid choosing analysis lines with conflicts were molybdenum and neodymium. Molybdenum 3902.963 is the only important molybdenum line in that region of the spectra investigated. This line, with an intensity rating of 1000, had a major interference with iron 3902.948 with an intensity rating of 500. An attempt was made to estimate the contribution of the iron to the intensity of this line, through the use of an intensity ratio of the iron line to another iron line. However, it was found on subtracting that portion of the intensity calculated to be due to the iron line, one was left with a negative intensity for the molybdenum line for all twenty-three

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Table 1

Analysis Lines used in the Addition Procedure

Line	*Intensity	Interfering Lines	Intensity of Interfering Lines
Ce 4222 Å	80		
Cr 4254 Å	5000		
Fe 4383 Å	1000		
Fe 4260 Å	400		
Gd 4251.74 Å	500	Sm 4251.79 Å	200
Gd 4262.09 Å	150	Cr 4262.13 Å	40
La 4333 Å	800		
Mn 4031 Å	500		
Mn 4034 Å	250		
Mo 3902.96 Å	1000	Fe 3902.94 Å	500
Nd 4303.57 Å	100	Fe 4303.58 Å	25
Sc 4246.83 Å	80	Nd 4246.88 Å	10
Sc 4374.5 Å	100		
Sm 4256 Å	150	Zr 4256 Å Nd 4256 Å	25 40
Sm 4329 Å	300		
V 4379 Å	200		
Y 4374.94 Å	150	Sm 4374.98 Å	200
Y 4398 Å	150		
W 4294 Å	50		
Zr 4239 Å	100		

*From M.I.T. Wavelength Tables.

sphene samples. As a result molybdenum was dropped from the analysis elements. Neodymium 4303.575 also had a conflict with an iron line. The contribution of this iron line was corrected for, as will be described later, and yielded meaningful results.

SPECTROGRAPHIC PREPARATION

Sample Preparation

As mentioned earlier, the sphene samples used were available to the author as minerals separated from granitic rocks. A list of the samples, their location, the type of rock from which they came and the estimated percent contamination is given in Table 2. These separates were derived from rock samples of about fifty pounds, which were crushed and concentrated by gravity and magnetic procedures (Fairbairn, 1955).

The author took twenty-three separates and crushed each sample in a stainless steel mortar. The mortar was cleaned with distilled water after the crushing of each sample was completed. That portion of each sample which passed the two hundred mesh screen and was retained on the three hundred twenty-five mesh screen was used in the analysis. The samples were crushed this fine in order to free the included impurities from the sphene. This fraction of the sample then was run through a Frantz isodynamic separator. Each sample was run through several times with varying amperages and rates of feed in order to remove a maximum amount of contamination. Of course, some samples showed little or no improvement since the original contamination was so low. Estimates of contamination were made under a binocular microscope. In all cases more attention was paid to eliminating opaque and dark impurities than quartz and similar minerals, since one would expect the opaque mineral to contribute much more heavily to the elemental contamination than quartz. The processing of the crushed sample through the Frantz separator also had the important effect of eliminating any contamination of iron due to the crushing in a steel mortar.

After cleaning the samples an estimate was made of the percent contamination. This was done by spreading several hundred grains on a small

Table 2

Locality, Rock Type, Other Accessory Minerals, and Estimated
Percent Contamination of Samples Analysed

Sample	Rock Type	Locality	Other Accessory Minerals	Estimated % Contamination
3011	Granite	Leavitt quarry, 2 miles W. of Leominster, Mass.	Biotite,magnetite,apatite,tourmaline,zircon	6-quartz
3055	Granite	Hallowell, Maine	Biotite,muscovite,apa., fluorite,monazite,zir.	3-quartz
3014	Granite	Curry quarry,Mass.,2½mi. ESE of Wrentham sta.Mass.	Biotite,chlorite,epidote apatite,fluorite,zircon	max. 9-quartz
3058	Quartz monzonite	Sprucehead Island, Maine	Biotite,epidote,apatite, tourmaline, zircon	7-quartz
3071	Granite	St. Gideon, Que.-Lake St. John area	Bio.,chlor.,amph.,magn., ilmn.epd.tour.fluor.zir.	2-quartz
3080	Granite	On route 198, 2 mi. N. Mt. Desert, Maine	Biotite,chlorite,magn., ilmn.,epidote,zircon	5-dark min. and quartz
3139	Granite	Route 11, 13.5 mi. E. of Mt. Laurier, Que.		2
3051	Granodiorite	North end of N. Attleboro, Mass.	Chlorite, ilmenite, epidote, zircon	5-quartz
3060	Granite	Mt. Waldo, Maine	Biotite,pyrite,apatite, tourmaline, zircon	3-quartz
3061	Rhyolite	Moosehead Lake, Maine on route 15	Biotite,chlorite,magn., amph.,epd.,fluor.,zircon	4-dark min. and quartz
3062	Granite	Route 201, 5.5 mi. S. of Jackman, Maine	Chlorite,magnetite,epidote, apatite, zircon	9-(½ quartz ½ dark min.)
3063	Granite	Hollingsworth & Whit.Rd. 6mi.W.from rte. 201, Me.	Biotite, chlorite, epidote, apatite, zircon	0
3079	Granite (rapakin)	On rte. 1, 1 mile S. of Jonesboro, Maine	Chlorite, epidote, apatite, zircon	3-quartz
3081	Granite	Barriefield,Ont.on outskirts of Kingston, Ont.	Amphibole,garnet,magn., apatite, tour., zircon	6
3082	Syenite	Kingston Mills, Ont., 6 mi. N. of Kingston	Biotite, pyrite, magn., ilmn., apatite, zircon	2
3485	Alaskitic Granite	Hope Lake, Kenora Dist., Ont.		2
3067	Syenite	Brome Mt., Quebec, on Iron Hill Road	Biotite,muscovite,ilmenite, apatite, zircon	4-quartz
3069	Tinguaite	St. Josef's Blvd., Montreal East	Amphibole, magnetite, apatite	2-quartz
3084	Granite Porphyry	Gaspe Nat'l. Park hiway 7 mi. S.of Gaspesie,Que.	Chlorite, magnetite, tourmaline, zircon	4-quartz
3085	Granite	W. end Mountainville, Deer Is. Quadrangle, Me.	Bio.,chlor.,amph.,pyrex, magn.,epd., apa., zircon	0
2093	Quartz Diorite	Dauphine quarry, Birchtown, Nova Scotia	Biotite,chlorite, apatite, zircon	6-pyrite and quartz
3013	Granite	Blanchard quarry, 1½ mi. WNW.of Uxbridge Sta.Mass.	Biotite, magnetite, fluorite, zircon	4-dark min.
3138	Granite fine pink	Rte. 58, 14.1 mi. W. of Mt. Laurier, Que.		12-opaque or dk. min.

grid under a binocular microscope, counting two to three hundred grains, and recording the number of non-sphene grains in this count. Due to the extremely small size of the grains used, it was not possible in the time available to determine what the impurities were. That portion of the impurities that were opaque minerals is listed with the estimates of contamination in Table 2. Quartz wherever discernible has also been noted.

Mixing

All mixing was carried out using a small agate mortar and pestle, both of which were scrubbed with cleanser and then well rinsed with distilled water before mixing each sample with either carbon or additive oxides. In the case of the samples to which oxides of the analysis elements were added, mixing in the mortar was carried on in the mortar for at least thirty minutes. During this time the sample was swept into a small pile in the center of the mortar at least six times. This procedure was followed in order to get a uniform mixing of the additive oxides with the sphene standard. The rest of the mixings consisted of mixing one part of the addition sample or pure sphene sample with two parts of carbon by weight. The mixing with carbon was carried out for at least five minutes with at least five coning procedures.

Electrodes

Each sample was run in duplicate. It was found in preliminary qualitative work that one eighth inch electrodes with a cylindrical cavity one sixteenth of an inch in diameter and three sixteenths of an inch deep was the best available size to use for the sample electrodes. Spectrographically pure graphite electrodes were used for all samples throughout the

investigation.

The twelve electrodes used for the addition procedure were weighed before and after loading of the samples. The variation in the weights of the samples in these electrodes averaged about give percent. None of the other electrodes was weighed.

Photographic Materials

Kodak 103-O spectrographic plates were used in all cases. After arcing, each plate was put in a developing tank for four and a half minutes at a temperature of twenty degrees centigrade. Then the plate was fixed for at least fifteen minutes, usually longer. Finally, the plate was washed for at least thirty minutes.

Photometry

Measurement of line and background intensity was done with a Hilger non-recording microphotometer. Measurement of both line and background was made on all analysis lines.

Spectrograph

The analysis instrument was a twenty-one foot, 30,000 lines per inch concave grating spectrograph on a Wadsworth mounting. This instrument has a dispersion of about 2.5 Å per millimeter. The good dispersion of this instrument was the basis of the choice of this instrument. The near coincidence of many of the rare-earth lines requires a large dispersion in order to get maximum possible separation of the lines of the different elements. The region used in this investigation lay from about 3900 Å to 4500 Å. A slit width of 0.015 inch and slit height of about 8.0 millimeters was used.

Arcing Conditions

All samples were arced to completion using anode excitation at about seven amperes. The electrode separation was about seven and a half millimeters. One eighth inch spectrographically pure graphite electrodes containing the sample were used at the anode. The counter electrodes used were three sixteenths inch spectrographically pure carbon rods, sharpened to a fine point. Counter electrodes were changed after each sample and resharpened for later use. The average completion arcing time was about one minute and fifty seconds, with a variation of about five percent. The variation of arcing time is to some extent related to the amount of sample arced (see figure 1). However, this relationship was not determinable. It undoubtedly depends on many other things also, such as matrix, amperage, electrode size, etc.

Sector

In order to reduce the intensities of certain lines to the point where they could be measured quantitatively, a sector was used. An eight step sector with a factor of one-half per step was used for the addition procedure on sphene 3085 and for three other sphene samples. A newly prepared sector with a step factor of one-fourth was found to be more useful, and was used on all the remaining samples. This sector had five steps. What is meant by a step-factor of one-fourth can be explained as follows: assuming constant intensity over the entire area of the sector, the first step allows the passage of all the light, while each succeeding step permits the passage of a quantity of light equal to only one-fourth that allowed to pass on the preceding step.

SOURCES OF ERROR

There are two general types of errors involved in quantitative spectrochemical analysis. They are those inherently present in the sample and equipment used, and those introduced by the analyst.

In the first group are included errors due to contamination of the samples, development of the plates, non-linear step factor, and due to impurities of standards used in the addition procedure.

1. Contamination: The estimates of percent contamination are listed in Table 2. The average percent total contamination is about four and a half percent. However, it is very important to notice that in at least ten of the sphenes nearly all of the contaminating material was quartz. One would expect quartz to contribute very little to the contamination in the elements being analysed for. This is especially true when quartz is compared to minerals such as augite, hornblende, or hematite. Hematite for instance contains seventy percent iron, and a twenty milligram sample with a one percent contamination by hematite would have 7000 ppm of iron due to the hematite alone. This is very considerable contamination and is an extreme example. Hematite is quite unlikely to be present as a result of the separation procedure used. Most contaminating materials will contain many times less of the contaminating elements than hematite contains iron. Quartz can be expected to make essentially no significant contribution to the contamination of the sample in any of the analysis elements. On the basis of this consideration and the observation of ten samples, whose only visually detectable granular contamination was quartz, the estimated average effective contamination is about

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two and a half percent. This lies well within the error introduced by the analyst.

2. Plate Development: Errors due to development are extremely small on the same plate. Errors from plate to plate due to variations in the plates and in the development of each plate are thought to have been largely compensated for by calibrating each plate in three separate wavelength regions and by the use of comparison standards on each plate. Error due to this source is considered to be negligible in relation to errors introduced by the analytical procedure.

3. Error due to Non-linear Step Factor: As explained earlier, a step sector with an assumed linear step factor of one-half and later one-fourth derived from the g eometry of the sector was used during the investigation. Actually, however, the intensity of the light in the arc varies with the position in the arc gap, and thus the intensity of the light reaching different steps on the sector varies (see Dennen, 1949). In order to minimize the error from this source, intensity readings were made on the same step wherever possible. However, this was not possible in many cases and thus since the factors of one-half or one-fourth were assumed, error has resulted. Based on the work of Dennen (1949, illustrated in figure 11 of his manuscript) concerning this problem, light from the center of the arc was as accurately as possible caused to fall along the slit. Dennen found that the intensity in the central portion of the arc was the most nearly constant. In this way it is felt that the error from this source was minimized. It has been assumed in this investigation that this source has not

contributed significantly to the error.

4. Errors due to Impurity of Standards Used: Oxides of the analysis
    elements used in preparing the addition standards are in general
    quite pure and contribute errors which are very definitely negli-
    gible, and actually in most cases lie below the detection limit.
    This is the case for the oxides of zirconium, iron, yttrium,
    vanadium, tungsten, chromium and scandium used in this study.
    (The oxides are listed in Table 3.) However, in the case of the
    rare-earths, it is much more probable that larger errors, signifi-
    cant ones perhaps, may have been introduced due to impurity of the
    oxides used in preparing the standards. The reasons for this lie
    basically in the great similarity of the various rare-earth ele-
    ments and thus the greater ease with which they substitute for
    one another. The kind or degree of contamination of the rare-
    earth oxides used is not known. It is known that they are old,
    however. It is felt that error from this source, especially in
    the cases of samarium and gadolinium may be real. But since no
    data is available on the purity of these oxides, it was not pos-
    sible to make any corrections and it was assumed that only the
    analysis element of the oxide was present.

In the second group are errors introduced in weighing and mixing of
additive oxides, loading and arcing of the samples, measurement of line in-
tensity, construction of curves and errors due to loss of unvolatilized
sample.

1. Weighing Errors: All weighings of the additive oxides were made
    to the nearest tenth of a milligram. Error due to this source is
    certainly considerably less than a percent.

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2. Mixing Errors: Errors due to non-uniform mixing of the oxide additive is unknown. The mixing procedure described earlier is considered to have rendered error from this source to be negligible.

3. Error due to Loading and Arcing of the Samples: From twelve loaded electrodes used in the addition procedure it is estimated that the error in the sample weights arced is of the order of five percent. This variation in sample weights, of course, is also responsible in some measure for variation in arcing time and thus exposure. As mentioned earlier the arcing time showed about a five percent variation also. The nature of the relationship between sample weight and arcing time is not known, and was not investigated in this study. However, some indication of a relationship between variations in sample weight and arcing time may be seen in figure 1.

4. Errors due to Measurement of Line and Background Intensities: Errors from this source are, from general experience in the Cabot Laboratory at M.I.T. where this work was carried out, considered to be of the order of one percent.

5. Errors due to Loss of Unvolatilized Sample: Errors due to this source are unknown, but considered to be small, less than a percent. The arcing conditions and weight ratio of sphene to carbon used gave a very steady and smooth arc, with very little sputtering. None of the samples used in the analysis had any significant noticeable sample loss. All samples were arced to completion.

6. Errors due to Construction and Use of Curves: Errors from this source can be introduced at three stages in the particular

Figure 1
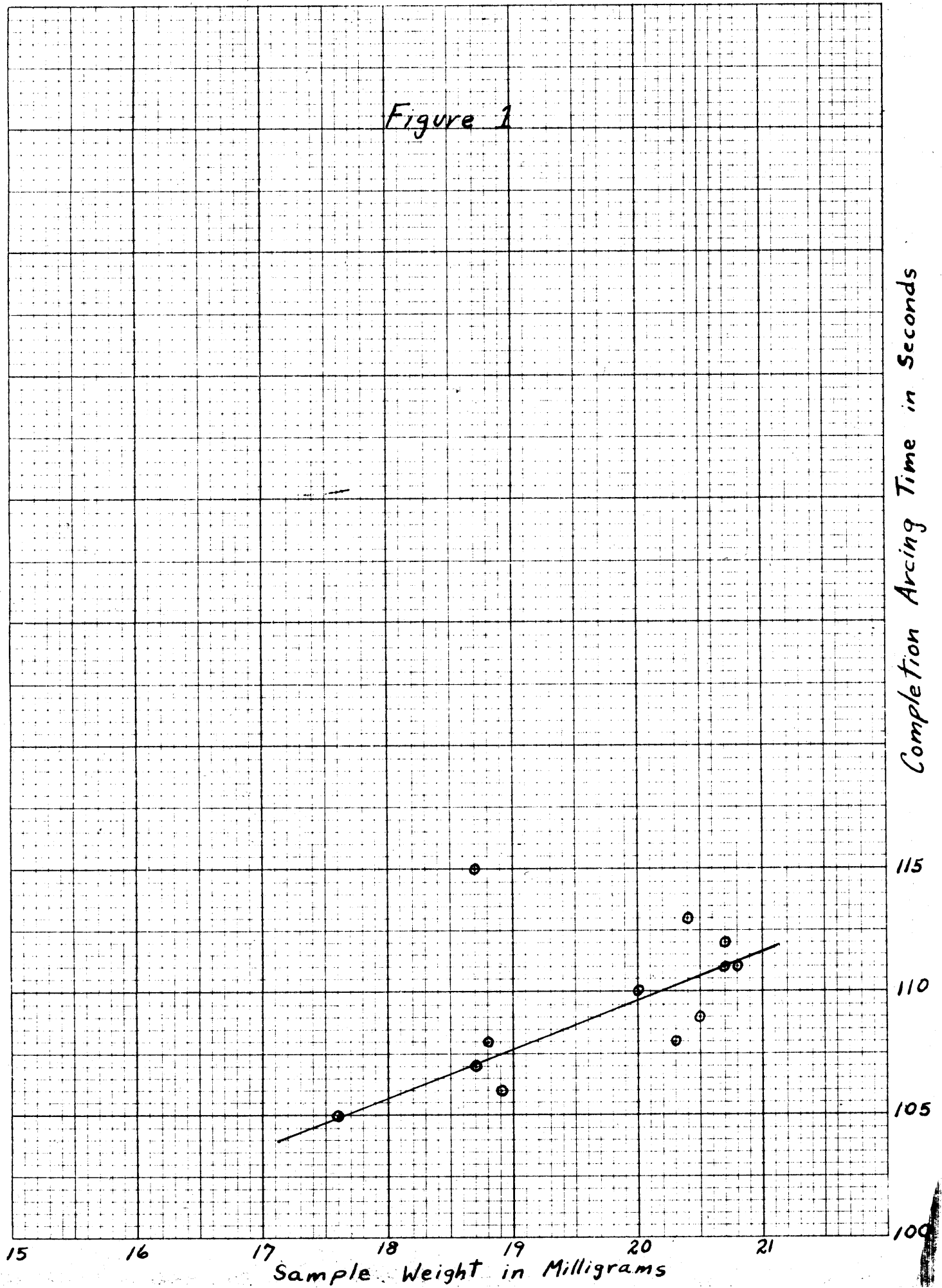
procedure used in this investigation. Errors are introduced in the plotting of the addition curves used to determine the original amount of each element present in sphene 3085. These curves also introduce error after plotting, in the interpolation to determine the original concentrations of the various elements. This problem is discussed under the section dealing specifically with the addition procedure. It is sufficient here to note that errors in this part of the study will have an important effect on determinations in all the samples, since it is by the standard (3085) that the concentrations in all the rest of the samples are determined. The effect will be a shift of all determinations in the same direction from some absolute value.

A second place where errors are introduced through graphical procedures is in the plotting and the use of calibration curves. This error, while probably not as critical or as generalized in effect as the error involved in the addition plots, could be significant. It is felt, however, due to the construction of many such curves, that the slope of these curves is subject to a comparatively small error.

The remaining graphical error is that involved with the working curves for each element. This also is discussed in more detail elsewhere.

No actual estimate of the error due to the construction and use of these curves is available. However, it seems reasonable to expect that an error of from five to ten percent may be introduced from this source.

It is estimated that the total probable error involved in the determinations reported lies between about ten percent to perhaps as much as twenty percent. Different elements will have somewhat different probable error. While these sound like, and are, sizeable errors that need to be allowed for, it is important to realize that the importance say of a twenty percent error quantitatively speaking is dependent on the general level of concentration of the particular element. Thus with a 100 ppm level of concentration similar to the values obtained for chromium, the actual value lies between 80 and 120 ppm. While in a case such as iron with a general level of about 20,000 ppm, the possible values range between 16,000 and 24,000 ppm.

ANALYTICAL PROCEDURE

Method of Analysis

In order to make quantitative measurement of the elements of interest, it is necessary to construct a "yardstick" using one of the samples. Once this has been done, this standard can be used to make determinations of these same elements in the rest of the samples. I chose sample 3085 as the standard since it contained no visible impurities. The addition method was employed to determine the original concentrations of the analysis elements in sphene 3085.

In this method an oxide mix containing equal or nearly equal amounts by weight of each of the fourteen original analysis elements was prepared. A list of the sources of these analysis elements and the percentage of the source that is made up by the analysis element is given in Table 3. This oxide mix was then mixed with sphene 3085 in such a proportion that each analysis element had an approximate concentration of one percent or 10,000 ppm. Then one part of this prepared addition sample was mixed with nine parts of pure sphene 3085. This gave an approximate concentration of about 1000 ppm in each of the analysis elements. In analagous fashion other addition concentrations of 5,000, 2,500, 350, 100 and 35 ppm were prepared. After mixing these samples one part to two parts of carbon by weight, they were arced in duplicate. Addition plots were then prepared to determine the original concentration of the analysis elements in the pure sphene 3085. The graphical procedure is discussed in the section concerning addition plots.

Table 3

Compounds of the fourteen original analysis elements used in
the addition procedure and the percent of each comprised by
the analysis element

Compound	Percent of Analysis Element
Ce_2O_3	85.4 Ce
La_2O_3	85.3 La
$Gd(NO_3)_3$	45.8 Gd
Nd_2O_3	85.7 Nd
V_2O_5	56.0 V
Y_2O_3	78.8 Y
MnO_2	63.2 Mn
MoO_3	66.7 Mo
W	100.0 W
ZrO_2	71.0 Zr
Cr_2O_3	68.4 Cr
Fe_2O_3	69.9 Fe
Sc_2O_3	65.3 Sc
Sm	100.0 Sm

Graphical Procedure

Three types of plots were used to determine the concentrations of the analysis elements. These are calibration curves, addition plots and working curves.

Calibration Curves: A calibration curve has to be used at each wavelength in order to convert deflections from the microphotometer to relative intensities. Calibration curves for different lines may have different slopes. A separate calibration curve was prepared for each line listed in Table 1 on the addition part of this investigation, which was all contained on one photographic plate. Examination of these curves showed that only three calibration curves were required. One was for use with molybdenum 3903, a second used for manganese 4031 and 4034, and the third was used for the region 4200 $\overset{o}{A}$ to 4500 $\overset{o}{A}$, which region included the rest of the analysis lines.

Addition Plots: Two plotting techniques were used for each analysis line in the addition part of the procedure. The first of these was the standard addition plot discussed in Ahrens (1955, page 33). This is merely a plot of the relative intensity of the line of an element as the ordinant versus the amount of the element added to the sample, on the abcissa. A curve is then drawn through a succession of these points. Ideally this is a straight line which is then extended to intersect the abcissa. The point of intersection of the abcissa and the extended addition curve indicates the original concentration of the analysis element in the sample.

The second type of plot is the same in all respects except that the intensity of the analysis line was ratioed to the intensity of one of the major element lines, calcium or titanium. These major elements were

assumed to be present in an essentially constant proportion. This method then is really just the internal standard method applied to the addition plot.

To the best of the author's knowledge the only previous use of this ratio method with addition plots, was that of Ahrens and Gorfinkle (1951). In this article little more was said of the method other than stating the fact of its use.

In the particular case of this investigation, calcium, comprising about twenty percent of sphene was used as the constant internal standard element for all analysis elements except chromium and zirconium. The calcium line used was 4302. In the cases of chromium and zirconium, titanium, making up about twenty-five percent of sphene was used. Since there does seem to be some relation between the weight of sample and arc-ing time, there is presumably some effect also on the measured intensity of the lines. It was hoped that by using this ratio of intensities, that variation in the sample weight in the addition procedure would be compensated for and result in addition plots whose points would be the same as if there had been no variation in sample weight.

It is important to note here, as concerns the graphical procedure, that while both of these types of addition plots ideally give a straight line, this is not the case in actual experimental work. One important suspected cause of the non-linearity of the addition plots, is that as the concentration of the analysis element increases, the amount of self-absorption also increases. This of course varies with the element. This would have the effect of reducing the intensity of the line at higher concentrations and thus result in a decrease in the slope of the addition plot at

these higher concentrations. This decrease of the slope of the addition curve with increasing concentration of the analysis element, especially at the 10,000 ppm added level, was noted in all cases except two or three of the ratioed addition plots. In nearly all cases the ratioing of intensities is observed to have reduced the amount of non-linearity as compared to that of the ordinary plots.

In constructing the addition plots and determining the original concentrations in sphene 3085, the straight line that best fitted the curve defined by the lower concentration points (0 through 5000 ppm added) was used. It does not seem that the ratioing of the intensity of the analysis line to that of the calcium or titanium line necessarily reduces the variation of the two points from the mean. However, the ratioed type of addition plot definitely does seem to increase the linearity of the addition curve in many cases. This definite improvement is illustrated in figures 2 and 3, which show the results for iron 4383 and iron 4260. As can be seen from the figures both iron lines give larger values for the original iron concentration in sphene 3085, in the standard addition plot, than they do in the ratioed addition plots. Also in each case the linearity of the ratioed addition curve is increased over that of the standard curve. This is particularly evidenced in the case of iron 4383, in which case a straight line can be drawn entirely within the envelope of intensity ratio variation at all points of concentration. This ratioed addition curve determination of iron was used as the experimentally determined iron content of sphene 3085. I have drawn as can be seen in figure 3 the best curve through the ratioed intensity points for iron 4260, which gives nearly the same value obtained from the ratioed iron 4383.

33

Standard and Ratioed Addition Plots for Iron 4383

x — Fe 4383
⊙ — Fe 4383/Ca 4302

Indicates a Concentration of 22,100 ppm

Indicates a Concentration of 15,900 ppm

Indicates a Concentration of

Intensity Ratio of Fe 4383/Ca 4302

Intensity of Fe 4383

Iron Added in Parts per Million

Figure 2

Standard and Ratioed Addition Plots for Iron 4260

X — Fe 4260
O — Fe 4260/Ca 4302

Indicates a concentration of 20,100 ppm
Indicates a concentration of 15,700 ppm

Figure 3

Intensity Ratio of Fe 4260/Ca 4302

Intensity of Fe 4260

Iron Added in Parts per Million
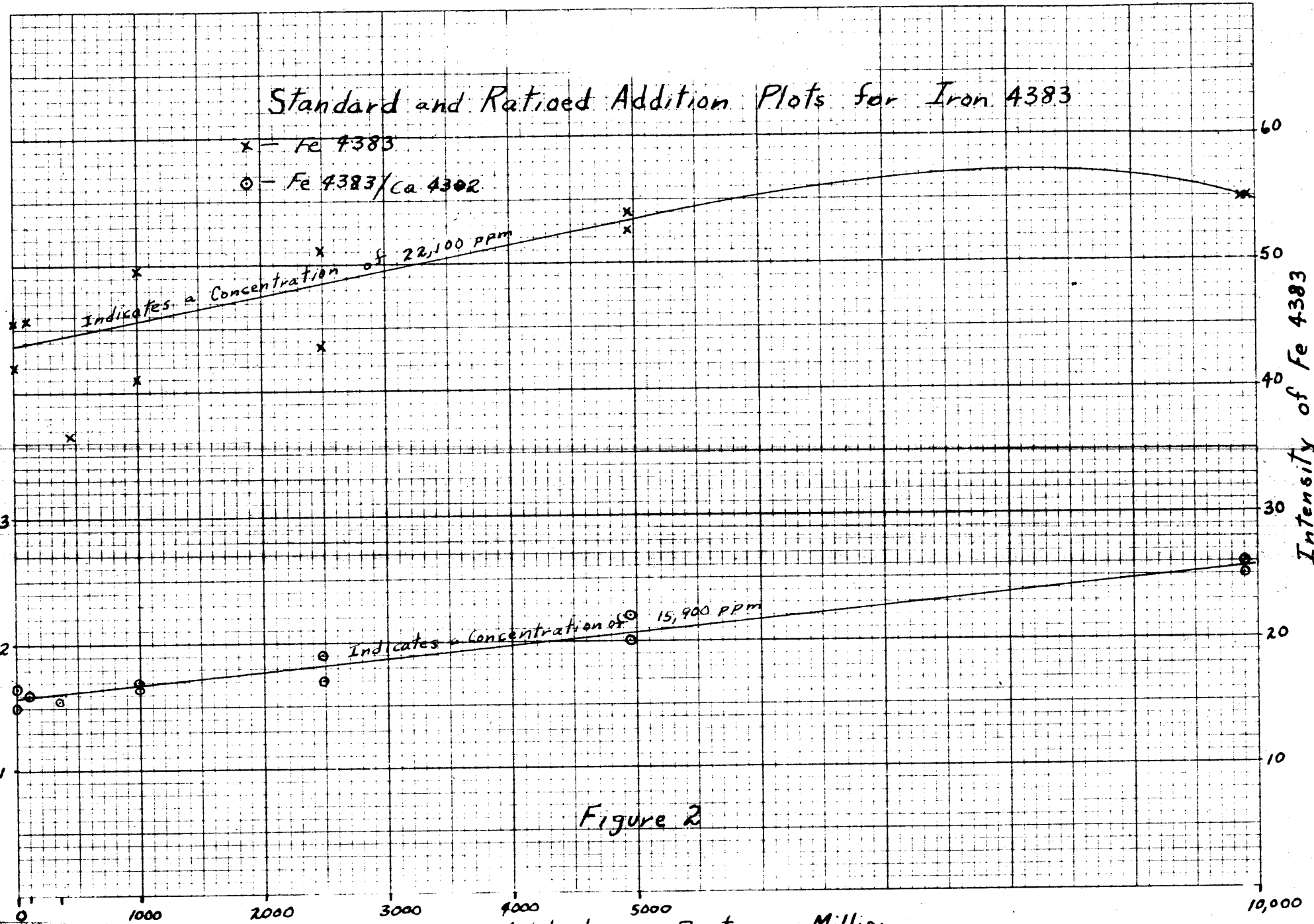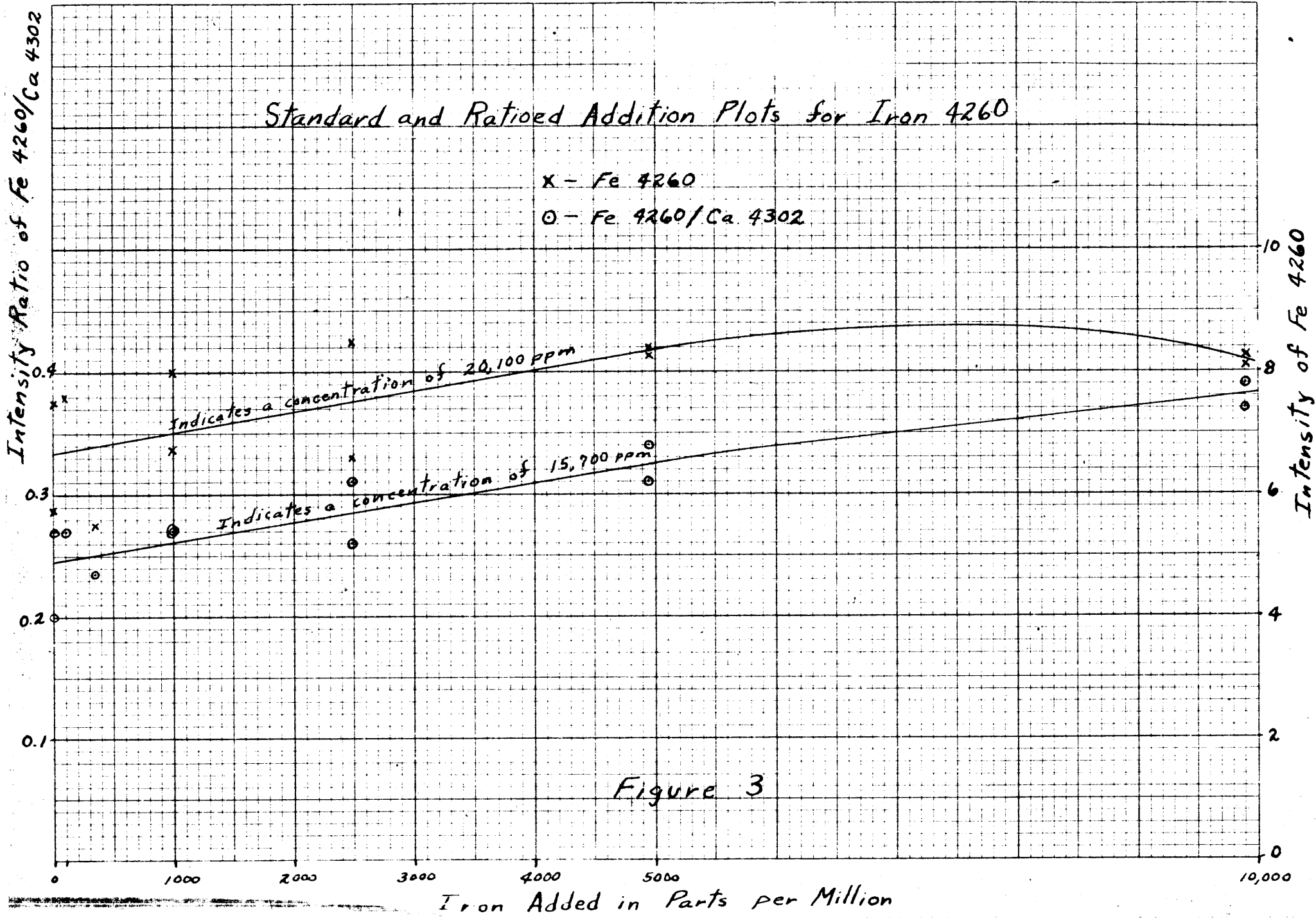
In most cases the ratioing did seem to give improved values. There were some cases, however, in which the ratioing did not improve the curve at all and may in a case or two have made it worse.

Working Curves: After determining the concentration of the various analysis elements in the standard, working curves were established and constructed for each element. A working curve was plotted for each element on each plate. This was done by plotting points from three different known concentration levels of the standard for each element on each plate. The slope of the working curve for each element was assumed to be forty-five degrees (Ahrens, 1951). The base experimental working curve was constructed from the addition data, using all the concentration levels prepared. In most cases the concentration determined from the addition plots gave a working curve with a slope of nearly forty-five degrees and thus agreed quite well the assumed slope suggested by Ahrens. In the case of chromium, yttrium and gadolinium, minor adjustments were made in the original concentrations of these elements in sphene 3085, until the working curve was within a degree or two of forty-five degrees. The exact procedure used in this adjustment is as follows. When the angle of the working curve is much greater than forty-five degrees, the original concentration used for the working curve was too high, while an angle less than forty-five degrees indicates that the original concentration used was too low.* This procedure was used in detail with manganese, which is discussed below.

In the case of manganese, two analysis lines, Mn 4031 and Mn 4034, were chosen for purposes of furnishing a check throughout the investigation. The original concentration of manganese in sphene 3085 as determined

*Personal communication from Dr. W. H. Dennen.

from the best addition plots, was 4700 ppm from Mn 4031 and 3800 ppm from
Mn 4034. For both lines all the working curves for all the plates used
were plotted for each of the two assumed original concentrations in sphene
3085. In all cases except the working curve from the addition material
for Mn 4031, the angles of the curves for the 4700 ppm concentration were
considerably greater than forty-five degrees. On the basis of the above
mentioned criteria the 4700 ppm value was regarded as being too large.
The angles of the working curves for the 3800 ppm concentration were in
all except the case of the addition plot for Mn 4031, very close to forty-
five degrees. Thus 3800 ppm was the concentration value used for manganese
in pure sphene 3085.

In the determinations of the analysis elements from the working curves,
only one line of each element was used. Selection of the line used in each
case was based on considerations of apparent sensitivity (as revealed by
the addition plate) and minimum interference. The only exception to this
general method of selection was manganese. In the case of manganese, the
working curves indicated that Mn 4034 gave more reliable intensity values
for the remaining twenty-two samples. Thus, for these samples, intensity
values for Mn 4034 were used in preference to those of Mn 4031. The
analysis lines used in the final working curve stage were:

Fe 4385 Å
Mn 4034 Å
Y 4398 Å
Sm 4329 Å
Gd 4258 Å
V 4379 Å
Ce 4222 Å
Cr 4254 Å
Zr 4239 Å
Nd 4303 Å
Sc 4374 Å
La 4333 Å
W 4294 Å

Molybdenum was discarded as an analysis element in this stage, when it was found that overcompensation had occurred for every sample when a correction factor was applied.

DISCUSSION OF RESULTS

The concentrations of each analysis element in each sample are tabulated in Table 4. Each value shown in the table is in all cases, except a few, the average of two determinations. Also given in Table 4 is the average percent deviation from the mean or probable error for each element. This figure was calculated for each element by dividing the deviation from the mean of each pair of determinations, by the mean itself, and then totaling all these deviations and dividing by the total number of samples for which two quantitative determinations were made. This answer was then expressed in percent. Thus in the case of chromium the average percent deviation from the mean is 6.78 percent. This means that any reported determination for chromium has a fifty percent chance of being within 6.78 percent of the correct value. The error of the average of two determinations is then simply the probable error of a single determination divided by the square root of two, i.e., $6.78 / \sqrt{2}$ for chromium. It was not possible to make quantitative determinations in all cases. In these cases the elements were not detected or at best just gave trace indications. The best that could be done was to make a rough estimate of the maximum possible concentration. This was done in all cases except one for tungsten and numerous times in the case of scandium.

The averages of the two determinations for each element of each sample are plotted both by element, graphs 1-9, and by sample, graphs 10-20. Semilogarithmic paper has been used in the plots in order to accommodate the wide differences in concentration, and maintain relative variations of the elements. The results will first be discussed by element and then by samples.

Table 4

Average Concentration of Analysis Elements in Each Sample
(All values given in parts per million)

| Sample	Fe 4383	Mn 4034	Y 4398	V 4379	Cr 4254	Zr 4239	Ce 4222	La 4333	Nd 4303	Sm 4329	Gd 4262	Sc 4374	W 4294
3011	8250	5200	1600	1010	360	680	500	340	2720	1650	1650	140	ND
3055	9300	1930	2320	860	600	1000	490	470	2450	1220	1390	<75	ND
3014	21350	6150	11400	470	28	4450	550	530	2120	4900	5000	510	ND
3058	16150	3650	3720	1080	70	490	200	260	1400	2100	2050	130	ND
3071	20350	4100	7850	220	28	520	320	275	1910	5800	3950	<75	ND
3080	27500	4620	22000	650	165	2250	820	450	3780	9450	5800	980	ND
3139	24000	5320	4120	300	18	2280	1360	1660	2500	3020	2950	130	ND
3051	24200	6400	14850	440	26	750	1160	520	2680	7800	5900	<75	ND
3060	21100	5950	9550	600	78	580	1620	950	4050	4500	4000	360	ND
3061	20400	3900	6320	860	100	2800	1030	700	1750	5700	3900	280	730
3062	18250	5300	3640	760	31	2350	4250	4020	8350	3980	1980	160	ND
3063	18150	4780	4400	1060	67	2800	4020	2180	8500	6500	3850	210	ND
3079	22300	4050	13650	880	85	820	4780	1780	11200	5450	3700	380	ND
3081	20750	2760	3700	570	125	3120	3600	2290	6100	3650	2080	<75	ND
3082	20800	3350	2420	130	22	1900	1480	1330	1880	1700	1100	<100	ND
3485	18250	2680	1860	860	91	2380	8150	3980	10350	5250	2060	<75	ND
3067	21950	5170	2120	310	36	5900	3580	3550	4950	2600	3820	<75	ND
3069	15500	2750	995	1040	23	3900	2850	2680	4550	1450	2420	<100	ND
3084	13000	620	740	1060	92	1760	3820	2280	5150	2000	1500	210	trace
3085	15900	3800	2700	800	70	3100	4200	3000	4200	1850	1800	150	ND
2093	11600	1940	2480	940	635	2180	820	8700	1550	2020	1650	<75	ND
3013	15250	8550	15500	240	38	18900	100	100	<500*	970	2200	<100	ND
3138	51500	4750	4050	1160	16	2280	1340	1000	<580*	3480	2600	180	ND
Ave. % Dev. from Mean	4.10	4.37	3.03	5.33	678	4.44	5.64	2.79	4.78	3.81	3.85	7.65	---

* overcorrected for iron conflict   ND— not detected, less than 200 ppm

Discussion of Results by Element

1. Iron: Iron (graph 1) is present in all samples. The iron content varies from about 8,000 to 28,000 ppm, with the exception of over 51,000 ppm in sample 313S. It is almost a certainty that much of this last value is due to contamination, as indicated by the estimated twelve percent contamination consisting of opaque grains (Table 2). Most of the iron values seem to lie in the neighborhood of 20,000 ppm. One can notice some degree of similarity in the shape of the curves for gadolinium (graph 8), samarium (graph 7), and iron.

2. Chromium: Chromium (graph 1) is also present in all samples. Chromium values are much more variable proportionately than iron and are a great deal lower. All the samples analysed contained less than 700 ppm. The majority of the values, as may be seen from either Table 4 or graph 1, are less than 100 ppm. It is noticed that the three samples containing the highest concentrations of chromium also have the three lowest values of iron. These samples are 3055, 3011 and 2093.

3. Manganese: Manganese (graph 1) is present in all samples, with most of the values lying in the range of 4000 to 6000 ppm. There appears to be general similarity in the shape of the curves for manganese (graph 1) and gadolinium (graph 8).

4. Zirconium: Zirconium (graph 2) was found to be present in all samples. The variability in concentration is rather high. About half of the values obtained lie between 1800 and 3000 ppm. An unusually high concentration of almost 19,000 ppm is reported for sample 3013. It would seem likely that some of this is due to
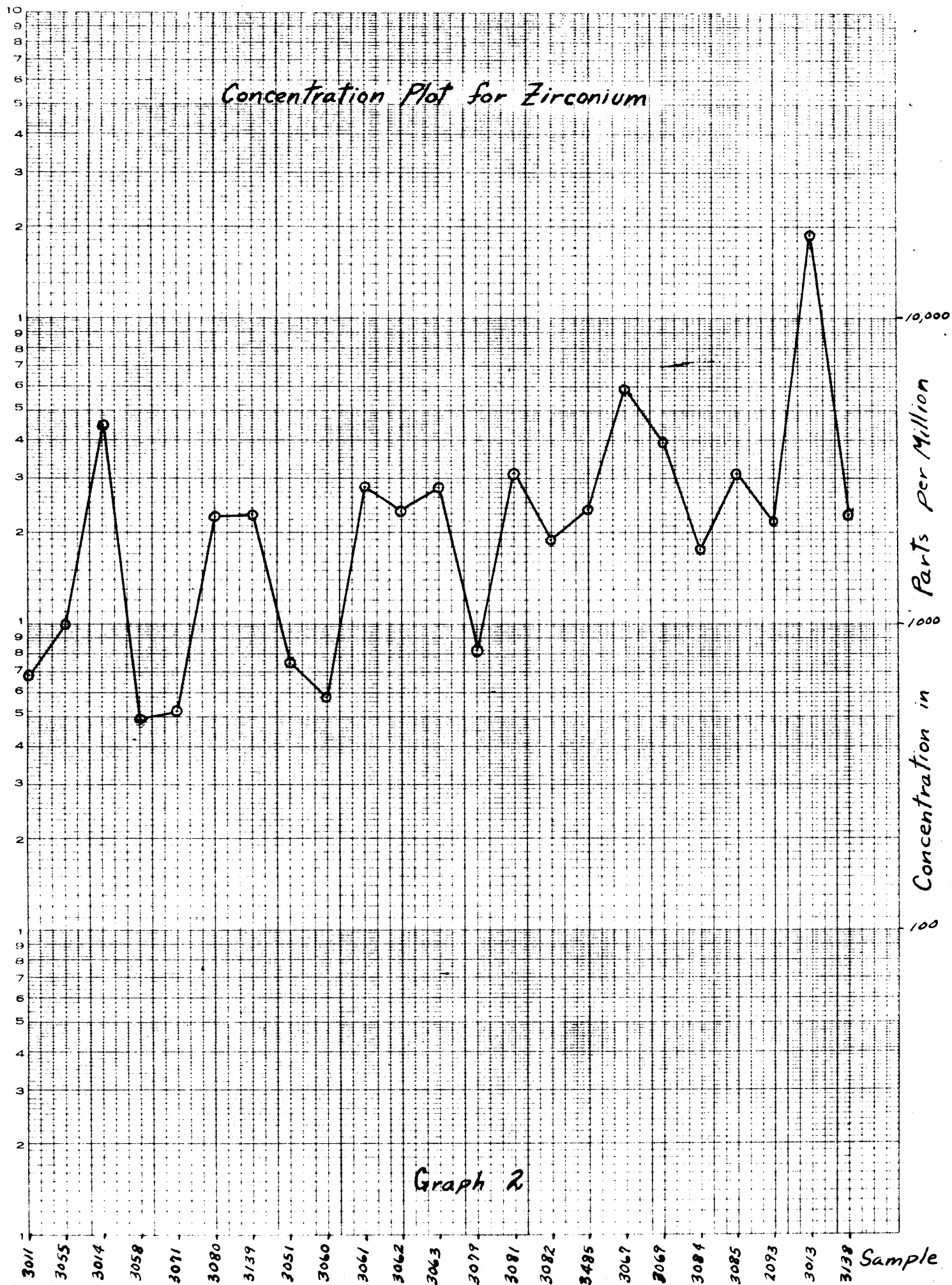
Concentration Plots for Iron, Manganese and Chromium
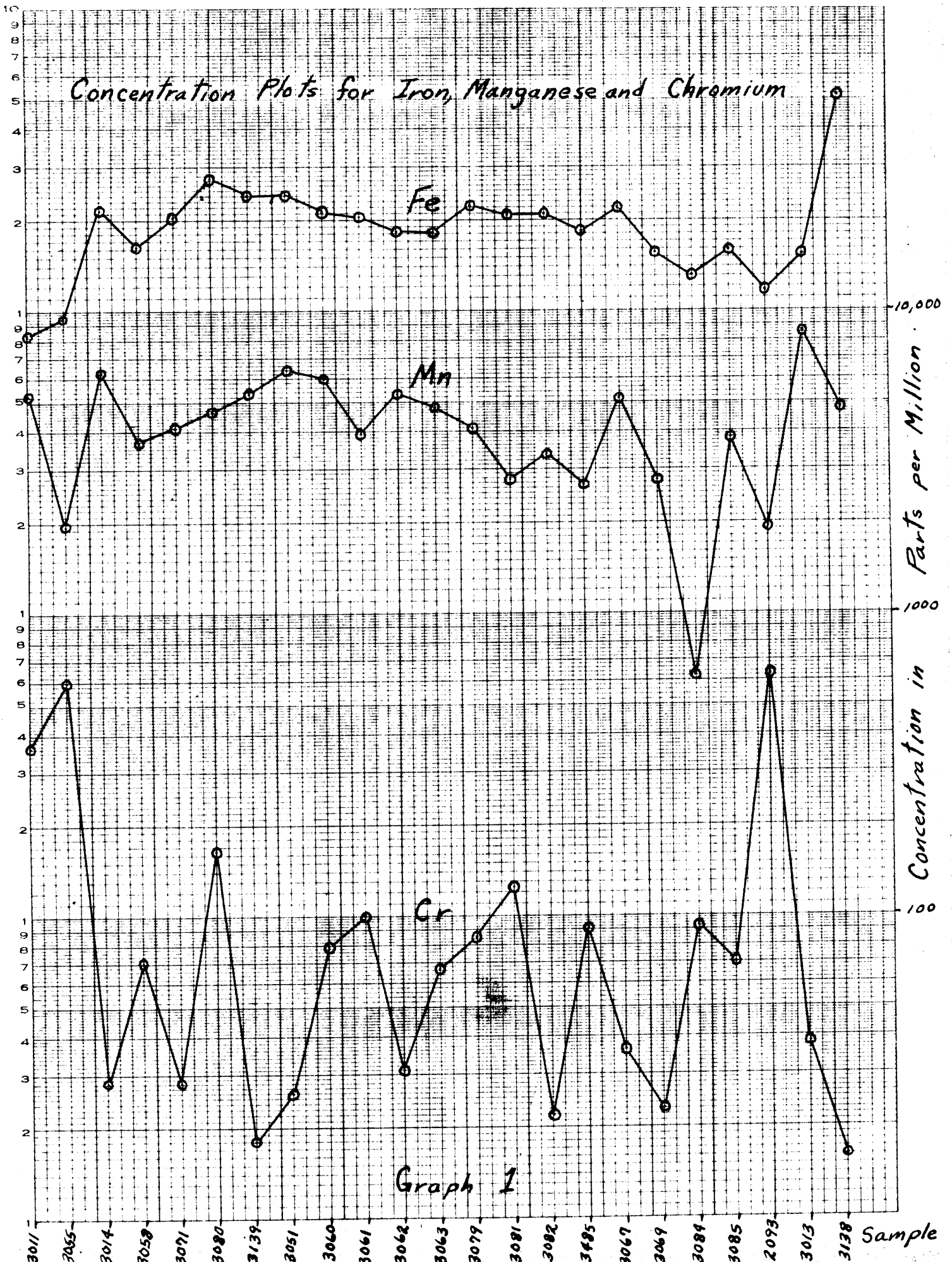
Graph 1
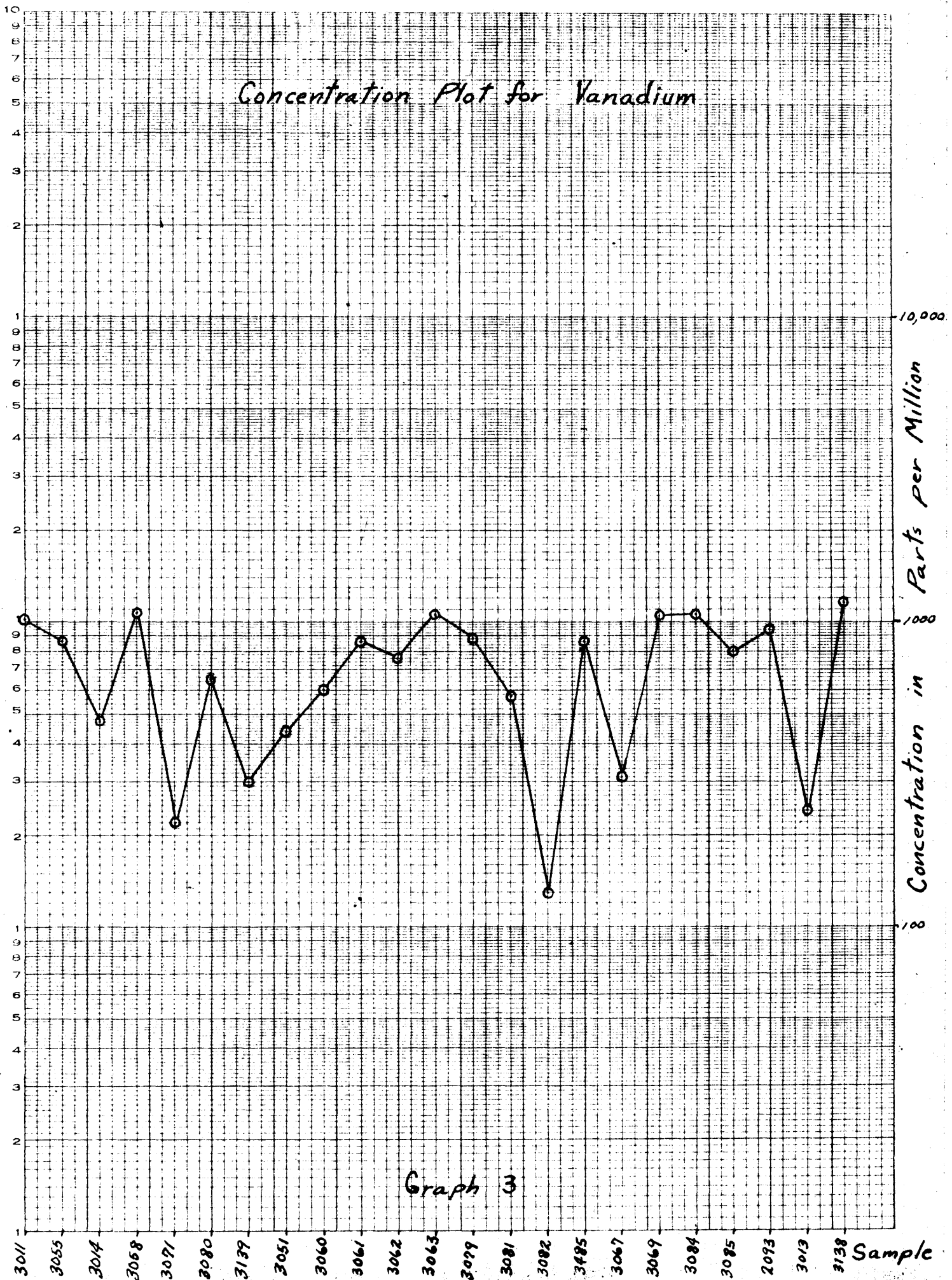
Concentration Plot for Zirconium

Graph 2

contamination, perhaps by zircon.

5. Vanadium: Vanadium (graph 3) was found in all samples and varies from about a 100 ppm to about 1200 ppm. Most of the samples had values between 800 and 1200 ppm.

6. Yttrium: Yttrium (graph 4) shows a wide range of variation from about 700 ppm to about 22,000 ppm and is present in all samples. Most of the values lie in the range 3500 to 6500 ppm. It is possible that a few of the very high values may in part be due to contamination as all samples with high values have at least three percent contamination.

7. Lanthanum: Lanthanum (graph 5) was found to be highly variable in concentration and was present in all samples. Except for a few extreme cases the values lie between 300 and 4000 ppm. Lanthanum generally seems to have values which are the inverse of yttrium, i.e., in general when a sample has a low yttrium concentration, the lanthanum value is reasonably high and vice versa. As may be seen from graphs 5 and 6, there is a definite parallelism of the concentrations of lanthanum, cerium and neodymium. When a sample is low in one of these elements it is also low in the other two.

8. Cerium: Cerium (graph 5) was found in all samples and was highly variable in concentration. The values determined ranged from about 100 ppm to about 8000 ppm. There seems in general to be an inverse relationship between cerium and yttrium values.

9. Neodymium: Neodymium (graph 6) varies over a range of 130 ppm to about 11,000 ppm, and was found to be present in all samples except two, which is discussed below.
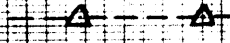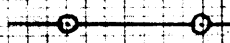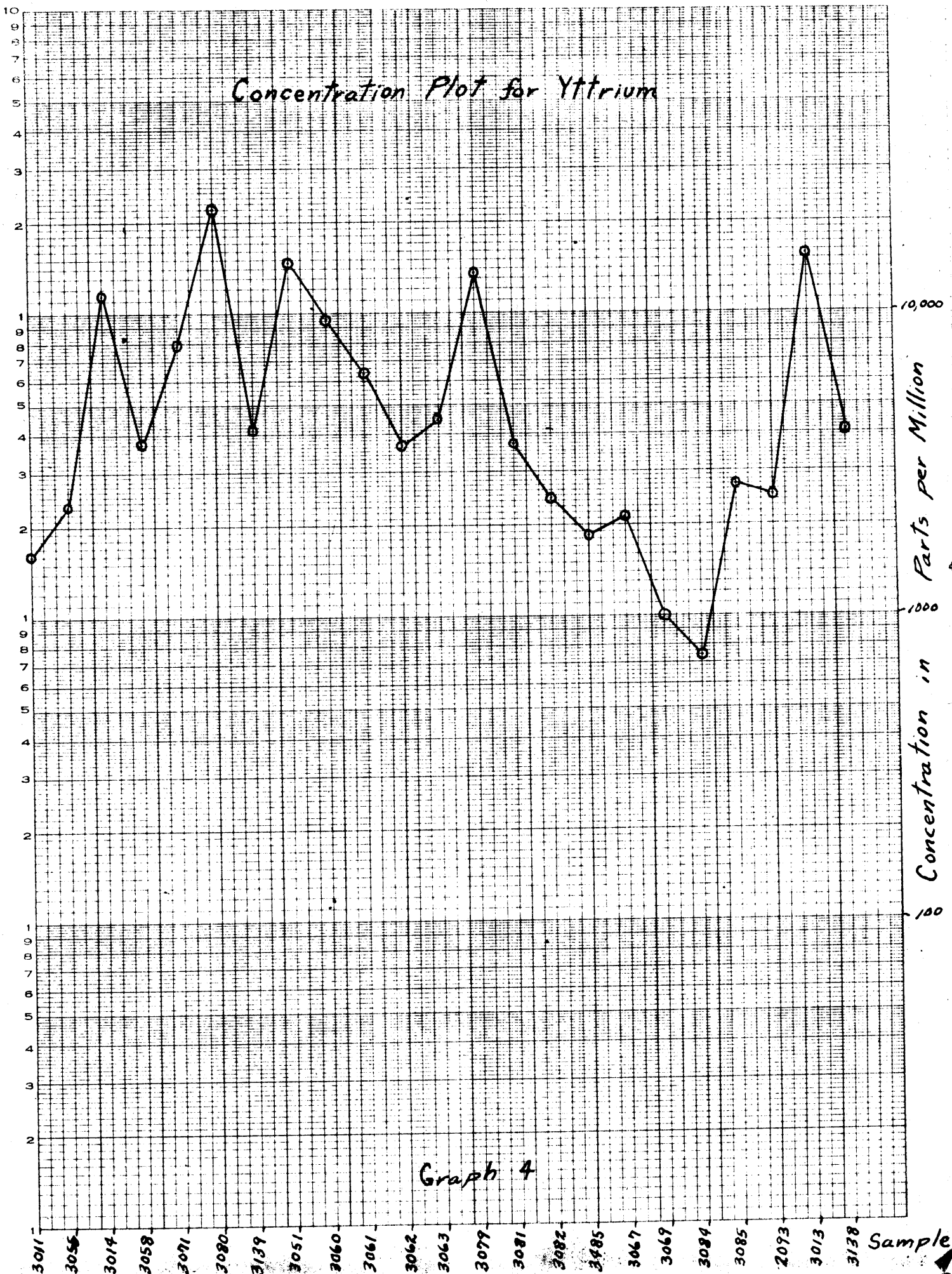
Concentration Plot for Vanadium

Concentration in Parts per Million

Graph 3

Sample

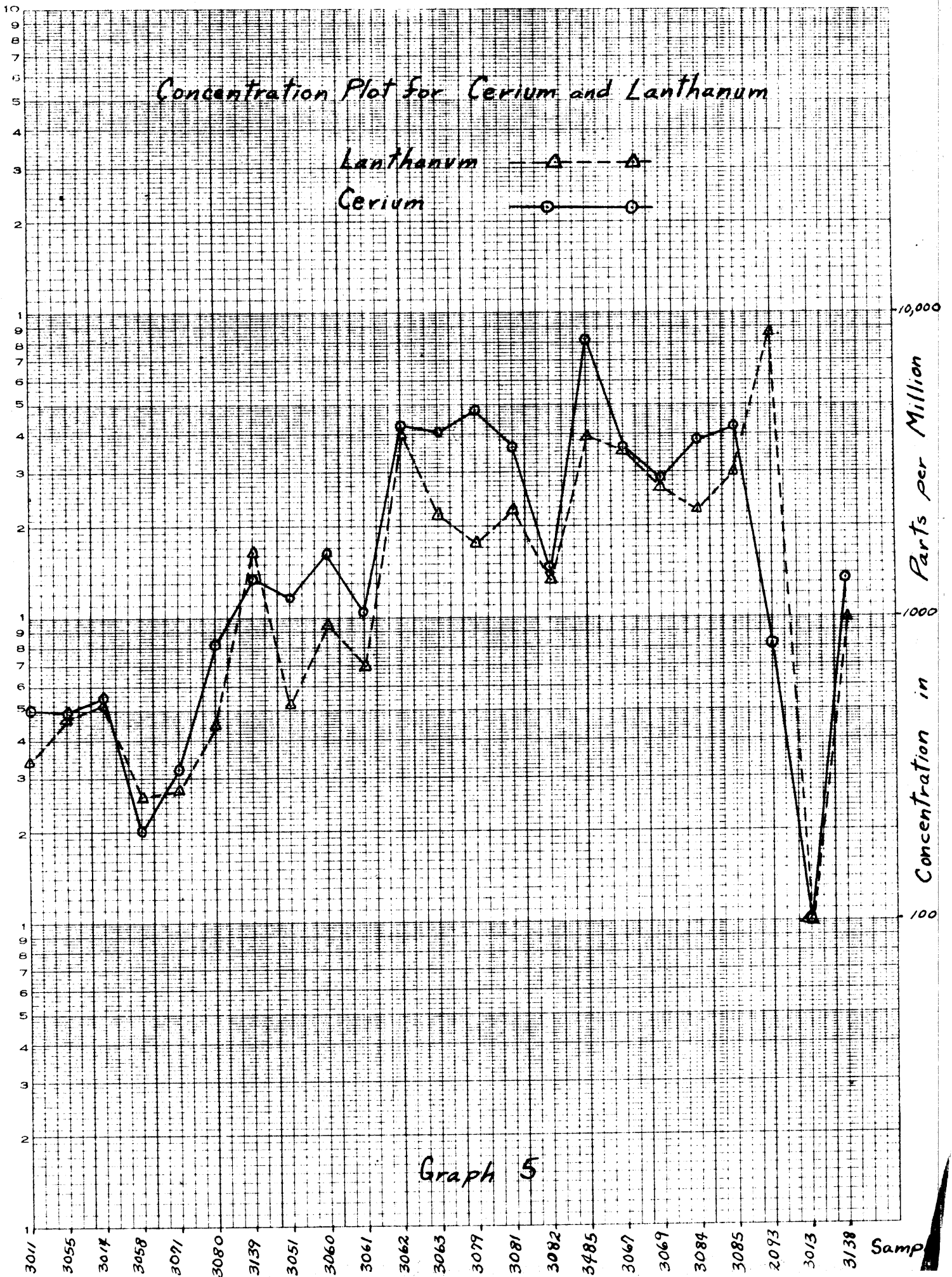Concentration Plot for Yttrium

Graph 4

Concentration Plot for Cerium and Lanthanum

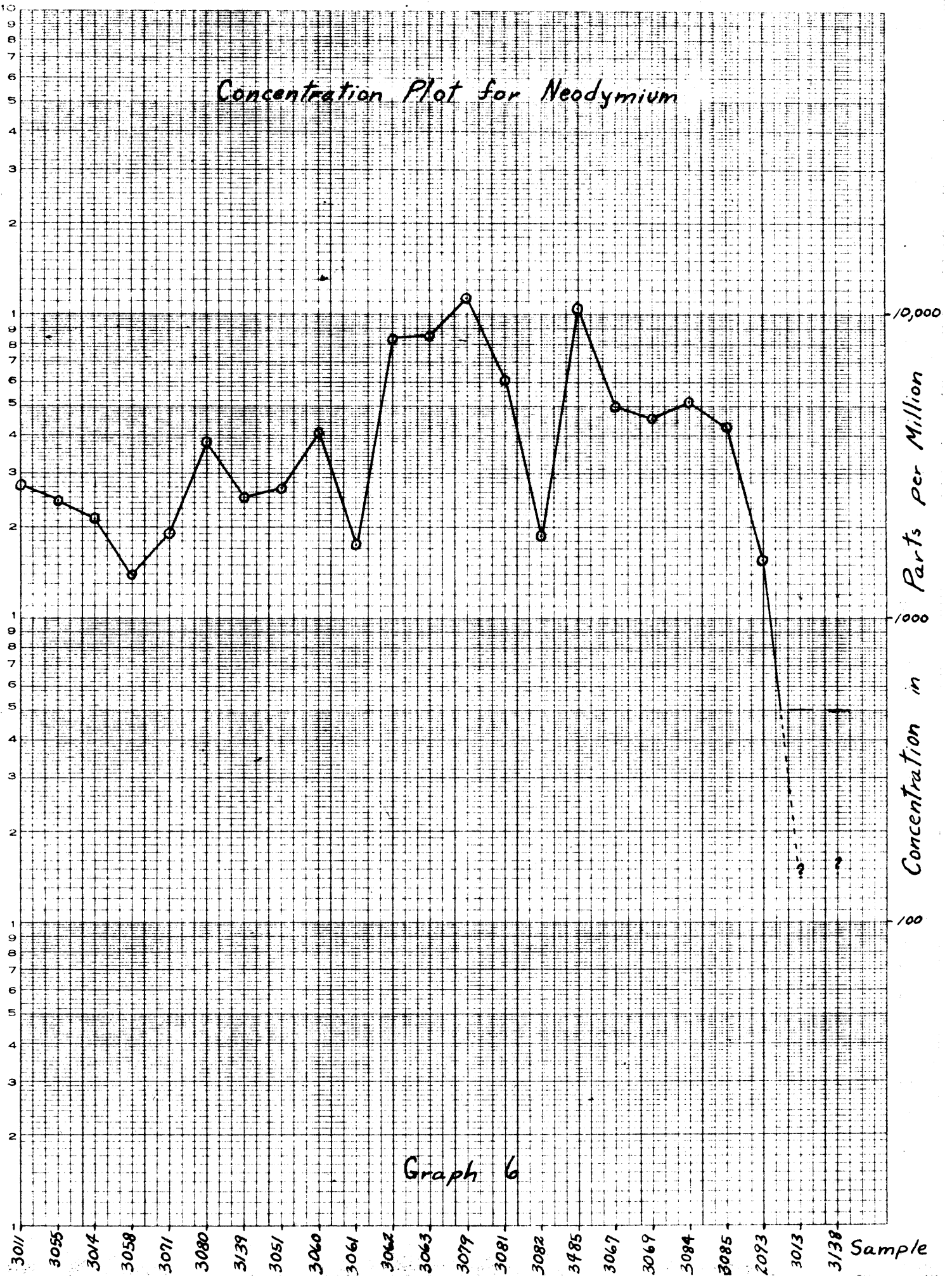Lanthanum — △ — — △
Cerium ⊙——⊙

Graph 5

As mentioned earlier Nd 4303 has a conflict with an iron line at about that same wavelength (see Table 1). In order to remove that part of the intensity of this line due to iron, the following procedure was followed.

A sample containing a mixture of ferric oxide and quartz was arced. Then the ratio of the intensities of Fe 4303 to Fe 4383 was calculated. Since the Fe 4383 intensity was known for each sample, it then became theoretically possible to calculate how much of the intensity of the line at 4303 was due to iron. This value was then in each case subtracted from the measured intensity, theoretically leaving just the intensity due to the neodymium present.

In all cases except two this procedure gave positive intensity values, which are meaningful. However, in the cases of samples 3013 and 3138, negative intensity values resulted. This certainly indicates that these samples were quite low in neodymium relative to the other samples, and it has been assumed in this study that they were also low in absolute concentration. The negative intensity values, which have no real meaning, do indicate that there is some sort of an inaccuracy in the correction factor used. It would seem that there has been some overcorrection to give these negative values. Thus it is probable that all the samples have been somewhat overcorrected. Since most of the samples already have high neodymium values, the elimination of this overcorrection would simply increase the peaks for this element seen in the sample plots. In the cases of samples 3014, 3061, 3067, 3082 and 3085,

Concentration Plot for Neodymium

Graph 6

Concentration in Parts per Million

Samples: 3011, 3055, 3014, 3058, 3071, 3080, 3139, 3051, 3060, 3061, 3062, 3063, 3079, 3081, 3082, 3485, 3067, 3069, 3084, 3085, 2093, 3013, 3138

neodymium, while reasonably high, does not constitute a peak, but might become a peak value in these sample plots if not overcompensated. This would eliminate one of the more common discrepancies noted in the discussion of results by samples. However, both 3013 and 3138 would still be low in neodymium relatively speaking.

10. Samarium: Samarium (graph 7) was found to be present in all samples and varies from approximately 1000 to almost 10,000 ppm. In all except two or three cases, the concentrations of samarium and gadolinium (graph 8) parallel each other. In addition to the general parallelism observed in graphs 7 and 8, one notices that the actual concentrations of each of the elements are in many cases similar numerically.

11. Gadolinium: Gadolinium (graph 8), like samarium, was present in all samples and varies over a range of 1100 ppm to about 6000 ppm.

12. Scandium: Scandium (graph 9) was not detected in seven of the samples. It is estimated that the concentration of scandium in these samples is 75 ppm or less. A trace amount of scandium was detected in three other samples and are tabulated as having values near 100 ppm. The remaining samples have values varying from 130 to almost 980 ppm.

13. Tungsten: Tungsten was detected in only two samples. The non-detection is estimated as indicating that less than 200 ppm of the element is present in the sample.
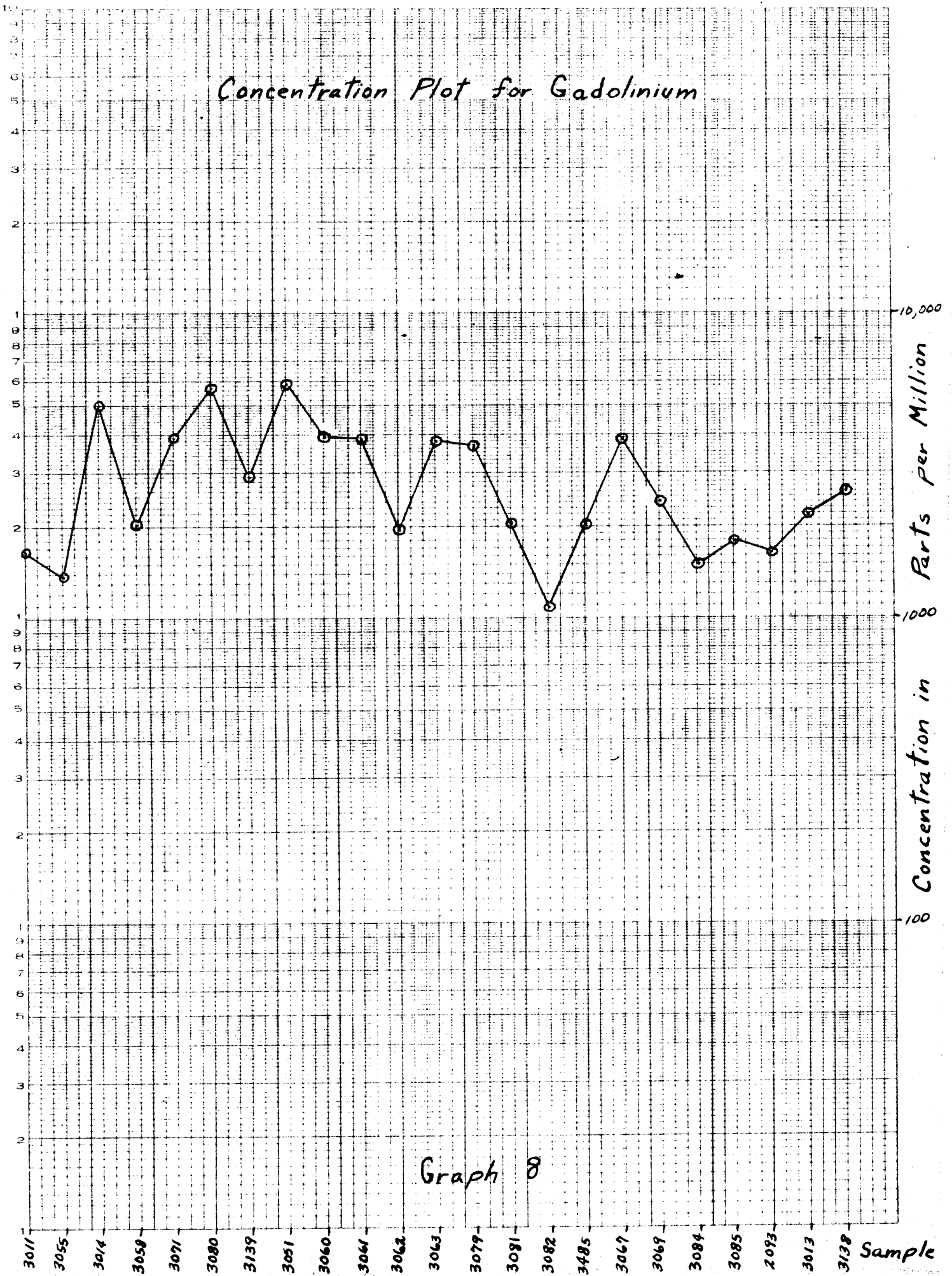
Semi-quantitative estimates have been made for strontium and aluminum. The strontium estimates were made using line Sr 4215.5 and the aluminum estimates were made from line Al 3961.5. Sample 3069 has an estimated
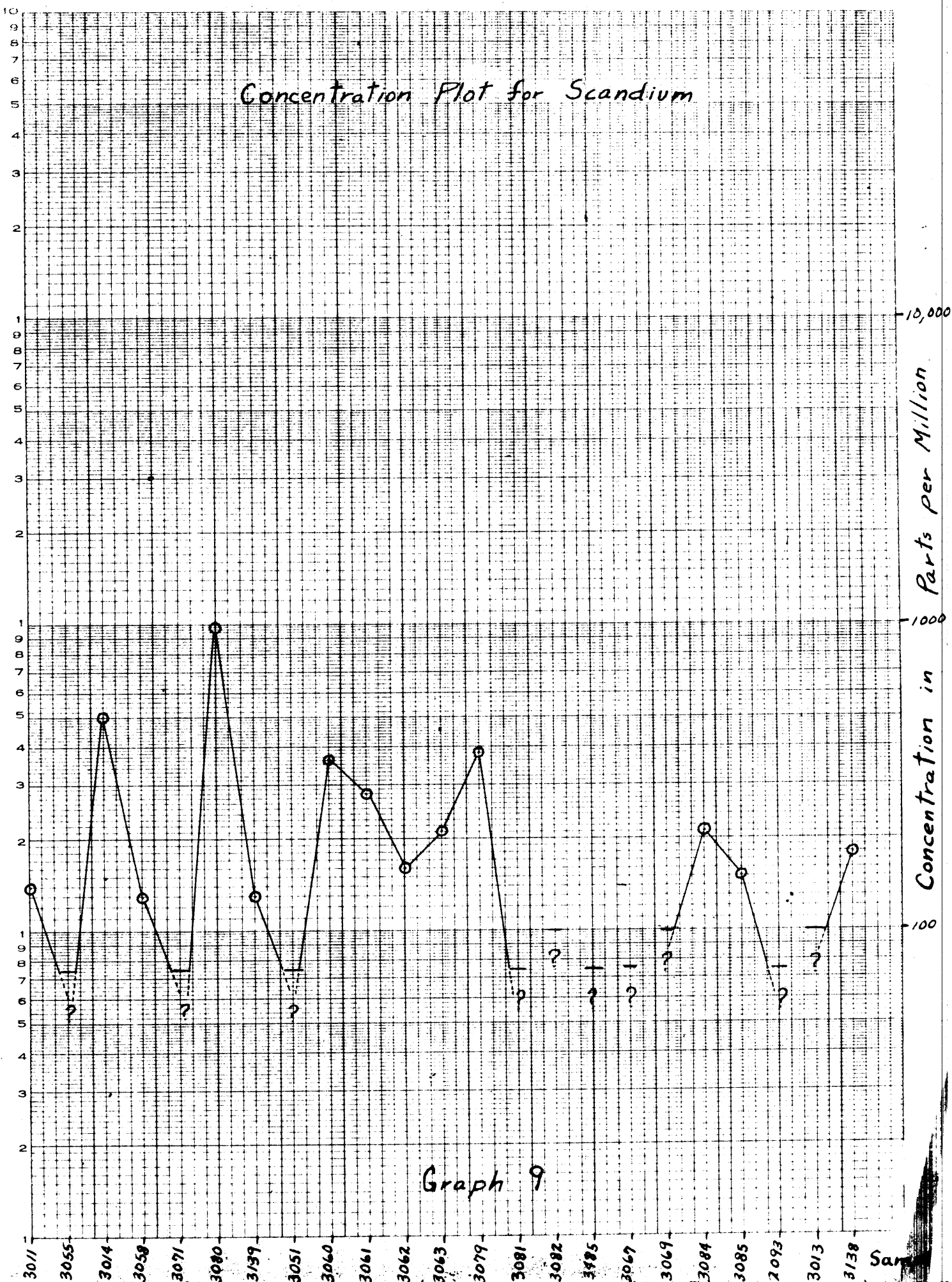
Concentration Plot for Samarium

Graph 7

Concentration in Parts per Million
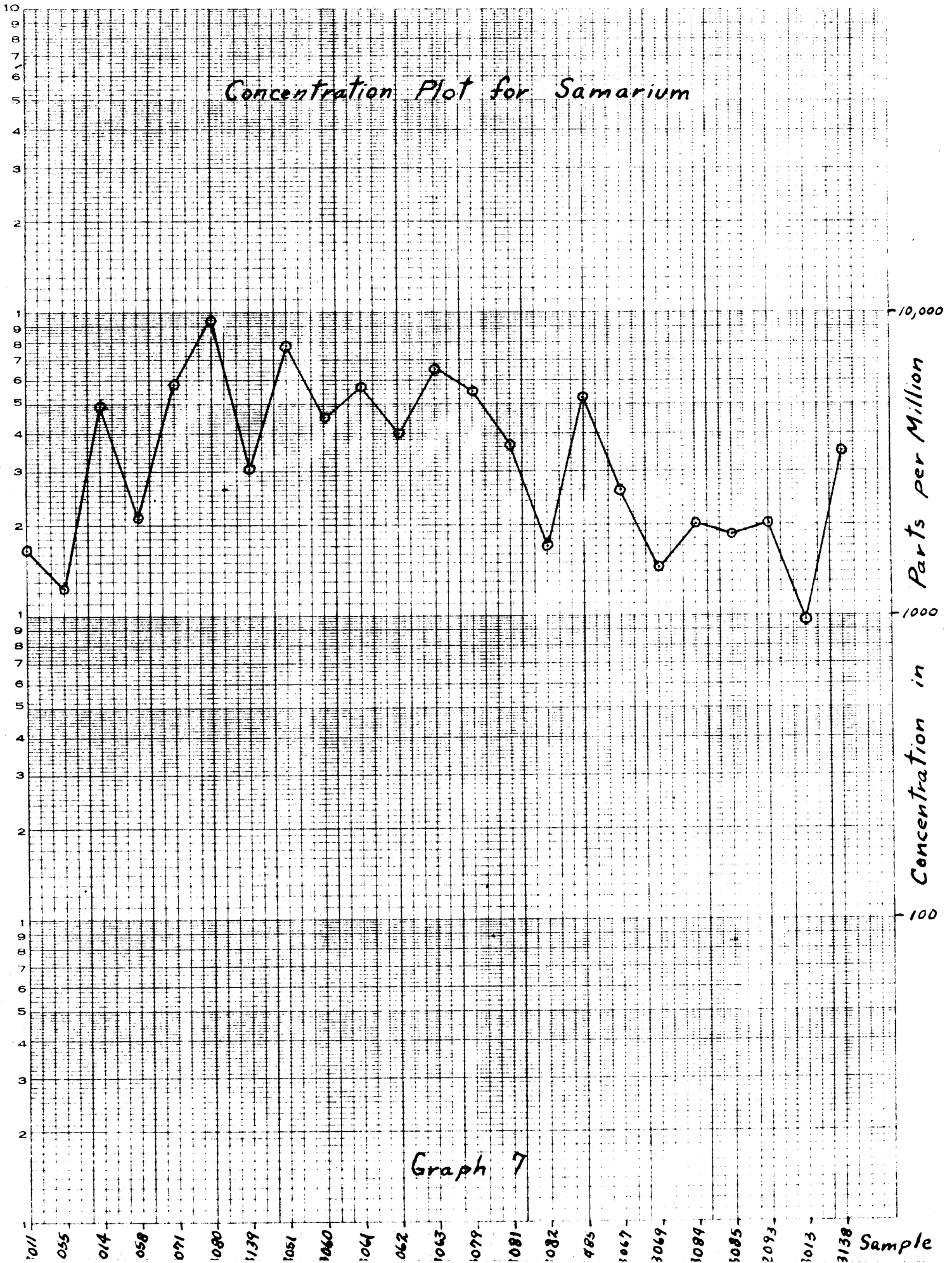
Sample

Concentration Plot for Gadolinium

Graph 8

Concentration Plot for Scandium

Graph 9

2600 ppm of strontium and sample 3139 an estimated 1200 ppm. None of the other samples showed any detectable strontium. All of the samples contained aluminum, estimated to be present in quantities of 10,000 to 20,000 ppm in each sample.
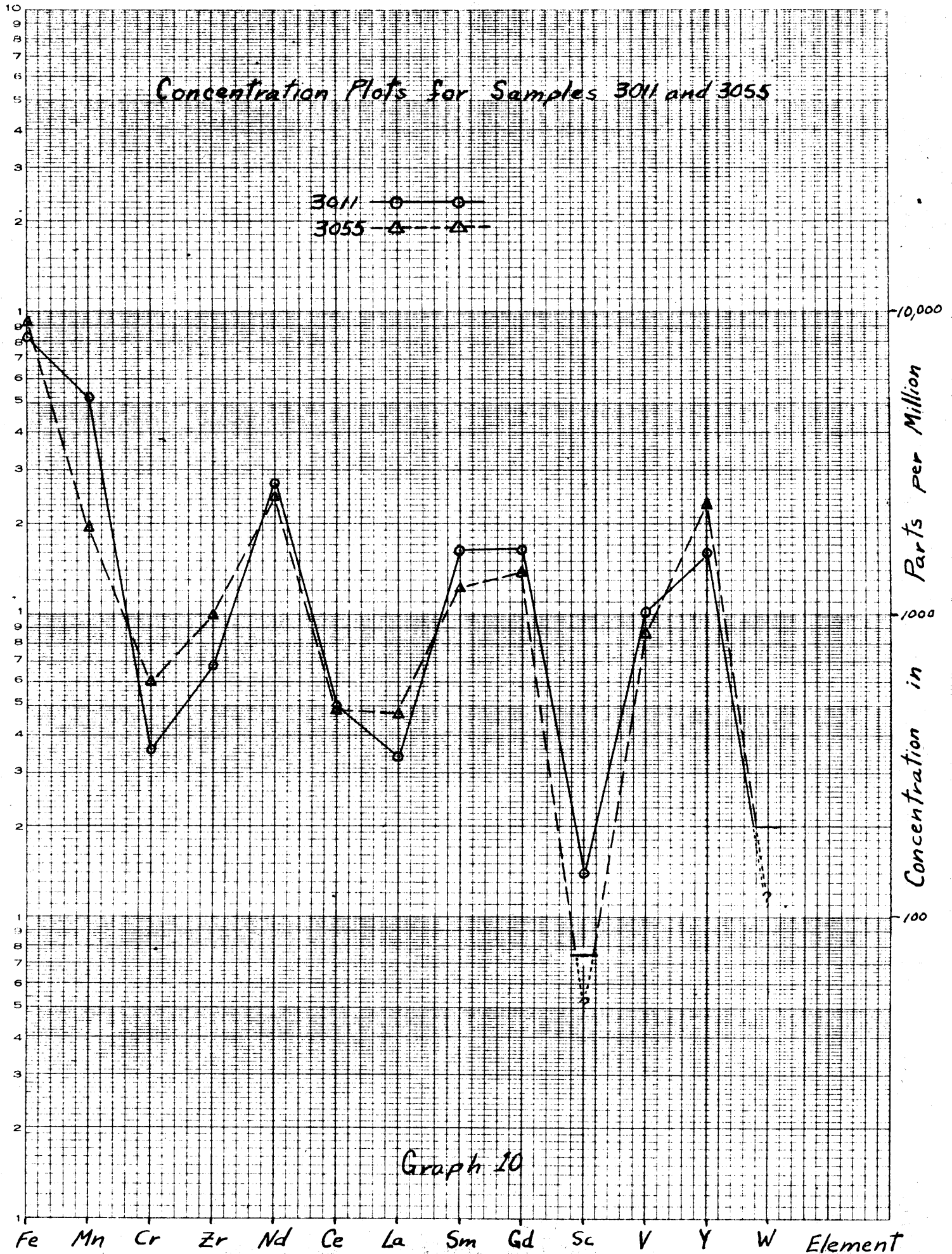
Discussion of Results by Sample

In this presentation and discussion of the data by samples, I am attempting to determine by trace element analysis if any of the sphenes might be from genetically related rocks. Reasonable evidence of genetic similarity or relationship between two sphenes and also presumably between the two rock sources from which they were separated, is taken to be a parallel relationship between the plots of the concentration of the elements in each of the two samples. It seems reasonable to expect that two sphenes from genetically related rocks would illustrate similar relations between elements. It seems well to point out here that there may not always be complete agreement or similarity due to the errors involved in the determinations, but that a general similarity is necessary. If two samples have nearly the same concentration of the elements, one might suspect they came from not only from genetically related sources, but that the sources were also in close geographical proximity.

The samples are discussed by groups arranged on the basis of the author's impression of significant similarity and relationship. The only relationship among the samples of the last group is that they have little or no similarity to any other samples in the author's opinion.

In the first group are samples 3011, 3014, 3051, 3055, 3058, 3060, 3061, 3062, 3063, 3071, 3079, 3080, and 3139. In general these samples have high peak concentrations in yttrium, iron, neodymium, samarium, and gadolinium. Samarium is usually higher than gadolinium. These samples also have minimum values for scandium, lanthanum, dhromium and tungsten. Cerium is often nearly as low as lanthanum. Closer similarity between some of the samples than between others was noted within the group. The
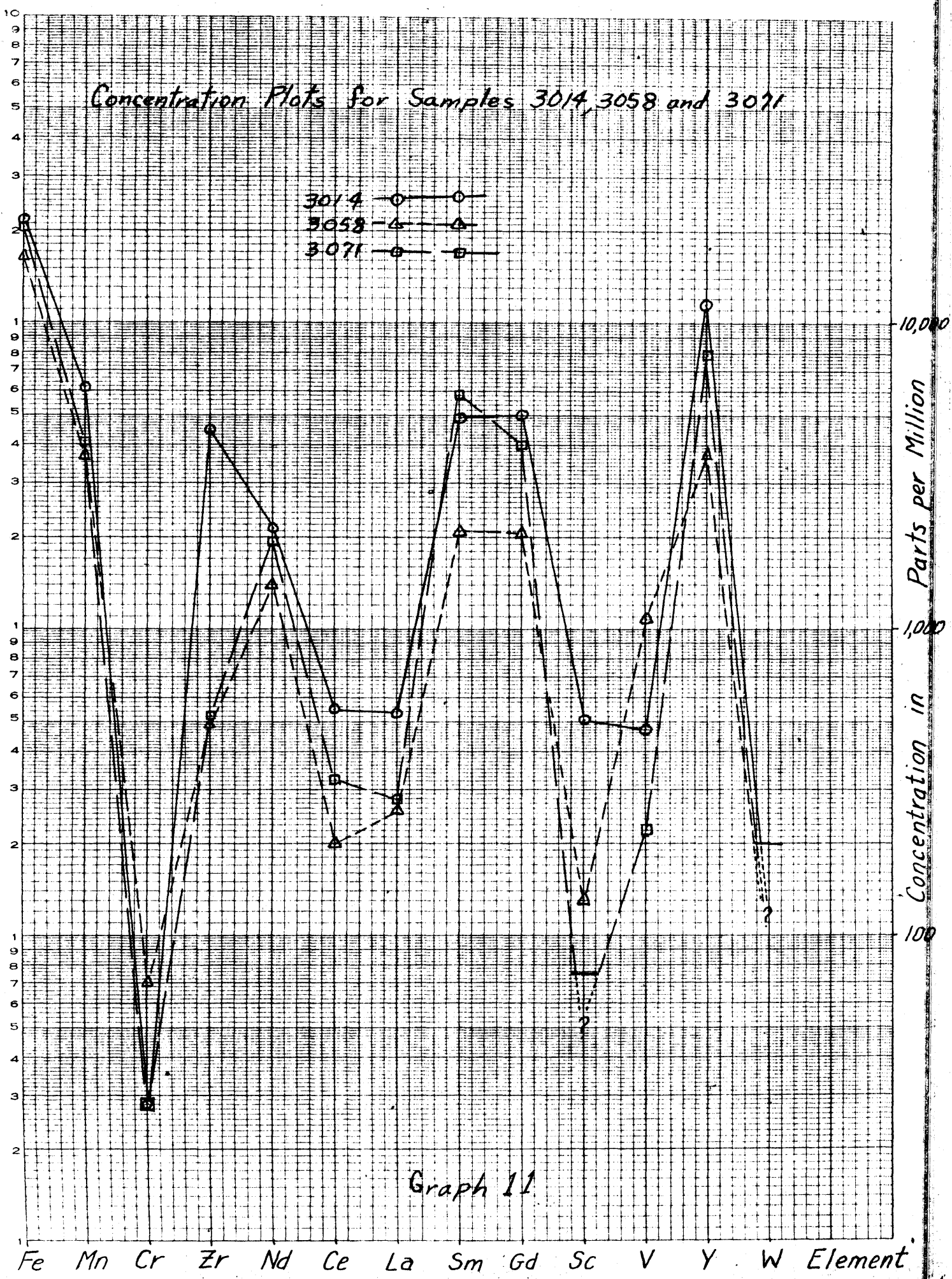
Concentration Plots for Samples 3011 and 3055

3011 ——o——o——
3055 --△----△--

Graph 10

Element: Fe Mn Cr Zr Nd Ce La Sm Gd Sc V Y W

Concentration in Parts per Million

samples of this group will be discussed in relation to these apparent closer similarities within the group primarily for convenience, as it is felt there is a significant similarity between all of the samples of this group.

The first subgroup of group one contains samples 3011 and 3055 (graph 10). There appear to be two distinguishing characteristics of these samples. First, both have decidedly higher chromium values and decidedly lower iron values than any of the other samples in this group. Second, the peak concentrations, while agreeing with the general case for the group as far as elements are concerned, are considerably lower than the concentrations of the same elements in the rest of the samples of group one. This is especially noticeable in the cases of yttrium and iron. In the case of iron both of these samples have less than 10,000 ppm, while the rest of the samples all have at least 16,000 ppm.

The second subgroup of group one contains samples 3014, 3058, 3071, 3080, and 3139 (graphs 11 and 12). These samples are distinguished from the other samples except those in subgroup one on the basis of their cerium values, which are nearly as low as the lanthanum values and in the cases of 3058 and 3139 are somewhat lower. The first subgroup also possesses this quality. The second subgroup was separated from the first on the observation that in subgroup two the samarium and gadolinium values are in all cases greater than the values for neodymium, while in subgroup one the neodymium values are in all cases greater than both the samarium and gadolinium values. Sample 3014 (graph 11) shows a dissimilarity, with a peak concentration for zirconium. This, if not a real variation, could be due to too large a zirconium value or too small a neodymium value. It
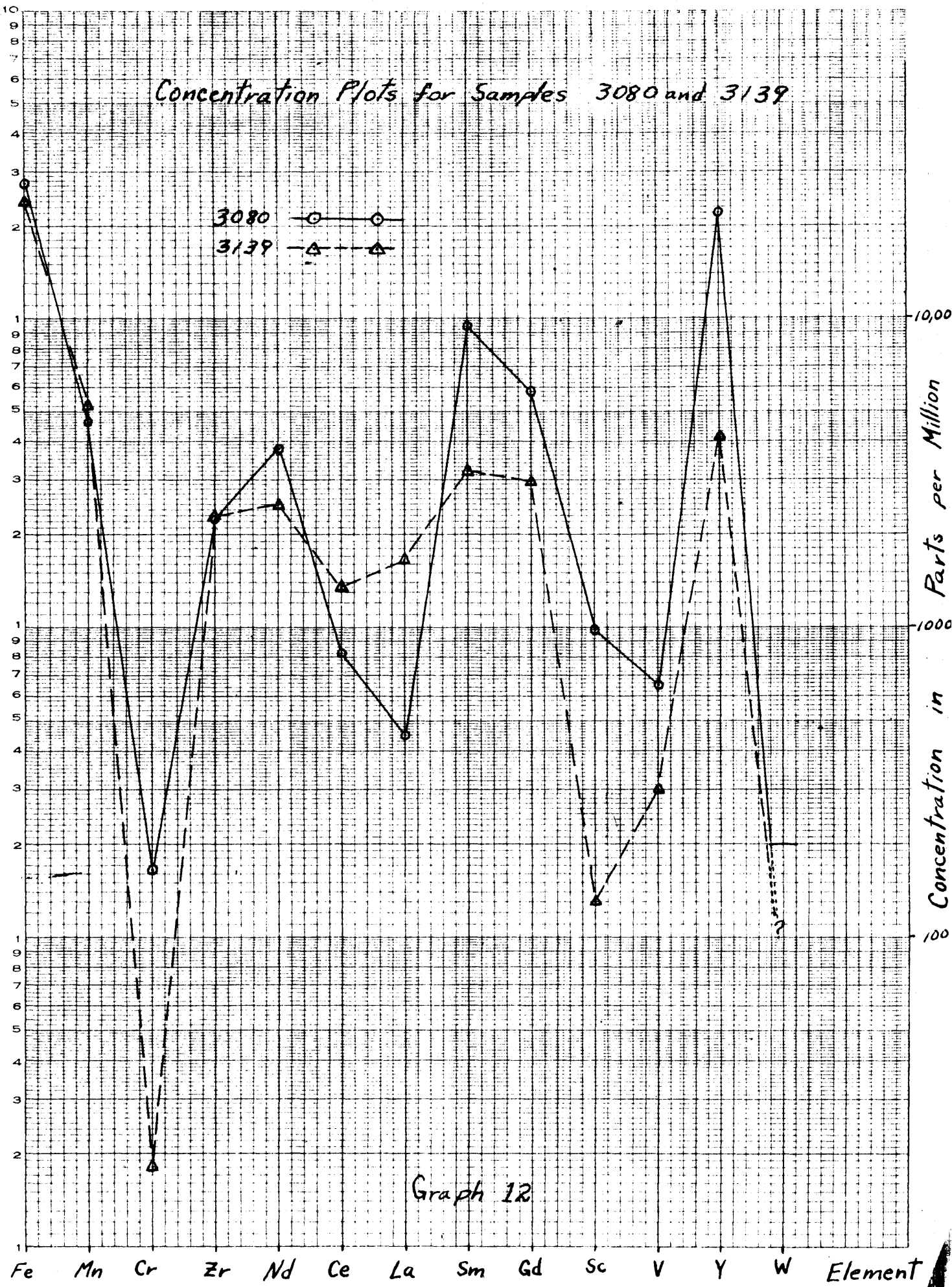
Concentration Plots for Samples 3014, 3058 and 3071

Graph 11

Concentration Plots for Samples 3080 and 3139

3080 ○——○
3139 △--△

Concentration in Parts per Million

Graph 12

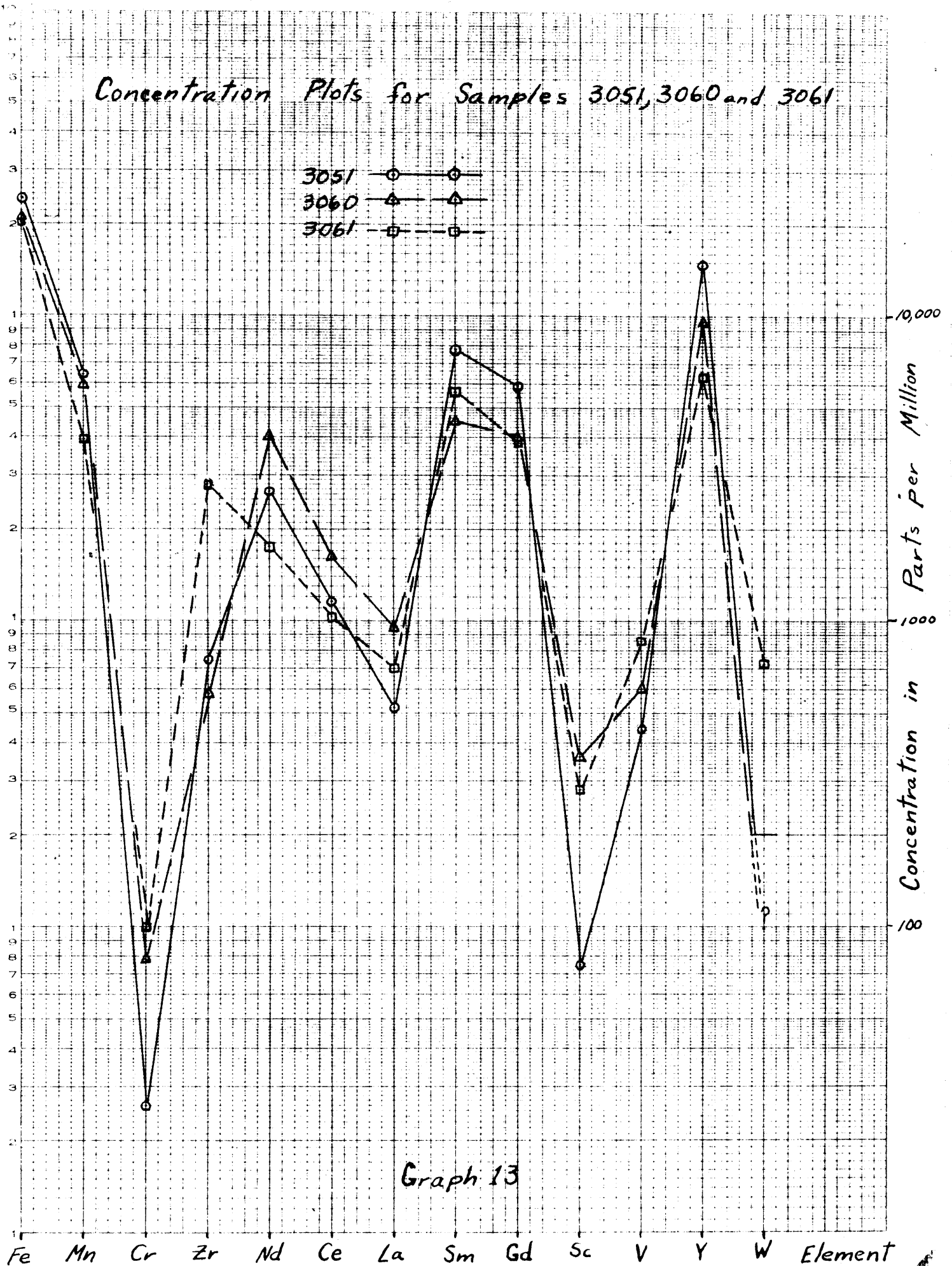Fe Mn Cr Zr Nd Ce La Sm Gd Sc V Y W Element

might be due to contamination by some zircon, as we notice from Table 2 that this sample has an estimated nine percent contamination. It should also be noted that the scandium values in samples 3014 and 3080 (graph 12) are higher than in most samples of this group.

The third subgroup of group one contains samples 3051, 3060, and 3061 (graph 13). This subgroup differs from the first two in that the cerium values are substantially higher than the lanthanum values. This subgroup differs from the fourth and last subgroup in that the samarium and gadolinium concentrations are substantially larger than the neodymium concentration. Sample 3061 has an apparent discrepancy in a peak value for zirconium, which may be due in part to contamination. This is not necessarily true, as it can be seen from graph 2 that this value for zirconium is in the general range of zirconium values.

The fourth subgroup of group one contains samples 3062, 3063, and 3079 (graph 14). This subgroup differs from the first two, in that it does not have a minima for cerium. It differs from the third subgroup by virtue of the fact that samarium and gadolinium values are lower in each sample than the neodymium value. In the case of sample 3062, the lanthanum value does not show a minima or low point, but was determined to be slightly greater than samarium. This is the only discrepancy within this subgroup, and it can be seen that if this lanthanum value (4000 ppm) were lowered by twenty-five percent this discrepancy would be eliminated. This percent change is not too much greater than the estimated ten to twenty percent possible error. It may well be that this relatively high lanthanum value is due to contamination. The estimated nine percent contamination could conceivably account for an additional 2000 ppm of lanthanum above that normally present
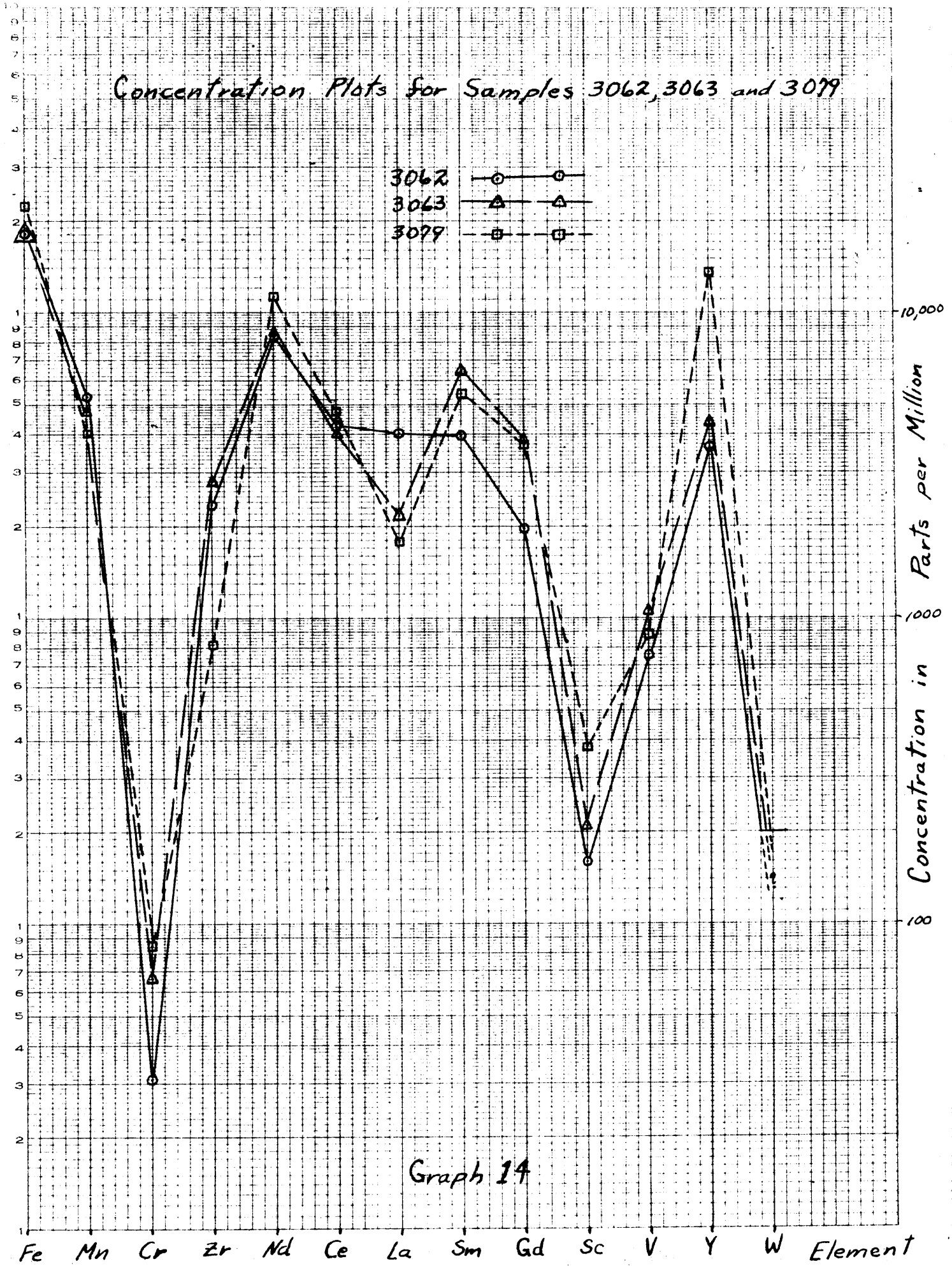
Concentration Plots for Samples 3051, 3060 and 3061

3051 —⊙——⊙—
3060 —△——△—
3061 —☐——☐—

Graph 13

Concentration in Parts per Million

Element: Fe Mn Cr Zr Nd Ce La Sm Gd Sc V Y W

Concentration Plots for Samples 3062, 3063 and 3079

3062 ⊙——⊙
3063 △——△
3079 ⊡——⊡

Concentration in Parts per Million
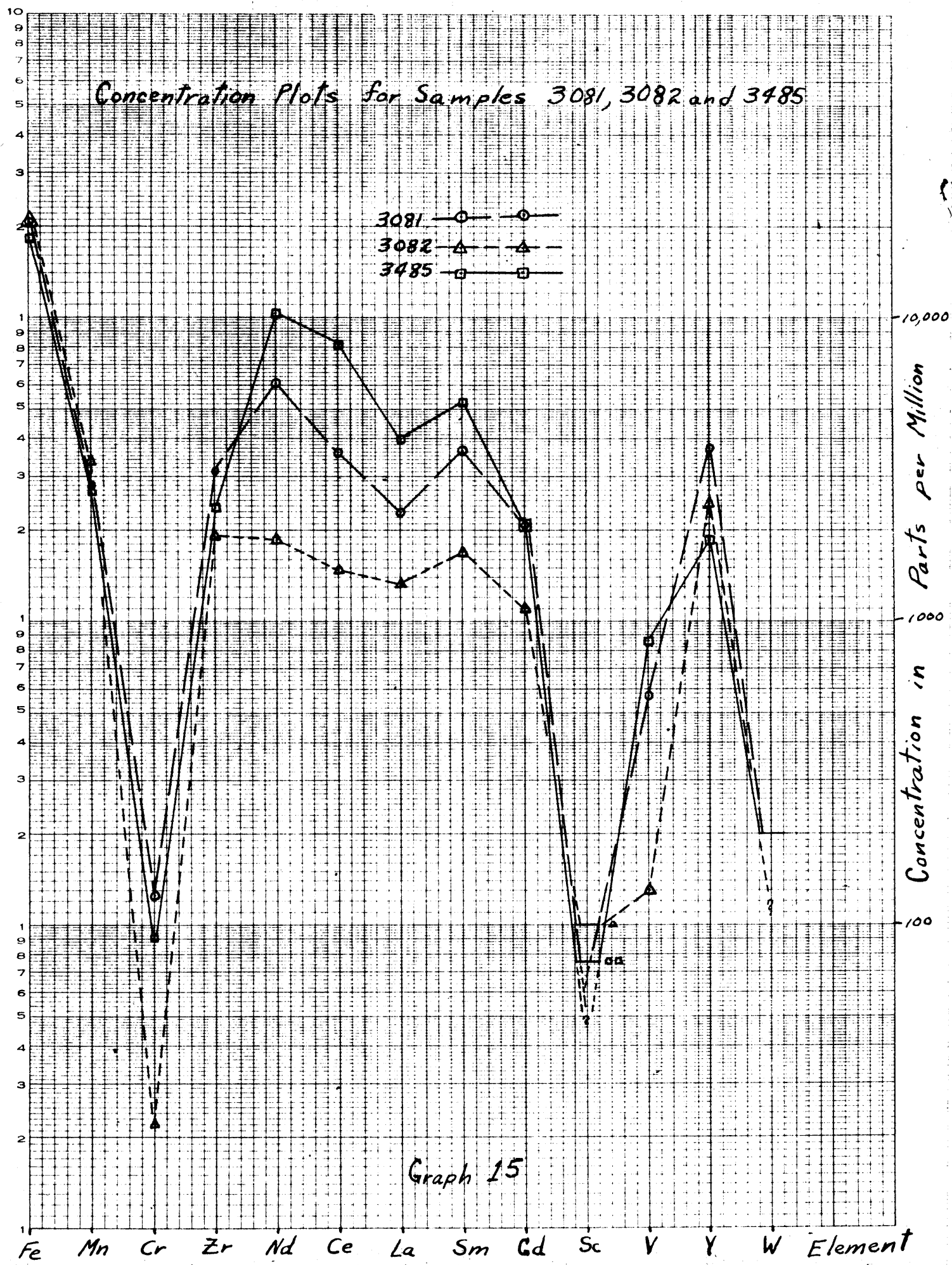
Graph 14

Fe Mn Cr Zr Nd Ce La Sm Gd Sc V Y W Element

in the sphene. Sample 3062 has been included in this subgroup after the above consideration and on the observation of definite similarity in the cases of all other elements. Actually, samples 3062 and 3063 not only show a parallel relationship, but in all elements except three, they show nearly equal concentration levels. As can be seen from the map of sample locations these two samples are within about five miles of each other. The above mentioned observation about the similar quantities of the analysis elements present would seem to indicate that the rocks from which these samples came are very closely related. They may be from the same igneous body.

The second group contains samples 3081, 3082 and 3485 (graph 15). This group like the first group has peaks for iron, neodymium, samarium and yttrium. There are minimas for chromium, scandium and tungsten. This second group differs from the first group in that the zirconium, neodymium, cerium and lanthanum values all are greater than the gadolinium values for their respective samples. Also the lanthanum is much higher relative to samerium in this group than is the case in the first group. Sample 3082 is slightly out of phase by its lack of a peak for neodymium.
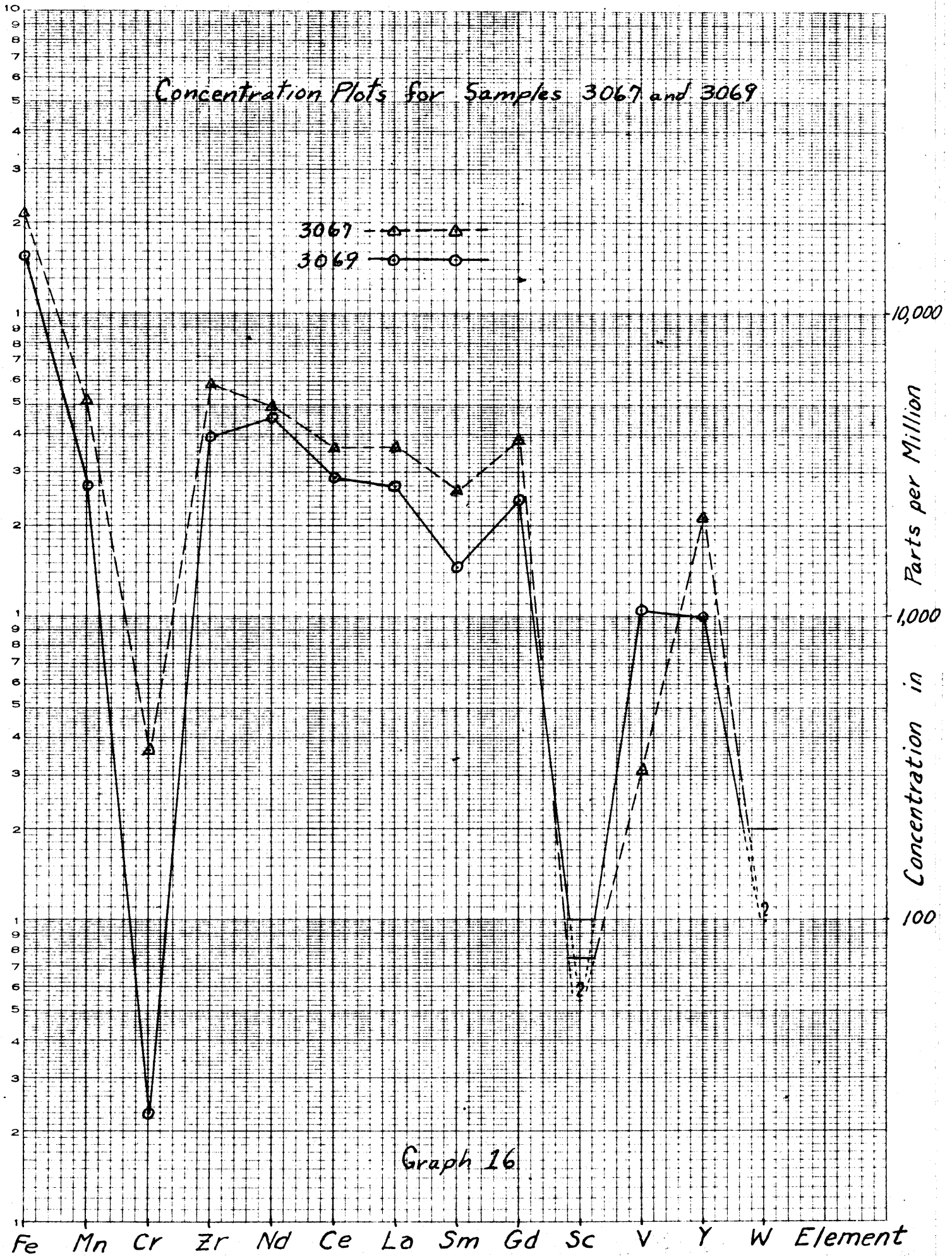
The third group contains samples 3067 and 3069 (graph 16). Here again chromium, scandium and tungsten are low and iron is high. Other general patterns present in the other groups are changed. Cerium and lanthanum, while not attaining peak values, are quite high relatively. They certainly are not low values. Also the samarium concentrations in both cases are significantly lower (about 1000 ppm) than the gadolinium values. It should be noted that these samples show different relations as regards zirconium-neodymium and vanadium-yttrium. However, their general similarity otherwise

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Concentration Plots for Samples 3081, 3082 and 3485

Graph 15

Concentration Plots for Samples 3067 and 3069

3067 —△— —△—
3069 —◯— —◯—

Graph 16

Concentration in Parts per Million

10,000

1,000

100

Fe Mn Cr Zr Nd Ce La Sm Gd Sc V Y W Element

is quite apparent.

The fourth group contains samples 3084 and 3085 (graph 17). This group differs in the occurrences of minima within the group of elements zirconium, neodymium, cerium, lanthenum, samarium and gadolinium. The lowest value in both samples is found to be that for gadolinium. This value is not overly low in relation to most of the above mentioned elements. The similarity between these two samples could be more striking. Sample 3084 has peak values for neodymium and vanadium, which 3085 does not. It would be possible with an adjustment or two for each sample in group three and group four, to bring the curves of these samples into general similarity with the samples of group two. The author, however, sees no justification or reason for doing so. In samples 3084 and 3085, for instance, a decrease of 400 to 800 ppm in the samarium concentration would bring these two samples into similarity with samples 3067 and 3069.

In the fifth group are samples 2093, 3013 and 3138 (graphs 18, 19, and 20). The samples of this group show no overall similarity either to each other or to any of the other samples. The zirconium value of nearly 19,000 ppm in sample 3013 is thought to be due in part to contamination. This value is about 13,000 ppm higher than the next highest zirconium value. Sample 3013 is also notable for its very low values for neodymium, cerium and lanthanum.

Sample 3138 (graph 20) is similar to the samples in group one with one very striking exception, namely a very low neodymium value. However, it should also be noted that this sample has an extremely high value for iron, over 51,000 ppm. This is more than 20,000 ppm greater than the next highest iron value for any of the other samples.
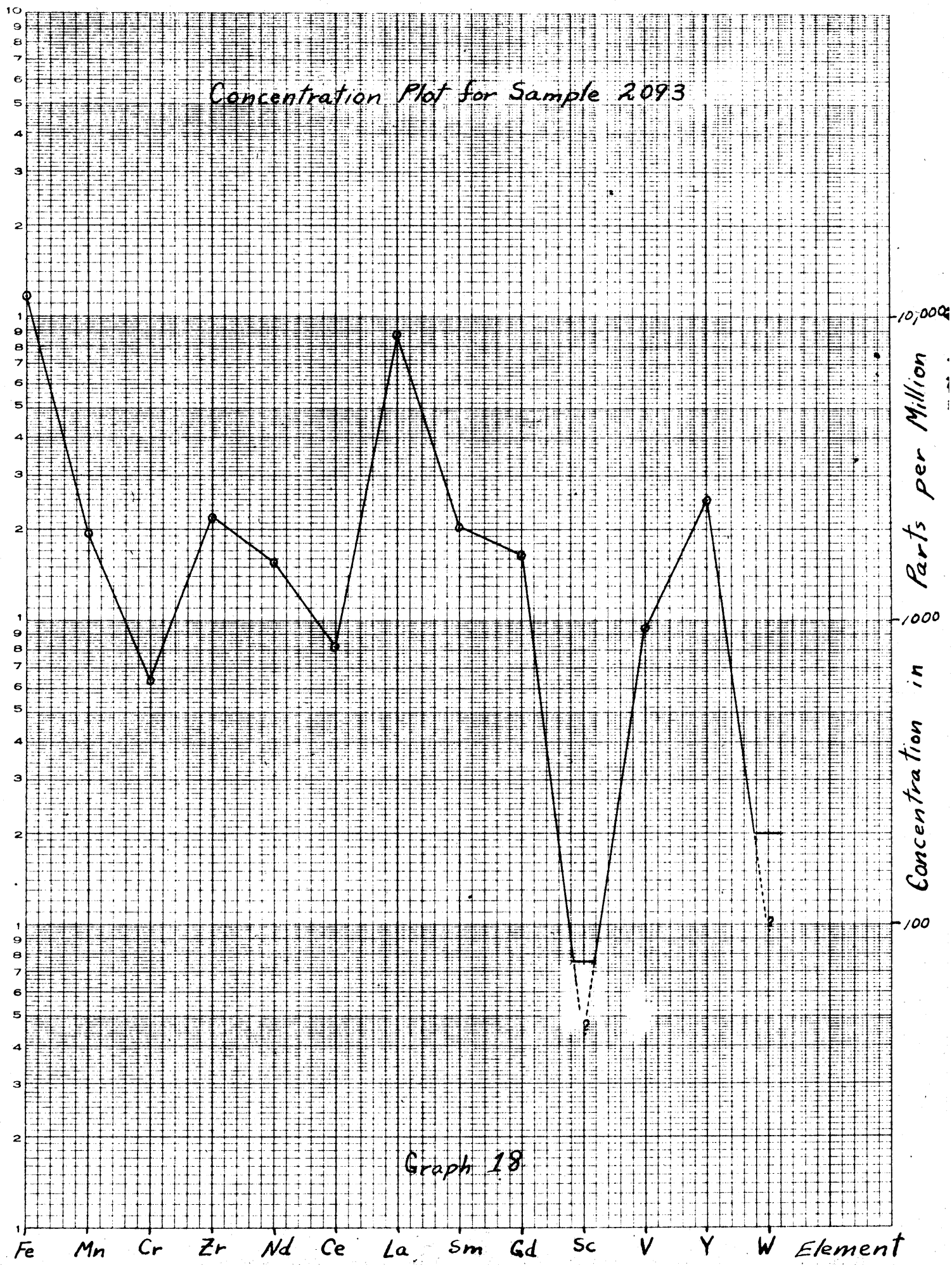
Concentration Plots for Samples 3084 and 3085
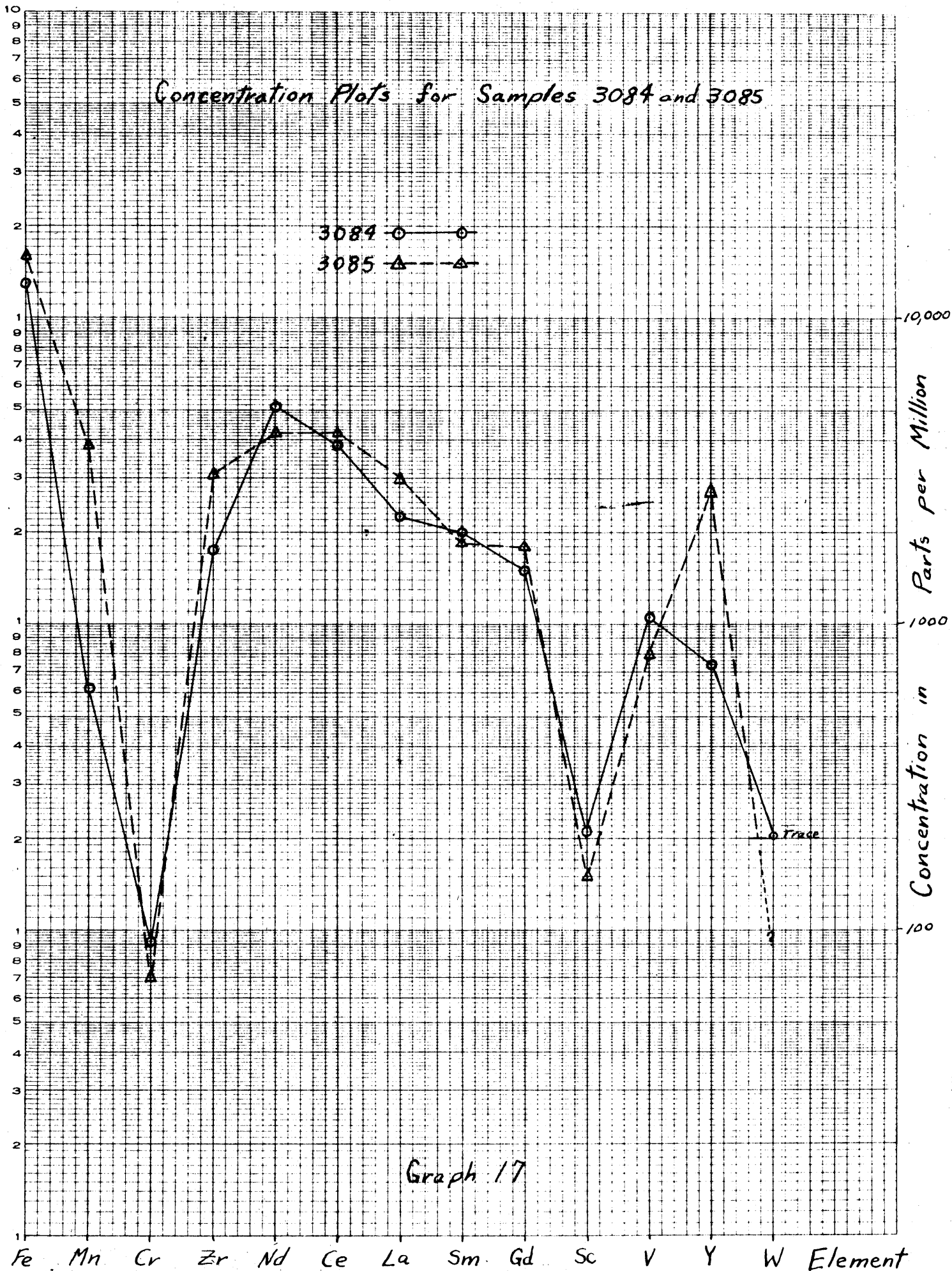
Graph 17
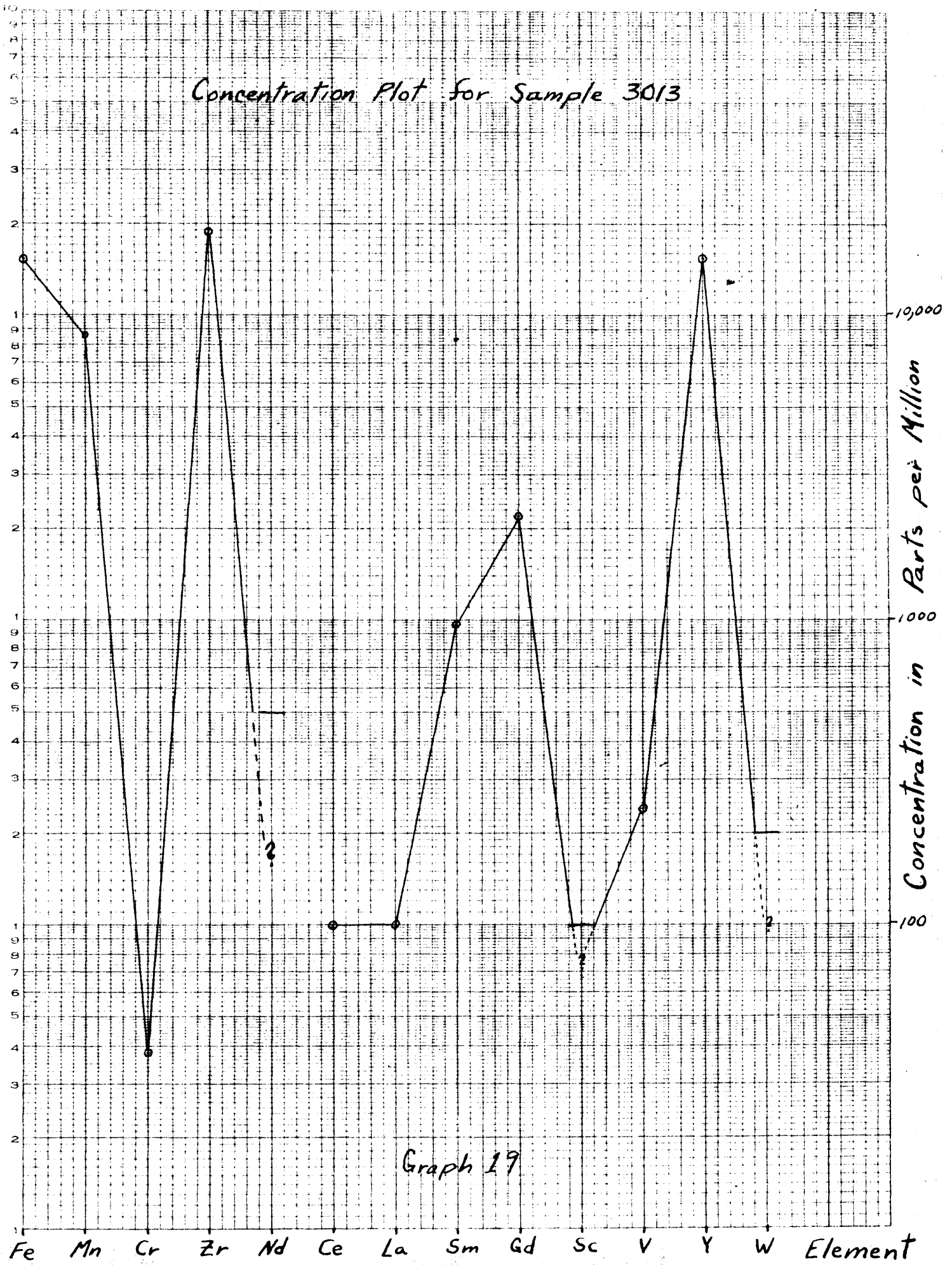
Concentration Plot for Sample 2093

Graph 18
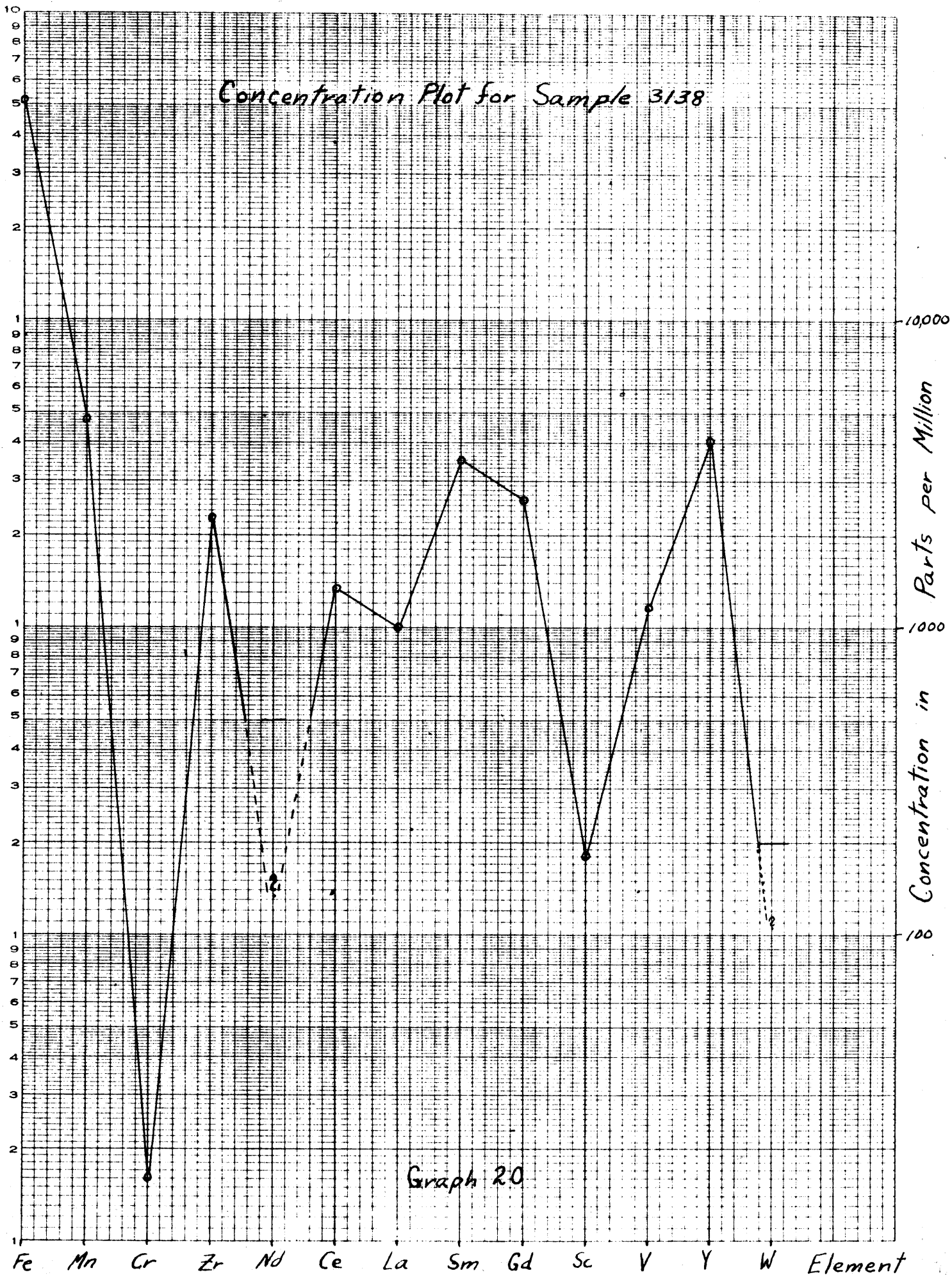
Concentration Plot for Sample 3013

Graph 19

Concentration in Parts per Million

Element: Fe Mn Cr Zr Nd Ce La Sm Gd Sc V Y W

Concentration Plot for Sample 3138

Graph 20

It is quite probable that a major portion of this value is due to contamination, estimated to be about twelve percent, all of which consists of opaque grains. The problem of overcompensation in the correction of the neodymium line was discussed earlier. However, it is possible that the overcompensation was unduly severe here due to the exceptionally high iron value. It is, of course, impossible to know if 3138 would show any greater similarity to group one if this overcompensation was eliminated.

Summary of Results and Conclusions

Results indicate that sphenes are generally low (up to several hundred ppm) in chromium, scandium and tungsten. Elements present in the middle range of concentrations from about 1000 to 3500 ppm, include lanthanum, cerium, gadolinium, samarium, zirconium and vanadium. Present in somewhat higher concentrations are manganese, yttrium and neodymium. All the above elements were only occasionally present in quantities greater than a per-cent. Iron values are very much higher than any of the other elements studies, averaging about two percent. This is as might be expected due to the greater geochemical abundance of iron as compared to the other elements. A portion of this high value for iron doubtless is due to contamination. Aluminum, while not determined quantitatively, is estimated to be present in the range of one to two percent.

There very definitely appears to be parallelism between the values of lanthanum, cerium and neodymium present in sphene. A sample high in one of these elements is also high in the other two. Samarium and gadolinium also show very striking parallelism. These relations are as might be ex-pected from considerations of ionic radii (see Table 5). An inverse re-lation is noted between iron and chromium in cases of highest chromium or lowest iron values. Lanthanum and cerium show an inverse relationship with yttrium.

Of the thirteen samples of group one, chosen as having significant similarities by the author, eleven are from New England, and two are from Quebec. Of the eleven from New England, three are from Massachusetts out of four samples from that state, and eight are from Maine of nine samples from there. The only Maine sample not listed in group one is the standard

Table 5

Tabulation of Ionic Radii of Certain Elements

Element	Valence	Radius in °A		Element	Valance	Radius in °A
Ca	+2	1.06		Ti	+4	0.64
Y	+3	1.06		Al	+3	0.57
La	+3	1.22		Cr	+3	0.65
Ce	+3	1.18		Fe	+2	0.83
Nd	+3	1.17		Fe	+3	0.67
Gd	+3	1.11		V	+3	0.75
Sm	+3	1.13		V	+4	0.61
Mnn	+2	0.91		Mo	+4	0.66
Sr	+2	1.27		Mo	+6	0.62
U	+4	1.05		W	+4	0.68
Th	+4	1.10		Si	+4	0.39

(From Appendix   Stillwell, 1938 and The Handbook of Physics and Chemistry)

3085. The locations of the samples except for 3485, in far western Ontario, can be seen on the map of sample localities (figure 4). The samples of group two, 3081, 3082, and 3485 are all from Ontario. Samples 3081 and 3082 are within ten miles of each other, while 3485 is about eight hundred miles away. Similarity is also noted between samples 3067 and 3069, which also show some geographical proximity. The remainder of the samples show relatively little trace element similarity and no geographical relationship. There thus does appear to be some definite geographical grouping of the samples, with New England being by far the most obvious group. The reason other geographically groupings are not so obvious may well be due to the much fewer number of samples from these areas.

The grouping of samples by similarity of their plots for the thirteen analysis elements, would seem to indicate that trace element analysis of sphenes can be used, given enough samples from an area, in correlating rocks that have some genetic and geographical relationship. It is possible that this is due only to the general selective nature of sphenes, selecting the various elements in certain proportions to each other in nearly all cases. It would seem, though, f rom the fact that only little more than half the samples (group one) show general similarities amongst themselves, while the rest seem to be significantly dissimilar from this group, that there is some genetic relationship indicated. The author concludes that trace element analysis of sphenes may be helpful in establishing due fact of genetic relationship between rocks. Of course, additional work is necessary, as will be suggested briefly under recommendations for future work.

It is concluded with respect to procedure, that the use of intensity ratios of an analysis element with a similarly behaving element present in
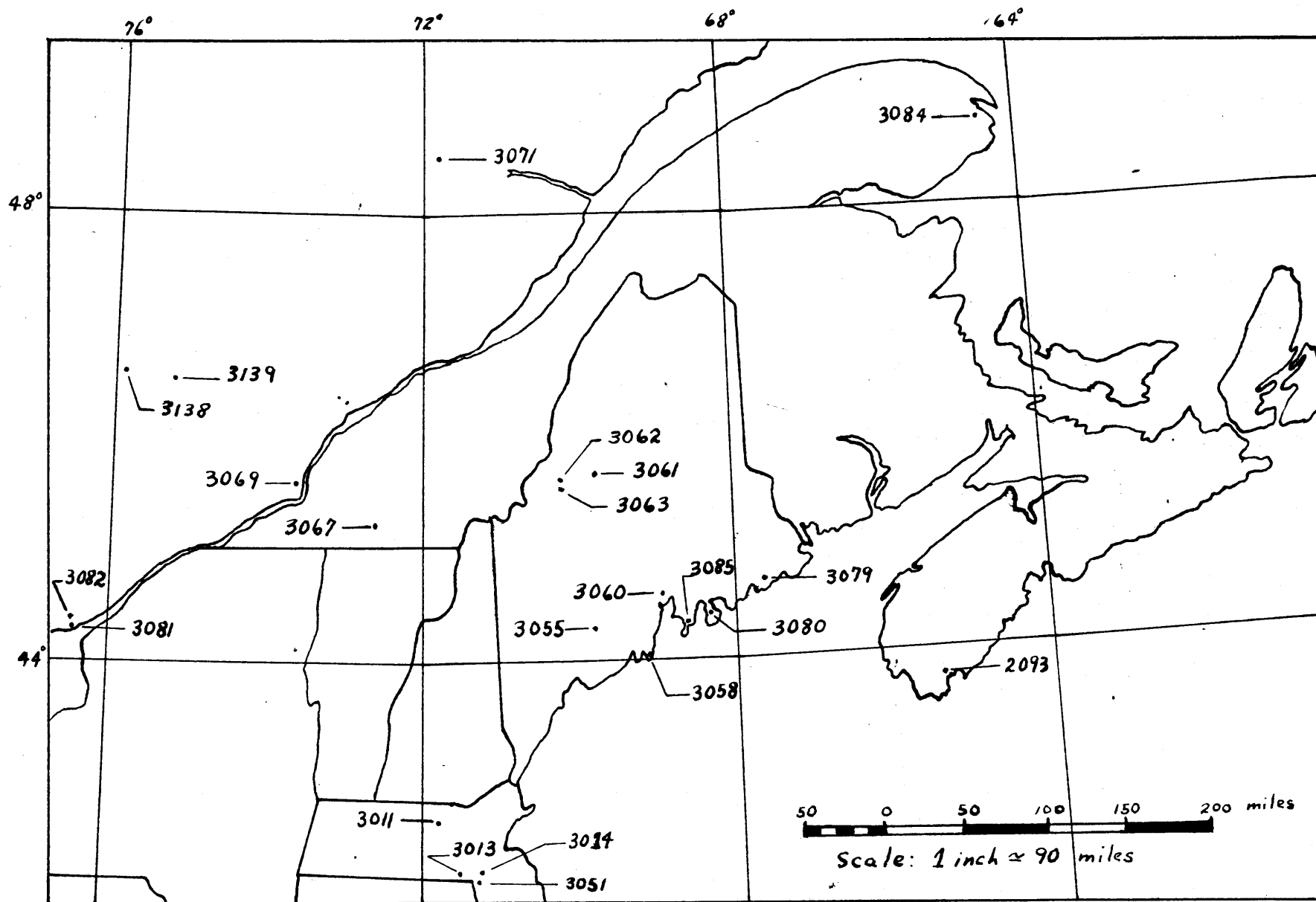
Figure 4. Map of Sample Localities

nearly constant proportion in additionplots is quite helpful. It was found in this investigation that this intensity ratio in most cases improved the addition plots, making them more nearly linear and thus making it easier to determine the original concentrations of the analysis elements in the standard. The use of these ratios for this purpose is recommended.

A tabulation of elements and their concentration ranges in sphene by various analysts is presented in Table 6.

Table 6

Elements and their Concentration Ranges in Sphene
by Various Analysts

(All values given in parts per million)

Oxide of Element	Sahama (1946)	Prince (1938)		Element	Rose (1959)
Fe_2O_3	0-19,100	9500-61,700		Fe	8250-27,500
FeO	1000-6900	0-10,700			
ZrO_2	500-1100	1100		Zr	500-5900
Cr_2O_3	100-200			Cr	15-635
La_2O_3	200-500			La	100-8700
Ce_2O_3	600-1900	}35,800		Ce	100-8150
Y_2O_3	200-9600			Y	740-22,000
Nd_2O_3	600-800			Nd	500-11,200
Gd_2O_3	100-300			Gd	1100-5900
Sm_2O_3	100-300			Sm	970-9450
MnO	100-800	0-500		Mn	620-8550
V_2O_5	50-1100			V	130-1160
				W	200-730
Sc_2O_3	300			Sc	75-980
Al_2O_3	0-44,400			Al	10,000-20,000
SrO	40-4400			Sr	1200-2600
Nb_2O_5	300-16,000				
Ta_2O_5	100-17,500				
Pr_2O_3	0-200			Cb	(1)500-10,000
Dy_2O_3	0-200			U	(2) 25-1270
Er_2O_3	0-100			Th	(2) 40-3150
Yb_2O_3	0-100				

(1) Jaffe (1947)
(2) Hurley and Fairbairn (1957)

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Recommendations for Future Work

Analysis of the rocks from which samples of sphene came for major elements would furnish useful information. Petrographic studies of the rock and sphene would also be helpful if time and purposes of the study permit. It would be very helpful in an investigation of the type reported in this thesis to check the determinations of each element by a different method, especially for the standard. Quantitative determinations in the standard are the ones needing the most verification, since these values are used to determine the values in other samples. The above suggestions for additional work would furnish greater confidence and reassurance in the results obtained and thus also in the interpretations made.

However, more important purposes would be served by analysing additional sphene samples and establishing greater geographical density of trace elements analyses for the mineral, especially in areas from which few sphenes have been analysed. In order to draw any really well based conclusions concerning the topic of this thesis it is necessary to have a statistically significant number of analyses.

Even more significant and indicative would be a similar trace element analysis of several accessory minerals from each of the rock samples. If several mineral phases indicated that certain rocks appeared to be genetically related, one would be much more confident in his conclusions.

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