MINOR ELEMENTS IN SOME CARBONATES

By

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SCOPE AND CONTENTS: An investigation of minor elements distribution in sedimentary and metamorphic carbonates was made. A copper oxide D.C. Arc Technique of spectrographic analysis was developed for determination of minor elements in carbonates. Forty-five samples of carbonates extracted from Palaeozoic limestones of Alberta and Ontario, Precambrian marbles of Ontario and from Grenville Lens and Vein Carbonates of Ontario and Quebec were analyzed, and the concentrations of Mg, Mn, Fe, Sr, Ba, Pb, Al, Si, Ti, B, Cr, and Ni were determined.

The structure and some chemical properties of carbonates were discussed. An attempt to locate the minor elements in the crystal structure was made.

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INTRODUCTION

Carbonate minerals form an important group of sedimentary and metamorphic rocks which include limestones, dolomites and marbles.

Recent research in geochemistry has concentrated on igneous and sedimentary rocks, meteorites, and (to a much lesser extent) metamorphic rocks whereas the carbonate metamorphic rocks have been largely ignored.

In the past few years a considerable number of limestone analyses have been reported although most of them, if not all, consider bulk rock compositions. While the carbonate component is the most important part of the rock from the genetic as well as the geochemical aspect, it is rarely analyzed separately.

In such circumstances it was felt that a study of minor and trace element distribution in unaltered carbonates (Paleozoic limestones) compared with carbonates from rocks affected by strong metamorphism and possibly other processes (Grenville rocks) could provide some information on the compositional differences in carbonate minerals of different environments.

A study of the minor and trace element content of three genetic groups of carbonates has been attempted. The following groups of carbonate rocks were chosen: Paleozoic limestones, Grenville marbles, and Grenville Lens and Vein carbonates. From these rocks almost pure carbonate samples have been extracted for analysis.

Recent developments in spectrographic instrumentation and analytical methods have provided a considerable improvement in precision and reproducibility for rapid analysis of rocks and minerals, particularly for the elements at low concentration. However, most of the spectographic methods have been developed primarily for silicate minerals analysis because they include most of the minerals in the earth's crust. Only a few of these methods are suitable for the analysis of carbonates.

Therefore, an investigation of several spectrographic methods already described in the literature was carried out for minor and trace element analysis in various groups of carbonates. This resulted in the development of an analytical method employing a sample-copper oxide-graphite mixture excited in the D. C. arc discharge using the airjet.

II SHORT NOTES ON RELEVANT GRENVILLE GEOLOGY

The carbonates studied in this work (except those from Paleozoic limestones) are from Ontario and Quebec areas in the Grenville sub-province of the Canadian Shield.

Grenville Series

The oldest rocks in this sub-province are the Grenville series of highly metamorphosed sediments: marbles, amphibolites, schists, gneisses, quartzites, and some other related metasediments; in some places pyroclastic beds, volcanic flows and sills of plutonics occur interbedded with them. It is commonly assumed that these rocks accumulated in the early Precambrian sea in form of limestones, marls, clays, graywackes, and sandstones while volcanic activity was present.

The original structures and textures of all the members of this series are highly modified or completely destroyed, probably by several periods of metamorphism. As a result, standard criteria for determination of stratigraphic succession and correlation cannot be applied with any accuracy to most of these rocks. Consequently, no definite age relations between the different parts of the sub-province or the different members of the series can be established although in some places banded sequences of limestones possibly representing original bedding-planes are noted.

The calcareous rocks of the Grenville series (limestones and marbles) are pure white to gray in colour. The presence of one to two per cent of graphite, iron oxides, and sulphides often causes banding. The weathered portions of the rocks are commonly brown or blue-gray although sometimes remain gray or white.

In most of the marbles one or more of the following accessory silicate minerals may occur: phlogopite, diopside, tremolite, hornblende, olivine, chondrodite, muscovite, talc, quartz, feldspar, and scapolite; lesser amounts of graphite, sphene, serpentine, iron oxides, and sulphides are found. Although no dolomite is found in the marbles, its presence can be suspected in Mg enriched carbonates.

Intrusive Rocks

The Grenville series is intruded by plutonic rocks of different ages and variable composition. The basic intrusives include gabbro, diabase, and amphibolite. Some of the gabbros have igneous textures and are relatively unmetamorphosed rocks, whereas other facies display metamorphic texture and are rather amphibolites. The diabase is fine grained and has a typical ophitic texture.

Silicic intrusives are represented by granite, granodiorite, aplite, granitic pegmatites and gneissic granite. The last rock, however, cannot always be included in the group of intrusive rocks since similar gneisses can be produced by metamorphism of impure sandstones. Migmatitic rocks of hybrid origin and gneissic appearance are abundant and are derived from Grenville rocks mixed with granitic material.

One member of the plutonic group, the origin of which is closely connected with that of the Skarn rocks (described below), is pyroxene granite or syenite. Their textures vary from normal coarse-grained to pegmatitic or gneissic. These changes in texture and composition are rapid over very short distances and therefore metasomatic processes probably contributed to their origin

Skarn Rocks

Skarn is a Swedish word and was originally defined as a contact metamorphosed rock which had experienced Fe-Mg metasomatism.

The term "skarn" is differently interpreted by various authors. In this work the meaning of the term is that used by Shaw (1956 and 1958) for description of the group of coarse-grained rocks which are rich in lime-silicates and are not uniform in the texture, colour, and mineralogical composition.

This meaning of term skarn corresponds to Korzhinsky's (1955) term "skarnoids" which describes metamorphic and metasomatic rocks formed from the rocks containing lime and silica in their original composition (such as marbles, calcareous tuffs, etc.), but without introduction of Ca and Si from other sources. Following Korzhinsky, these more or less deformed rocks, which occurred often in bedded series, contain a considerable amount of lime-silicate minerals and differ from the typical (mono - or bi-mineralic) skarns by the presence of three or more contemporaneous minerals and by the absence of metasomatic zoning.

Throughout the Grenville sub-province there are widespread skarn rocks of varying mineralogy. Most are late in the Precambrian history of the region and are believed to be coeval. They are widely known because of economically interesting minerals such as uramnite, uranothorite, mica, apatite, molybdenite, magnetite etc. which are often present.

Shaw (1956) suggested that the petrology of this skarn series can be explained by the concept of metamorphic facies, since all these rocks are formed of different assemblages of ten major components, namely: plagioclase, microcline, scapolite, pyroxene, amphibole, phlogopite, sphene, fluorite, apatite and calcite with addition of quartz which is stable under almost all metamorphic and metasomatic conditions.

On these grounds Shaw sub-divided the series into following members:
1) Pyroxene syenite-granite group
2) Fluorite rocks
3) Pegmatitic facies
4) Pink calcite rocks
5) Scapolite-pyroxenite rocks
6) Pyroxenites, and transitional facies from these into marbles, gabbros, amphibolites, and granites.

All these rocks contain corbonates (mostly calcite) in different forms.

The pyroxene syenite-granite rocks contain well formed crystals of calcite together with feldspar and pyroxenes in drusy cavities.

In the fluorite rocks, which form small veins and irregular bodies in various rocks, dark purple fluorite, calcite, pyroxene and amphibole are the most abundant minerals. Calcite grains seldom have crystal shape; they are medium to very coarse and are mostly coloured salmon-pink. In some bodies of this rock fluorite-rich and calcite-rich bands can be detected in the central fluorite-calcite core, which is surrounded by coarser aggregates of pyroxene and amphibole grading into the country rocks.

Pink coloured calcite is also abundant in all the rocks of pegmatitic facies associated with various other minerals.

The pink calcite rocks are mostly coarse grained and have a gneissic texture of alternating calcite-poor and calcite-rich bands. They occur in lenticular masses, pockets, lenses and veins in other rocks. The major component is calcite, accompanied by variable amounts of other minerals. The colour of the calcite is of primary origin and it is usually salmon-pink although pale brown and flesh-coloured varieties are present. Calcite is generally interstitial to other minerals and when euhedral crystals occur, they often contain inclusions of diopside and mica.

The scapolite-pyroxene rocks form lenses and bands conformable with the country rocks and contain calcite as an accessory mineral.

In the metamorphic pyroxenites, which are composed mostly of green pyroxene, calcite occurs as an accessory mineral together with phlogopite and amphibole.

Carbonate samples were collected for this study from the marbles and from some rocks of the "Skarn Series" and consist mainly of $Ca\ CO_3$. The presence of other divalent elements indicates, however, that other components are present in the calcite.

III THE CARBONATE MINERAL GROUP

Composition and Isomorphism

Carbonates are an important group of rock-forming minerals. Limestone, dolomite, and marble are some of the sedimentary and metamorphic rocks in which carbonates are principal constituents.

The major constituents of the simple carbonates are the $CO_3^{=}$ group and the divalent metals Ca, Mg, Fe, Mn, Sr, Ba, Zn, Pb, and Cd. They form two "isostructural" groups, the rhombohedral calcite group and the orthorhombic aragonite group. Calcium carbonate is included in both groups, although metallic elements with ionic radius smaller than that of calcium belong to the calcite group and those with larger radius belong to the aragonite group.

Bragg (1937) gives the following distribution of the metals between the two carbonate groups in accordance with their radii:

Calcite type:	Mg	Fe	Zn	Mn	Cd	Ca			
radius (Å)	0.78	0.83	0.83	0.91	1.03	1.06			
Aragonite type:						Ca	Sr	Pb	Ba
radius (Å)						1.06	1.27	1.32	1.43

Description of Structure

The Calcite Group:-

Bragg (1937) made an X-ray analysis of the calcite structure as early as 1914. His work led to a description of atomic positions within a unit cell with a rhombohedral angle of 46° 7', or in the cleavage rhombohedron with a rhombohedral angle of 101° 55'. This study indicated that calcite has a distorted NaCl type structure in which the cubic cell is compressed along a three-fold axis and has Na atoms replaced by Ca atoms and Cl^- atoms by CO_3 groups thereby resulting in a rhombohedral face-centred cell.

The triangular CO_3 group has a central C atom and each of the coplaner oxygen atoms at a distance of about 1.24 Å from the carbon and at the corners of an equilateral triangle and each about 2.3 Å apart. It lies in a plane perpendicular to the threefold axis. The Ca atoms and the CO_3 groups are alternatively situated on the (111) plane. The CO_3 group lies halfway between two groups of three Ca atoms so that each oxygen touches two Ca atoms since all the Ca atoms are in approximate cubic close-packing. (Bragg, 1937; Graf and Lamar, 1955).

Dolomite has a unit cell analogous to that of calcite, but with substitution of alternate Ca by Mg along any threefold axis resulting in a lower symmetry than that of calcite. There is also a disordered dolomite in which Ca and Mg positions are more haphazard.

Similar X-ray study of the other members of the calcite group indicated the same type of structure.

Bragg (1937, P.116) measured the parameters a and α for the true unit cell with the number of $CaCO_3$ molecules Z = 2, and the parameters a' and α' for the conventional (or cleavage) type unit cell analogous to that of NaCl with Z = 4:

Name	Rhombohedral Z = 2		Space Group $D_{3d}^{6} = R_{\bar{3}c}$	Z = 4
	a	α	a'	α'
Calcite $CaCO_3$	6.361 Å	46° 7'	6.4125 Å	101° 55'
Magnesite $MgCO_3$	5.61 "	48° 10'	5.84 "	103° 20'
Siderite $FeCO_3$	5.82 "	47° 45'	6.02 "	103° 05'
Rhodochrosite $MnCO_3$	5.84 "	47° 20'	6.01 "	102° 50'
Smithsonite $ZnCO_3$	5.62 "	48° 20'	5.87 "	103° 30'
Dolomite $CaMgCO_3$	6.00 "	47° 30'	6.18 "	102° 50'

The Argonite Group:-

Bragg (1937) placed the aragonite group in the orthorhombic space group Pbnm (V_h^{16}) with 4 molecules in the unit cell. While the Ca atoms in calcite are arranged in a cubic close-packing, in aragonite they are in an approximately hexagonal close-packing arrangement.

The CO_3 group is similar to that of calcite with the same C - O distance but rotated 30° (compared with calcite). Also, it lies between six Ca atoms but closer to the upper three with each oxygen touching three calcium atoms. This explanation of the aragonite structure is in agreement with its greater density compared with calcite and with the pseudohexagonal character of the twinning.

The replacement of calcium by the other metals of the aragonite group occurs to a lesser extent than in the calcite group. The unit cell data for minerals of the aragonite group after Bragg (1937, P.117) are as follows:

Name	Orthorhombic	V_h^{16} (Pbnm)	Z = 4
	a	b	c
Aragonite $CaCO_3$	4.94 Å	7.94 Å	5.72 Å
Strontionite $SrCO_3$	5.12 "	8.40 "	6.08 "
Witherite $BaCO_3$	6.25 "	8.83 "	6.54 "
Cerrusite $PbCO_3$	5.14 "	8.45 "	6.10 "

Bonding

The X-ray diffraction measurements of Schiebold (1919) and those of Wyckoff (1920) disclosed the presence of discrete CO_3 groups of identical size and shape in various carbonates corresponding to the infrared reflection maxima of $CO_3^{=}$ groups obtained by Schaefer and Schubert (1916). The existence of these discrete units is also supported by the application of Pauling's rule (1929) for distribution of positive valency of each cation equally among the surrounding anions: C $\underline{\;4/3\;}$ O and Ca $\underline{\;1/3\;}$ O in calcite and Ca $\underline{\;2/9\;}$ O and C $\underline{\;4/3\;}$ O in aragonite.

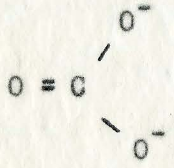
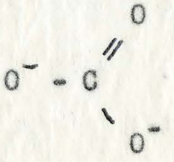
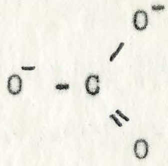
On the basis of the above observations, it can be concluded that the C - O bonds within the CO_3 group are stronger than the other bonds present in the carbonate structures.

However, this simplified conceptiom of carbonate bonding is complicated by the fact that the C - O distance of 1.31 Å in the carbon group is smaller than the sum of ionic radii of C^{++++} and $O^{=}$ which is 0.15 Å + 1.40 Å.

Graf and Lamar, referring to Zachariasen (1931) and Evans (1948), explain this phenomenon by the presence of polarization affecting $O^{=}$ ions or by the strong covalency of the C - O bonds. In their opinion a high polarization of the large $O^{=}$ ions by the nonsymmetrical coordination of other ions, including a small highly charged C cation, can be expected.

An ion's deformation is measured by its molecular refractivity: the value obtained for carbonates by Fajans and Joos (1924) indicates a highly deformed state of $O^{=}$ in CO_3 group since it is about one-half of that in the free state.

Pauling (1931) noted that carbon must be excited for the formation of three equivalent bonds at 120° in a plane, therefore the carbonate group resonates producing three principal structures with each C - O bond possessing 1/3 double-bond character.

Graf and Lamar (1955) concluded from a literature survey that Ca - O bonds in carbonates have more ionic character whereas C - O bonds in $CO_3^{=}$ group are predominantly but not completely covalent.

II ANALYTICAL METHOD

Previous Work

Methods for the spectrochemical analysis of carbonates have been developed to a lesser extent than those for the analysis of silicates as the latter include most of the rock forming minerals. Leininger (1950) described a method for the analysis of major components in limestone by use of the DC arc with a graphite-sample mixture and a mutual standard method. Spectrographic determination of the minor and major components in carbonate material was described by Goldsmith, Graf, and Joensuu (1955). Hawley and MacDonald (1956) developed a method, mainly for analysis of various silicate rocks, using strontium and barium carbonates as internal standards and buffers applying a modified Stallwood air-jet to eliminate selective volatilisation and other variable matrix effects. The same method was used also for the analysis of carbonate rocks. The major disadvantage of this method for the writer is that the adapted buffers do not permit the analysis of Ba and Sr which are important minor elements in carbonates.

Jaycox (1953) suggested a DC arc technique with a variable proportion of copper oxide as the internal standard and buffer for the analysis of ceramics and other non-metallic materials. Greenius and the author (Sibakin and Greenius 1955) adapted the principle of this method for an AC arc micro-crater electrode technique used for the analysis of open hearth and blast furnace slags. In the present study, after investigation of several buffers and internal standards, CuO used simultaneously as internal standard and buffer in a DC arc technique proved to be satisfactory for the analysis of minor and major constituents of carbonates.

Development of Method

A preliminary search was made for a proper buffer and internal standard using a set of artificially prepared standards, which were mixed in various proportions with the buffer and internal standard (when the latter was also used). The arc current, screen filter, and air-jet pressure were adjusted to achieve a wide analytical range and a suitably high sensitivity.

It is a widely accepted opinion (e.g. Ahrens, 1954) that a well chosen buffer and internal standard provide satisfactory grounds for disregarding the "total energy" method for quantitative determinations. Nevertheless, it was felt that the tendency of many metallic oxides to form hard-melting carbides during arcing affects considerably the amount of the element excited (Rusanov, 1948) and therefore it would be advisable to burn the sample to completion while using both an internal standard and a spectrographic buffer.

In the earliest stage of the investigation a mixture of the sample with graphite containing 0.2% $PdCl_2$ was tried. The results were unsuccessful; the arc burn was not smooth and the line to background ration was low.

The adaption of the $K_2\ SO_4$ and $SrCO_3$ methods described by Hawley and MacDonald (1956) and the parallel study of $LiCO_3$ and KCl as possible buffers with In and Pd as internal standards were the next steps of the investigation. The spectra showed that KCl and $LiCO_3$ decrease sensitivity considerably making these buffers unacceptable. Although $SrCO_3$ did not affect the spectrum so much, its successful application required a thin-walled electrode crater. This involved an inconvenient change in the standardized practice of electrode cutting. Considerable spitting during arcing without the air-jet and also the impossibility of analyzing Sr were the other factors which led to abandonment of this buffer. K_2SO_4 proved useful for the analysis of trace elements but the excessive intensity of most useful major element lines made it unsatisfactory for a complete analysis.

Description of the use of $CaCO_3$ in the literature as a successful buffer (Ahrens, 1954 P.156 and PP. 115-116) as well as the above described experiments showed that for the analysis of carbonates neither a strong buffer nor a high concentration of moderately acting buffer are necessary. Being composed mostly of $CaCO_3$, carbonates are strongly self-buffering compounds. They are rather poor conductors, however, and require admixture of a conducting material. For this purpose CuO was successfully adapted. Copper has an ionization potential of 7.68 volts, thus the sensitivity was not depressed and being an excellent conductor CuO improved the arc burn and provided a considerable number of internal standard lines of different intensities. The addition of CuO in excess, as used in the original Jaycox method, proved unacceptable. Several runs of the standards mixed with graphite and CuO in various proportions led to the acceptance of the ratio; sample: CuO: graphite = 4:1:5.

The semi-quantitative analysis of several representative samples had shown presence of two groups of elements with different ranges of concentrations. One group had concentrations from .01% to more than 1.0%; the other group had concentrations below .01%. Accordingly, two different excitation conditions for each sample were chosen, one with moderate and the other with high sensitivity of the analytical lines.

Excitation conditions were finally established as follows:

Condition I (for abundant elements)

primary slit opening 30 microns: exposure 75 seconds; 2 screen filters; rotating step-sector, steps 4 - 7; wave length range 2200 - 4900 Å; power source 240V (open circuit), 8.0 A; air-jet ½ psi.

Condition II (for trace elements)

primary slit opening 30 microns; exposure 85 seconds; 1 screen filter; rotating step-sector, steps 3 - 6; wave length 2200 - 4900 Å; power source 240V (open circuit), 10 A.

Further details of instruments and technique follow:

Spectrograph - Jarrell-Ash 21 foot Wadsworth grating instrument, first order dispersion 5 Å per mm.

Optical system - 25 cm. focal length cylindrical lens (horizontal axis) at the slit; 6.7 cm. focal length cylindrical lens (vertical axis) 16.1 cm. from the slit; diaphragm with 5 mm. aperture 27.5 cm. from the slit; 10 cm. focal length spherical lens 58.1 cm. from the slit; arc located 72.5 cm. from the slit.

Primary slit - 4.5 mm. length, 30 microns width.

Intensity control - step sector - step ratio Log I_1/I_2 = 0.2; 1 or 2 screen filters.

Arc gap - 8 mm. manually adjusted during excitation of the sample.

Power Source - ARL DC arc unit; current continuously adjusted during excitation time

Polarity - lower electrode anode

Electrodes - Sample: 1/8" graphite rod (National Carbon Co., "Special Grade") crater 6 mm. deep, 1.5 mm. diameter; counter electrode, 1/8" rod.

Air-Jet - Modified Stallwood air-jet; ½ psi pressure

Exposure sequence - At least one standard was exposed on each set of plates to check working curves; samples were analyzed in triplicate, one on each of three pairs of plates.

Photographic Processing - Eastman Kodak emulsion type SA-1 plate for the range 2200 - 3500 Å; and Type III-F plate for the range 3560 - 4900 Å; development 3 minutes in Kodak D-19 developer at 32°C; stop bath 10 sec.; 10 minutes fix; 20 minutes minimum wash.

Densitometry - ARL instrument; galvanometer readings between 1.0 and 95.0 were used; background correction applied in the case where 1 screen filter had been used; clear plate reading (100) before each measurement.

Emulsion Calibration

Previous work in the laboratory had indicated that, at least for equipment available at McMaster University, an emulsion calibration based on the spectra of standards and samples with the use of analytical and internal standard lines was superior to a calibration based on the iron spectrum exposed on the same plate. In this work a short investigation of the same problem was carried out.

An iron arc was exposed on the plates together with the standards. Line transmission readings were obtained in the same wave length areas for both the iron and standard spectra, using Cu-lines and analytical lines for the latter. The two step method was applied to plot calibration curves for both spectra. Four separate curves were drawn for the excitation condition I; for the wave-length regions 2400 - 2600 Å, 2600 - 2900 Å, 2900 - 3150 Å, and 4200 - 4600 Å. For the excitation condition II, two average curves were drawn; for the wavelength region 2500 - 3400 Å and 4200 - 4600 Å. A calculation of log. line intensity (log I) on both sets of curves showed that the results obtained from curves based on the spectra of the standards are more reproducible than those obtained from the iron spectrum curves on the same plate. Further check of established calibration curves was made with the seven step method for each set of plates.

Preparation of Standards

The artificial standards were prepared in a matrix of "Specpure" calcium carbonate with the added metal oxides. (Johnson, Matthey and Co. Ltd.). Two original matrices were prepared, one with 0.1% content of all the elements to be sought and another with 1.0%. All the constituents were mixed in an agate mortar with methyl alcohol to produce a fluid paste, then dried under a light bulb and ground again. These were diluted with calcium carbonate to produce a series of standards containing 1.0, 0.6, 0.3, 0.1, 0.06, 0.03, 0.01, 0.006, 0.003, 0.001, 0.0006, 0.0003, 0.0001% of each element.

The standard mixture of graphite and copper oxide in the ratio 5:1 respectively was made in a similar way.

Analytical Line Pairs and Working Curves

Table I shows the analytical line pairs used and the ranges of concentration covered by the method. The wide range of the element concentration required two different excitation conditions (described above) and two corresponding sets of analytical line pairs.

The internal standard lines were chosen in the various calibrated regions of the plate in order that intensities be suitable for nearby analytical lines. Although the lines Cu2406.6, Cu2766.4, and Cu2768.9 were interfered by very weak iron lines, there was no change in their intensity resulting from the variation of iron content of the standards and samples. The line Cu4275.1 was clearly resolved from Cr4274.8 and the low Cr content in material analyzed did not affect its intensity. The line Cu3108.6 coincides with a low intensity Ca line, however, the more or less constant amount of Ca present did not noticeably affect the Cu intensity. The rest of the Cu lines were free from any interference.

The high-intensity ground level Mg lines were not suitable for the determination of high Mg concentrations. The line Mg2779 was used instead.

Harrison's (1939) Wavelength Tables were used for reference in this work.

The working curves for all analytical pairs listed in Table I were plotted in terms of log intensity ratio of analytical to internal standard line (log IR) versus element concentration in ppm. on semi-log paper. The averages of six replicates of each high concentration standard and ten to thirteen replicates of each low concentration standard were used for plotting. All the working curves, except for Cr, were drawn through the averages without statistical correlation. The working curve for Cr was correlated by a least-squares method.

The working curve for Ba showed slight curvature, but the others were straight except for the ends which were curved as a result of either self-absorption or background effect. These curved ends were considered unreliable and were not used. Unfortunately, a gap occurred between the high and low concentration curves for Mg as a resulf of discarding the curved portions. All the working curves are shown in the Appendix I (Fig. 1 to 13).

In recent work reported by Shaw (1958), the analysis of V in calcium-rich samples such as limestones which were made using the line V 3185.4 have been considered doubtful. Accordingly, in the present work the determination of vanadium was carried out with the line V 3185.4 with a background correction measured at Ca3186.4 and an additional check made with lines V 3102.3 and V 3110.7. All the samples produce the intensity of V 3185.4 lower than that of Ca3186.4 and showed the absence of V 3102.3 and V 3110.7. Consequently, the

TABLE I

Analytical Line Pairs and Concentration Range

Element	Analytical Line/Internal Standard Line	Concentration Range in ppm.	Excitation Condition	Rotating Sector Step Used
Ag	Ag3280.7/Cu3108.6	1-30	II	6
B	B 2497.7/Cu2768.9	6-100	II	3
Ba	Ba4554.0/Cu4248.9	6-100	II	4
Cr	Cr4254.3/Cu4248.9	3-100	II	4
Ni	Ni3050.8/Cu2768.9	6-300	II	3
Pb	Pb2833.0/Cu2768.9	3-300	II	3
Ti	Ti3372.8/Cu3108.6	6-300	II	5
Al	Al3082.1/Cu3010.8	300-6000	I	7
	Al3082.1/Cu3108.6	30-600	II	6
Fe	Fe2719.0/Cu2766.4	300-6000	I	6
	Fe2719.0/Cu2768.9	30-300	II	4
Mg	Mg2779.8/Cu2882.9	300-10000	I	6
	Mg2802.7/Cu3108.6	10-100	II	4
Mn	Mn2949.2/cu3010.8	600-3000	I	7
	Mn2949.2/Cu2768.9	10-600	II	4
Si	Si2516.1/Cu2492.1	300-10000	I	7
	Si2528.5/Cu2406.6	100-600	II	4
Sr	Sr4607.3/Cu4275.1	300-6000	I	5
	Sr4607.3/Cu4248.9	30-300	II	4

vanadium concentration was considered to be not detectable and the working curve was not completed.

Precision

In order to test the reproducibility of the method, one sample (A-5a) containing a moderate concentration of the elements sought was analyzed ten times. The first three exposures were made on three different sets of plates in the routine way of analysis. The last seven exposures were made on one pair of plates. In each case three different standards were exposed on each plate to check the working curves. The coefficient of variation (C) was calculated from the following equation:

$$C = \frac{100}{K}\sqrt{\frac{\Sigma d^2}{n-1}}$$

where:

K - average concentration in ppm.

d - difference of a given determination from the mean

n - number of determinations

Table II shows the results of analysis with the averages and coefficients of variations calculated.

TABLE II

Results of Analysis of the Sample A-5a

Concentration in ppm.

	B	Ba	Pb	Ti	Al	Fe	Mg	Mn	Si	Sr
Analytical Line	2497.7	4554.0	2833.0	3372.8	3082.1	2719.0	2779.8	2949.2	2516.1	4607.3
Internal Standard Line - Cu	2768.9	4248.9	2768.9	3108.6	3010.8	2766.4	2882.9	3010.8	2492.1	4275.1
Replicate 1	11	11	20	10	440	3200	1200	910	3200	660
2	11	10	20	10	490	3800	1300	770	2900	780
3	13	10	19	11	420	3700	1300	780	3300	760
4	11	12	16	11	370	3300	1300	840	3600	660
5	13	12	16	10	480	3000	1500	870	3700	620
6	13	11	16	10	450	3400	1400	730	3500	720
7	12	12	16	10	480	3400	1400	680	3300	780
8	13	12	16	11	460	3200	1200	790	3600	780
9	12	11	16	9	480	3000	1400	840	3900	550
10	11	11	17	10	400	3200	1400	780	3500	640
Average Concentration	12	11.2	17.2	10.2	447	3320	1340	798	3450	695
Coefficient of Variation in %	±7.5	±4.8	±11.4	±6.5	±8.9	±6.9	±7.2	±8.3	±8.2	±11.6

Accuracy

The accuracy of the method was checked by analysis of the National Bureau of Standards argillaceous limestone standard No. 1a. This is the only available standard which corresponds more or less closely to the composition of the samples. However, it does not provide analytical data for all the elements sought and the concentrations of Si, Al, Fe, and Mg in it are much more above the analytical range of the established method. Thus, these elements were determined as well as Sr in a mixture of standard No. 1a diluted 1:9 by $CaCO_3$ powder, which was later mixed with graphite and CuO in accordance with the established procedure. For the analysis of Ti and Mn an undiluted portion of the standard was used.

Table III shows the results obtained in the present investigation compared with the values reported by NBS. The last values were recalculated from the oxides to the element form.

TABLE III

Concentration of Elements in NBS Standard No. 1a

	Concentrations in per cent						
	Al	Fe	Mg	Mn	Ti	Si	Sr
Values recommended by NBS	2.20	1.14	1.32	0.029	0.096	6.58	0.20
Results by present method	2.30	1.06	1.29	0.039	0.140	6.20	0.24

The values for Al, Fe, Mg, and Si obtained with the present method are in satisfactory agreement with those certified by National Bureau of Standards. The agreement is not very good for Sr and Mn and it is worse for Ti.

A certain disagreement should be expected when a comparison of analyses of a sample is made, particularly when different laboratories participate and entirely different methods of analysis are used.

Fairbairn et al (1951) in a report on the interlaboratory investigation of the precision of rock analyses indicates a maximum disagreement for TiO_2 and MnO among 34 results of the same rock samples made by different analysts in different laboratories as shown in Table IV.

TABLE IV

Extraction from Table I

After Fairbairn, 1951

Sample	TiO_2, Min.	% Max.	MnO, Min.	% Max.
G-1	0.16	0.50	0.01	0.06
W-1	0.10	1.41	0.10	0.53

Further in the same report he noted that an increase in the analytical error of a chemical analysis with a decrease in concentration of the element sought is very prevalent. However, the error of spectrographic analysis is very much less variable in this respect owing to the logarithmic concentration scale.

An additional evaluation of accuracy, although made on an approximate basis, is illustrated in Table V which shows analyses of two pairs of samples made by W.O. Taylor, Ontario Provincial Assay Office, and by the author. Each pair is from the same locality, but were collected by different persons. Thus, a considerable sampling error can be expected.

TABLE V

Results of Spectographic Analyses of the Samples from the Same Localities

Concentrations in ppm.

Sample	B	Ba	Cr	Ni	Pb	Ti	Al	Fe	Mg	Mn	Si	Sr	Analyst
Average of ON30 (A,B,C)	27	48	ND	tr	33	45	162	5700	2000	3000	770	1700	W.W.Lapkowsky
54-S-209	30	70	ND	1	9	40	-	10000	-	7000	-	2000	W.O.Taylor
A-3	6	15	ND	tr	60	13	230	3200	1700	1200	1700	1000	W.W.Lapkowsky
54-S-155a	ND	ND	1	1	30	6	-	7000	-	1000	-	1000	W.O.Taylor
54-S-155b	ND	ND	ND	1	30	10	-	2000	-	1000	-	600	W.O.Taylor

The samples are 54-S-209 and ON30 (A, B, C) collected from a calcite-fluorite-apatite vein at the Fission Mine, Cardiff township, Ontario and 54-S-155a (pink calcite), 54-S-155b (white calcite) and A-3 sampled in the MacDonald Quarry, Monteagal township, Ontario.

Mr. Taylor's analyses were made for D.J. Satterly and are reported here by courtesy of the Ontario Department of Mines.

Taylor analyzed these samples semiquantitatively by a visual comparison with artificially prepared standards. The material was analyzed as a rock sample; i.e. no separation of carbonates from other minerals possible present was reported.

Thus, the relatively lower values of Fe and Mn obtained by the author may result from the magnetic separation which was used for the carbonate purification in the present work. A slight disagreement in the values for B and Ba is explained by the limits of detectibility noted by Taylor as being 2 ppm for B and 50 ppm for Ba.

The values of Cr, Ni, Ti, and Sr can be accepted as being in satisfactory agreement considering possible deviations in the visual comparison of the line intensity.

The disagreement in the Pb results appears to be caused by a systematic error in one of the spectrographic methods. However, the differences in the precision of quantitative and semiquantitative determinations, the purification of the samples, and the possible sampling error should be taken into account,

In spite of all the above inconveniences in the comparison of both spectographic results, they are in better agreement than the chemical (NBS) and spectographic analyses of the NBS standard.

The absence of other well-analyzed samples of carbonates or calcites forced the acceptance of these incomplete checks of accuracy.

It may be concluded that the present method appears to give satisfactory precision and that the accuracy shows no obvious cause for concern.

III ANALYZED SAMPLES AND RESULTS OF ANALYSIS

Samples Analyzed

The Carbonate Samples used in this study were obtained from various sources and prepared for analysis in two slightly different ways. They are divided in three groups in accordance with the types and ages of rocks containing the carbonates.

The Palaeozoic limestones (Group I) of precipitated and skeletal type had been collected by F.W. Beales in south-western Alberta and southern Ontario. The purification of this group was made by Mr. F.W. Beales by handpicking the purest limestone grains. Neither magnetic nor heavy liquid separation methods were used in their purification. Three of the analyzed samples; a recent Miami Oolite (from F.W. Beales), a vug calcite from Silurian limestone (from R.V. Best), and a spirifer from Devonian sediments (from D.M. Shaw) are listed with Palaeozoic limestones but their analyses are not included in the limestone average and are presented merely for comparison.

The samples of the following two groups (II and III) are carbonates from metamorphic Precambrian rocks of Grenville sub-province..

The carbonates from Precambrian marbles (Group II) were obtained from various localities in Ontario and Quebec, and were extracted from highly metamorphosed limestones of different mineralogical composition.

The Grenville Lens and Vein carbonates were extracted from the rocks of "Skarn series" (Group III) and were collected in the

Bancroft area of Ontario and Pontiac County by D.M. Shaw and H.S. Armstrong. The name Grenville Lens and Vein carbonates does not bear a structural meaning. It is used for distinguishing the carbonates from the "Skarn series" and those of marbles.

Carbonates from the last two groups were separated from the other minerals by the methods described below.

Detailed petrographic and mineralogical description of the rocks from which the analyzed samples were obtained has been made by D.M. Shaw (unpublished) for the Precambrian, and by F.W. Beales (1956) for the Palaeozoic rocks.

The list of the sample localities in Appendix II provides information on their age and composition.

Sample Preparation

Hand specimens of rocks were crushed to 1/8" fragments or smaller then the pure carbonate grains were hand-picked. These were then crushed in a steel mortar and sieved. The 100-150 mesh fraction was saved and finer material discarded. The separation of calcite from other minerals present was carried out with the Franz Isodynamic Separator. Adjustments of the current and tilt of the separator were variable, depending on the impurities in each sample.

The concentrate was then separated in Tetrabromoethane. Samples of almost pure calcite were examined under the binocular microscope and finally purified with a glass rod, using the electrostatic attraction. A count of grains in the final samples showed up to 0.01% of impurities except sample CA-84 in which 2-3% of graphite was impossible to separate. The pure calcite sample was then ground in an agate mortar to a fine powder.

Results of Analysis

The analysis results expressed in parts per million (ppm.) are shown in Tables VI, ~~IX~~ XI and ~~XI~~ XIII according to the types of parent rocks. They are given with two significant figures both for low and high concentrations since the working curves are logarithmic.

The symbol ND means that the analytical line was not distinguishable from the background, whereas tr. indicates that the line to background ratio was very close to 1.0 and no numerical estimate could be made.

As previously mentioned, no V was detected in any sample. Ag was present in nearly every sample in an amount below the limit of measurement. Both of these elements, therefore, are omitted from further discussion.

Carbonates from Palaeozoic Limestones

Thirteen carbonate samples from precipitated and skeletal Palaeozoic limestones were analyzed. The analysis results arranged according to age are shown in Table VI.

TABLE VI

Analysis Results for Carbonates from Palaeozoic Limestones (Group I)

Sample	Concentration in ppm.												Limestone
	B	Ba	Cr	Ni	Pb	Ti	Al	Fe	Mg	Mn	Si	Sr	Type
	A - Ordovician, Black River Group, Southern Ontario												
H-30	6	8	<3*	tr	tr	35	580	1900	3200	340	3300	320	Precipitated,- Bahamite
H-33	16	10	<3*	ND	ND	82	1100	900	4600	620	4600	310	" "
U-6-2	10	3	tr	ND	ND	29	500	800	2800	210	3600	400	Skeletal; Crinoid/Brach.
U-6-9	ND	3	ND	ND	ND	27	660	1900	4300	260	3400	370	?
U-6-16-6	16	6	<3*	ND	ND	76	1600	780	4700	130	4700	440	Skeletal; Crinoidal
Girvanella	12	3	<3*	tr	tr	41	900	1800	4700	180	8100	490	Skeletal; Girvanella
	B - Devonian, Palliser Formation, South-western Alberta												
P-1735	9	6	tr	ND	ND	65	1000	570	>20000**	32	2000	170	Precipitated; Bahamite
W-690	ND	2	ND	ND	ND	32	640	550	>20000**	30	3100	320	" "
P-1550	9	4	<3*	tr	ND	51	810	610	4200	41	2000	270	Skeletal; Crinoidal

TABLE VI (contd.)

Analysis Results for Carbonates from Palaeozoic Limestones (Group I)

Sample	Concentration in ppm.												Limestone Type
	B	Ba	Cr	Ni	Pb	Ti	Al	Fe	Mg	Mn	Si	Sr	
	C - Mississipian, Rundle Group, South-western Alberta												
JR-630	10	3	3	ND	ND	18	530	150	5500	16	1700	280	Precipitated; Bahamit
JR-530	8	4	<3*	tr	ND	36	560	540	5000	17	3600	270	" "
78	ND	2	6	ND	ND	9	150	670	3600	21	1800	310	" "
JR-100	6	3	6	ND	ND	27	520	670	20000	21	2900	110	Skeletal; Crinoid/Brach
	Other Samples from Sedimentary Rocks												
Miami Oolite	35	17	<3*	ND	tr	81	62	57	410	ND	10000	4800	Oolite
Spirifer	49	4	ND	tr	tr	37	1100	4900	2200	1200	3700	410	Fossil (Spirifer)
Vug Calc.	ND	2	ND	ND	tr	7	850	110	2900	2100	3100	140	Vug Calcite

* 3 ppm. is taken for calculations;

** 20000 ppm. is taken for calculations.

Although three other carbonate samples are listed with this group, their values are not included in the averages since they represent rather extreme deviations in their age or origin.

The arrangement of the results according to a precipitated or skeletal origin showed no significant differences in composition. So, in the carbonates of Ordovician limestones hardly any differences in composition of these two types is noticed, although here the amount of skeletal type samples is in the highest proportion. The type of the parent limestone for each sample is indicated in Table VI and more descriptive data is given in Appendix II.

The deviations of the B, Ba, Cr, Ti, Sr, Mn, and Si values from the mean within each age group are not large; the values for Al and Fe are slightly larger. The averages of element concentrations among the different age groups are considerably greater, particularly that of Mn, which is approximately from 2 to 10 fold (Table VII).

The high values of Mg in three samples were checked by the analysis of samples diluted 1:1 by $CaCO_3$. The results obtained were still slightly above the limit of the working curve, but the approximate values are given in Table VII and the values of 20000 ppm. were taken for calculation of the Mg averages shown in Tables VII, VIII and elsewhere in this thesis.

TABLE VII

Ranges and Average Composition of Carbonates from Various Age Groups of Palaeozoic Limestones

Element	Ordovician		Devonian		Mississipian		All Palaeozoic Limestone Carbonates	
	6 Samples		3 Samples		4 Samples		13 Samples	
	Range	Aver.	Range	Aver.	Range	Aver.	Range	Aver.
B	ND-16	10	ND-9	6	ND-10	6	ND-16	8
Ba	3-10	5	2-6	4	2-4	3	2-10	4
Cr[a]	ND- 3	3	ND- 3	tr	3-6	4.5	ND-6	2
Ni	ND-tr	tr	ND-tr	tr	ND-tr	ND	ND-tr	tr
Pb	ND-tr	ND	ND	ND	ND	ND	ND-tr	ND
Ti	27-82	48	32-65	49	9-36	22	9-82	41
Sr	310-490	388	170-320	253	110-310	242	110-490	312
Mn	130-620	290	30-41	34	16-21	19	16-620	147
Al	500-1600	890	640-1000	816	150-560	440	150-1600	735
Fe	780-1900	1347	550-610	576	150-670	507	150-1900	911
Mg[b]	2800-4700	4050	4200- 20000	14733	3600- 20000	8375	2800-20000	7846
Si	3300-8100	4617	2000-3100	2366	1700-2900	2500	1700-8100	3454

a - Cr values 3 ppm. were taken as 3 ppm. for calculations.

b - Mg values 20000 ppm. were taken as 20000 ppm. for calculations.

The composition of this group of unmetamorphosed carbonates is compared in Table VIII with other limestone analyses recently published, namely those of Pennsylvavian Limestones from Illinois (M.E. Ostrom, 1957) and Mississipian, Pennsylvanian and early Permian limestones from Kansas (R.T. Runnels and J.A. Schleicher, 1956) and also with the average composition of limestones (Rankama and Sahama, 1950, Table 5.52).

TABLE VIII

Composition of Different Limestones (in ppm.)

Elem.	Palaeozoic Samples (13)		Ostrom (92)		Runnels and Schleicher (288)		Rankama and Sahama
	Range	Aver.	Range	Aver.	Range	Aver.	Average Limestones
B	ND-16	8	1-200	18	0.5-300	6.9	3
Ba	2-10	4	10-10000	260	10-3000	68	120
Cr	ND-6	2^d	3-61	11	1-200	6.2	2
Ni	ND-tr	tr	ND-70	15	0.5-100	9.4	0
Pb	ND-tr	ND	6-100	26	10-200	9.1	5-10
Ti	9-82	41	tr-2400	400	10-6000	200	no data
Sr	110-490	312	240-810	490	14->20000	470^b	425-765
Mn	16-620	147	400-3700	1400	20-6000	850^b	385
Al	150-1600	735	-	-	$420\text{-}47060^c$	6720^c	4300
Fe	150-1900	970	3200-46000	13000	700-49210	9240	4000
Mg	2800->20000	7846^a	-	-	745-312000	30500	47700
Si	1700-8100	3454	-	-	714-112300	10740	24200

a - Mg values >20000 ppm. were taken as 20000 ppm. for calculations.

b - Average of samples in which the element was detected.

c - Included Ti, Mn, V. (325 samples chemically analyzed for major elements).

d - Cr values <3 ppm. were taken as 3 ppm. for calculations.

The results obtained in this work are in some agreement with figures given by Rankama and Sahama, except for Ba, Mn, Al, Fe, and Si, which are much lower in the present study but disagreement is more or less greater when they are compared with the results reported by other authors.

The averages for the writer's samples are all lower than those of Ostrom and of Runnels and Schleicher.

TABLE IX

Comparison of Elements Concentrations in the Natural Limestone Samples and their Acid Insoluble Residue

(Extracted from Strakhov, 1955)

Average Concentration in ppm.

	Fe		Mn		P		Cu		Cr		Ni		Co		V	
	A	B	A	C	A	C	A	C	A	C	A	C	A	C	A	C
Elements Distribution in the Natural Rock Samples																
Pashiysk and Domanic sediments with low organic carbon content	20600	12400	730	1470	650	350	23	11	12	nil	14	3	nil	nil	23	12
Domanic sediments with high organic carbon content	7900	3700	120	200	600	-	24	14	nil	nil	32	6	nil	nil	79	18
Element Distribution in Acid Insoluble Residue of the Same Samples																
Pashiysk and Domanic sediments with low organic carbon content	98700	161800	4490	14000	3130	5090										
Domanic sediments with high organic carbon content	46500	79400	710	2130	3900	-										
In all low-frasnian sediments							111	132	33	nil	64	40	nil	nil	118	143

A - Argillaceous Limestones - 14 Samples
B - Limestones and Dolomites - 3 Samples
C - Limestones - 9 Samples

However, these disagreements may be explained, to a certain extent, by the fact that values for purified carbonates are being compared with limestones. Ostrom (1957, P.1) expressed an opinion that: "Those limestones containing clay or shale as an impurity are likely to contain a greater amount of trace elements than pure limestones...". Facts supporting this point of view are reported by Strakhov et al (1955) who compare minor and trace element analyses of lower Devonian limestones and argillaceous limestones with analysis of the acid insoluble residue of the same samples (Table IX). This comparison shows that the concentration of trace and minor elements in the argillaceous impurities of the limestone is much greater than in the limestone carbonates. The same trend is seen when a comparison of values for argillaceous limestones with more pure limestones is made (Tables IX and X).

TABLE X

Average Trace Element Concentration in Limestones

of Voronezh Massif

(Data of E.S. Zalmanson, 1951;

extracted from Strakhov, 1955) in ppm.

Element	Argillaceous Limestone 2 Samples	Limestone 7 Samples
Cr	11	0
Ni	32	0
Co	15 (?)	3
V	10	10
Cu	46 (?)	25
$CaCO_3$%	82.5	93.46

These facts and conclusions reported by different authors indicate a lower concentration of minor and trace elements in the purified carbonates. Therefore, the purified Palaeozoic carbonates of this study are suitable for comparison with the other carbonates extracted from different parent rocks.

Carbonates from Precambrian Marbles

Table XI shows analytical results for 10 carbonates from Grenville marbles from various localities in Ontario and Quebec.

TABLE XI

Analysis Results for Carbonates from Precambrian Marbles

(Group II)

	B	Ba	Cr	Ni	Pb	Ti	Al	Fe	Mg	Mn	Si	Sr
CA-84	12	27	ND	ND	3	14	260	210	>10000 1)	130	1300	230
CA-103	4	11	ND	ND	ND	23	560	890	>20000	66	1700	500
CA-43	5	7	ND	ND	9	7	44	1200	>10000	110	440	310
PC-187	5	69	ND	ND	tr	17	780	890	>10000	610	3200	180
PC-189	32	44	ND	ND	tr	37	310	650	5-10%	380	>10000 1)	100
44-1941	12	16	ND	ND	tr	7	20	3600	5-10%	210	390	83
L-807	36	23	ND	ND	tr	6	51	4700	5-10%	470	1200	45
M-16	36	15	ND	ND	tr	19	290	3900	5-10%	360	3600	130
M-6116a	32	>200 1)	ND	ND	ND	9	1500	25	390	92	12000	450
FR-5	6	12	ND	ND	12	8	56	740	690	78	270	930

1) Ba > 200 as 200 ppm., Si >10000 as 10000 ppm. and Mg >10000 as 10000 ppm. and 5-10% as 75000 ppm. are taken for calculations.

In this group all the elements for which results were obtained show considerable variations in their concentrations from sample to sample. The "tr" values of Pb are in the approximate range of 1-2 ppm. However, the average for the whole group is calculated from three samples with determined values. Cr and Ni were detected in none of the samples. Mg was too abundant to be determined directly in all except two samples: high Mg contents were therefore estimated visually in diluted mixtures.

Averages and ranges of element concentrations of this group and sedimentary carbonates are compared in Table XII. The information on the degree of element enrichment or impoverishment will be discussed later.

TABLE XII

Average Composition of Palaeozoic and Precambrian Marble Carbonates

Element	Palaeozoic Carbonates (13)		Precambrian Marble Carbonates (10)	
	Range	Aver.	Range	Aver.
B	ND-16	8	4-36	18
Ba	2-10	4	7- 200	42.4
Cr	ND-6	2	ND	ND
Ni	ND-tr	tr	ND	ND
Pb	ND-tr	ND	ND-12	2.4
Ti	9-82	41	6-37	15
Sr	110-490	312	45-930	296
Mn	16-620	147	66-610	250
Al	150-1600	735	20-1500	387
Fe	150-1900	970	25-4700	1680
Mg	2800->20000	7846	390-100000	35100
Si	1700-8100	3454	270-12000	3410

Lens and Vein Carbonates from the Precambrian Skarn Series

Nineteen analyses of Lens and Vein carbonates are shown in Table XIII. They mostly represent samples from different localities as well but include slightly different carbonates from the same hand specimens in three cases.

TABLE XIII

Analysis Results for Lens and Vein Carbonates of Grenville Rocks

(Group III)

	B	Ba	Cr	Ni	Pb	Ti	Al	Fe	Mg	Mn	Si	Sr
A-1	23	36	ND	tr	17	16	110	6200	3200	2600	420	3800
A-2	20	98	"	tr	44	13	25	3700	3000	2000	110	5800
A-3	6	15	"	tr	60	13	230	3200	1700	1200	1700	970
A-4	17	30	"	ND	17	17	140	5800	2700	3000	1200	2500
A-5a	12	10	"	ND	21	10	460	3500	1300	830	3000	760
A-5b	12	90	"	ND	16	10	710	4400	2000	930	3700	740
A-5c	11	11	"	ND	22	9	670	5100	2500	950	2300	1300
A-6a	9	98	"	ND	4	36	260	3700	10000	440	2600	570
A-6b	10	98	"	ND	4	43	1700	3700	13000	380	11000	530
CA-105	22	6	"	ND	12	9	74	1400	1300	650	860	3700
Q-67	28	100	"	ND	27	7	380	1900	600	700	4400	2500
ON-6b	48	16	"	tr	18	23	540	2600	5500	1200	1500	1100
ON-15	10	16	"	tr	13	10	470	3500	1700	940	1900	1000
ON-26	25	79	"	tr	18	20	1100	5800	4700	2400	5400	5200
ON-30a	41	57	"	tr	45	45	83	6000	2000	3000	600	1900

TABLE XIII (contd.)

	B	Ba	Cr	Ni	Pb	Ti	Al	Fe	Mg	Mn	Si	Sr
ON-30b	21	50	ND	tr	29	46	97	5500	2000	2900	600	1400
ON-30c	20	38	"	tr	26	44	300	5500	2100	2900	1100	1700
ON-31	26	54	"	ND	12	10	78	1300	13000	430	930	2500
ON-39	44	96	"	ND	16	17	180	1500	12000	890	3600	6600

The samples ON 30 a, b, and c are carbonates of different grain size in the same parent rock: a - coarse, b - medium, and c - fine grain. In these samples the following changes in element distribution are indicated: a slight but gradual decrease in B, Ba, and Pb content from the coarse to the fine grain size: no clear changes in the Ti, Mg, Mn, Fe, Sr, Cr, and Ni contents and a large (2-3 fold) increase in the Al and Si contents of the fine-grained carbonates.

Samples A-5a, b, and c, and A-6a and b represent a transition in carbonate colour of two corresponding hand specimens A-5 and A-6. A-6a is a pink variety and A-6b a white one. Their compositions have no changes over the limits of variation in B, Ba, Pb, Ti, Fe, Mn, Sr, Cr, and Ni contents; a large increase in the Al and Mg contents as well as a large decrease in the Si content occur in the white carbonate. Samples A-5a (pink), A-5b (gray), and A-5c (white) were collected within 1" - 3" from a contact with hybrid gneiss and show rather more uneven element distribution. There are no significant changes in B, Ti, Pb, Cr, and Ni contents, but the Fe, Mg, and Mn contents increase gradually and in large amounts from the pink through the gray to the white variety while the Si content increases from the pink to the gray and then decreases considerably in the white carbonate. The highest Sr content is in the white carbonate, while the Ba content is highest in the gray one.

The rest of the analyses represent samples from different localities and vary considerably in the concentrations of all the elements sought.

The average and range of element concentration of this group is compared with those of marbles in Table XIV, which indicates further and more intensive enrichment of trace and minor elements in Lens and Vein carbonates, particularly Sr. This phenomena is discussed in more detail in the following section.

TABLE XIV

Average Composition of Carbonates from Precambrian Marbles and Lens and Vein Carbonates

Element	Marble Carbonates (10)		Lens and Vein Carbonates (19)	
	Range	Aver.	Range	Aver.
B	4-36	18	6-48	21
Ba	7-200	42	6-100	52
Cr	ND	ND	ND	ND
Ni	ND	ND	ND-tr	ND
Pb	ND-12	2.4	4-60	22
Ti	6-37	15	7-46	21
Sr	45-930	296	530-6600	2345
Mn	66-610	191	380-3000	1492
Al	20-1500	387	25-1700	400
Fe	25-4700	1680	1300-6200	3910
Mg	390-100000	35100	600-13000	4437
Si	270-12000	3410	110-11000	2470

Enrichment and Impoverishment of Different Carbonate Groups

A comparison of the average concentrations of elements sought shows significant changes from one genetic group to another.

On the grounds discussed earlier in this paper, the average composition of the carbonates from sedimentary rocks can be taken as first approximation of the average composition of original limestone carbonate. Thus, in further discussion, the other group averages are compared with it for a determination of enrichment or impoverishment of the other carbonate groups.

Carbonates from Sedimentary Rocks

The average composition of this group compared with the averages of its subdivisions by age is shown in Table VII and indicates considerable variations in the ranges and the averages of element concentration of these subgroups.

The following elements Fe, Mn, Si, Sr, and B show a decrease (from 1/2 to 2 but Mn ten-fold) in concentration from the carbonates of Southern Ontario Ordovician limestones to those of South-western Alberta, Devonian, and Mississipian limestones. The average concentration of these elements fluctuates slightly (Fe, Sr, Si) or retain the same level (B) in the limestones of the last two sub-groups except Mn which is lowest in the Mississipian samples.

The change in the Al and Ti averages are of a different character. They remain on the same level in the carbonates of Southern Ontario Ordovician and in those of South-western Alberta Devonian limestones, but are approximately twofold decreased in the carbonates of Mississipian limestones of South-western Alberta.

The group of elements found in smaller amounts Ba, Cr, or present as traces, Ni, display no pronounced variations in the composition of all three sub-groups of sedimentary carbonates. Since Pb is not detectable in all of these samples, it can be assumed that it follows the same pattern of distribution.

The approximate average values of Mg (in three samples, its concentration being above the range of working curve is estimated as 20000 ppm.) show the following distribution in the age sub-groups: The Mg concentration is lowest in the carbonates from Ordovician limestones. It is considerably increased in Devonian and slightly less in those of Mississipian limestones.

The Carbonates from Marbles and Lens and Vein Carbonates.

The results of analysis have shown that there is a considerable increase in the concentration of most minor and trace elements (except Ti, Al, and Si) from the carbonates of unmetamorphosed limestones through those of Precambrian Marbles to the Lens and Vein carbonates.

Table XV shows the average concentrations and the values of enrichment or impoverishment of each element in each group compared with those of sedimentary carbonates. The Lens and Vein carbonates are compared also with the carbonates from the marbles. The coefficient of standard deviation or analytical error (V) determined with sample A-5a is shown in this table as well.

TABLE XV

Enrichment and Impoverishment of Minor and Trace Elements in Carbonates (in ppm.)

	Group Average			Carbonates of Marbles comparing with Palaeozoic Carbonates		Lens and Vein Carbonates comparing with Carbonates of Marbles		Lens and Vein Carbonates comparing Paleozoic Carbonates		Coefficient of Standard Variation (Sample A-5a)
	Polaeozoic L-st.	Marbles	Lens and Vein							
	13	10		Enrichment	Impoverishment	Enrichment	Impoverishment	Enrichment	Impoverishment	%
B	8	18	21	10	-	3	-	13	-	7.5
Ba	4	42.4(25) 1)	52	38.4(21)	-	9.6	-	48	-	5.0
Cr	2	ND	ND	-	2	-	-	-	2	-
Ni	tr	ND	tr	-	tr	-	-	-	tr	-
Pb	ND	2.4	22	2.4	-	17.6	-	22	-	11.0
Ti	41	15	21	-	26	6	-	-	20	6.5
Sr	312	296	2345	-	16	2049	-	2033	-	12.0
Mn	147	191	1492	44	-	1301	-	1345	-	8.0
Al	735	387	400	-	348	13	-	-	335	9.0
Fe	970	1680	3910	1700	-	2230	-	2940	-	7.0
Mg	7630	34100	4437	29470	-	-	29663	-	3200	7.0
Si	3454	3410	2470	-	14	-	940	-	984	8.0

1) Figure 42.5 includes in the average calculations sample with 200 ppm. Ba as 200 ppm.

Figure 25 does not represent this sample.

Compared with limestones, marble carbonates show considerable increase in Mg, Ba, and Fe, slight increase in B and Mn, little change in Cr, Ni, Pb, Sr, and Si, and a decrease in Ti and Al.

The Lens and Vein carbonates display a large enrichment in Sr, Mn, and Fe, moderate enrichment in Pb, B, Ba, little change in Ni and Cr, a considerable impoverishment in Mg and Si compared with both limestone and marble groups; a little change in Al and Ti compared with marbles, and an enrichment in them compared with limestones.

Diagrams of element distribution in the samples of various genetic groups are attached in Appendix III, figs. 1 to 8.

The averages for the groups show considerable differences, which might be introduced by secondary processes such as metamorphism and/or metasomatism. Therefore, the total averages for all the analyzed samples are not calculated, being considered unrepresentative.

VII DISCUSSION

Location of Minor and Trace Elements in Carbonates

Two different types of location are anticipated for minor and trace elements in any mineral analyzed. One occurs in contamination by foreign grains, inclusions, and intergrowths with other minerals, while the other one is in the crystalline structure of the mineral itself.

The presence of contamination in minerals is possible and requires detailed discussion of sample purification.

Purity of the Samples

The main purification methods, described elsewhere in this paper, are based on two properties of minerals: Specific gravity and magnetic susaptibility. Therefore impurities differing in these particular respects were easily eliminated while those with similar properties as carbonates were separated only to a certain extent.

The final purification was made under binocular microscope by use of electrostatic attraction for picking up the impurities. At this stage the colour and appearance of foreign grains were used for their identification, and mineral grains similar in this respect to carbonates were difficult to eliminate.

Almost all of the samples studied (except sedimentary varieties) were extracted from Precambrian rocks containing numerous additional minerals. These minerals may be grouped as follows:

I. Minerals containing components not analyzed in this work:

graphite, fluorite, apatite.

2. Minerals easily separated from carbonates: sulphides, Feoxides, sphene, diopside, tremolite, chrondrodite.
3. Minerals difficult to separate from carbonates: phlogopite, scapolite, quartz.

In one sample (CA-84) 2 - 3% of graphite was impossible to separate but the rest of the samples did not contain much of the easily noticeable purple fluorite and green apatite which were separated during the final stage of purification.

The proof of satisfactory separation was not always possible to establish directly, i.e. by examination under binocular microscope, particularly for the grains with colour and appearance resembling carbonates. Some indirect reasoning, however, suggested that satisfactory purification of the carbonates had been achieved.

Thus, sample FR-5 representing silicated marble, in the case of poor purification, should contain considerable amount of Si, but the results of analysis for this sample show the lowest concentration of Si in all the group of marble carbonates, proving that silicates present in the rock sample have been very satisfactorily separated.

The degree of separation of magnesian silicates could additionally be checked by the proportion of Mg and Si in the samples enriched in Mg. If separation had not been satisfactory then the concentration of Si in these samples should vary in proportion to the concentration of Mg. The results computed in Tables XI and XIII, however, do not show any indication that such a relation occurs. On the contrary, the marble carbonates which are very rich in Mg contain less Si.

Moxham (1958) discussed in more detail the effect of sphene on the results of spectographic analysis of pyroxenes. He concluded that 1 grain of sphene per thousand of the sample will increase the concentration of Ti by approximately 250 ppm. It should be noted that very rare sphene grains occurred in the carbonate samples and were easily detected and eliminated at the final stage of purification.

The last group comprises two minerals which were poorly separated at the main stages of separation. The first mineral is mica flakes (mostly phlogophite) which were found in considerable quantity in almost all the samples. During final purification they were easily identified with the help of their appearance and separated by use of electrostatic attraction. Presence of some unnoticed grains can affect the concentrations of Mg, Al, and Si. However, no indirect control of this effect could be established since it is possible that micas of different composition were present in the samples.

The second mineral of this group, scapolite, was most difficult to separate since its properties are similar to carbonates.

Filby (1957) achieved purification of scapolites from carbonates by dissolving samples in dilute HCL. It is obvious that this method is of no use for purification of carbonates.

No successful method for scapolite separation was found in this work. Fortunately, a microscopic study made by Shaw (unpublished) has shown that most of the samples analyzed in this study contain little or no scapolite.

The amounts of Mg, particularly in the marble carbonates, indicate that some submicroscopic intergrowth of dolomite in calcite are probably present although microscopic investigation of the samples (Shaw, unpublished) did not show any evidence.

It appears that at the achieved degree of purification the contamination of the samples by the presence of foreign grains does not affect the results noticeably. In our case the analytical method (considering its coefficient of standard deviation) could introduce more variations in the results obtained than the achieved purity of samples. It is also clear that the effect of trace and minor elements in the impurities, in this case, should be much smaller or rather negligible.

No intergrowths were observed between carbonates and other minerals, but may have been present on a sub-microscopic scale. Contamination from such minute inclusions can never be ruled out, but is likely to be negligible.

From the above discussion the effect of contaminating factors in the samples is considered to be of no importance at the achieved degree of purity, and therefore it was not accounted for in changes of element concentration either among samples or groups of samples. As well, it will not be considered in the problem of locating elements in the carbonates.

Location of Minor Elements in the Structure of Carbonates

It is well known that many minerals contain elements which are not present in their theoretical formula. These elements either occupy structural sites or are situated in structural voids among other elements.

In geochemistry the substitution of minor and trace elements into the structure of a mineral and their relationship within the lattice is often explained by the concept of diadochy.

Rankama and Sahama (1950, P.121) give the following definition of this concept: "two atoms or ions occurring in a mineral are called diadochic if they are capable of replacing each other in the structure of the mineral, each occupying the other's position".

Thus, isomorphic mixtures with more strict compositional and structural requirements to the compounds participating are a specific case of this concept.

In the present study several of the elements found in the carbonates correspond to the requirements of isomorphous mixtures; they are Mg, Fe, Mn, Ba, Sr, and Pb.

Data of various carbonate analyses show that they also tolerate some quantities of Si, Al, Ti, Cr, Ni, and other elements. In the present study the above elements were found in variable amounts in all three genetic groups of carbonates. The possible location of these elements in the carbonates, whether as occupying structural sites or as held in the crystal in the form of a dispersed phase, will be discussed later.

The location of boron could be in the structural voids, if one assumes that it is present in form of cation, since its very small ionic radius would permit such implacement. It should not be overlooked that it might be present in the form of calcium or magnesium borates (Rankama and Sahama, 1950, P.490) as well as in the form of gaseous inclusions and submicroscopic inclusions of tourmaline.

The above estimate of substitution of some elements for various structural localities is based on Goldschmidt's empirical rule of ±15% tolerance in atomic radii for the guest element to the major element in the structure. In many cases, however, this rule does not hold (Shaw, 1954) and other explanations are to be sought for the distribution of the minor elements.

Most of these explanatory factors have been studied for silicates and mainly considered with respect to the formation of igneous minerals where ions can freely move in the magma and can be selected during crystallization in accordance with their concentration and properties.

The conditions are entirely different during formation of metamorphic or metasomatic minerals. The genisis of these minerals involves the problem of transportation to the site of reaction with possible compositional variation of incoming material. The bulk of the reacting material depends upon the composition of the rock in situ. Any soluble material produced by a reaction can be removed. Although the processes as well as the ionic substitution proceed in accordance with chemical laws, some alterations may occur, particularly when the presence of colloids is anticipated. Nevertheless, some of the factors explaining distribution of minor elements concerning igneous minerals will be very shortly mentioned.

Ramberg (1952) considered the silicates as increasingly polymerized compounds, and discussed in detail the Si-O bond. He shows how small cations of high charge (Mg, Fe) prefer the simplest member in the series (orthosilicates) while the larger and low charged cations concentrate in the most complex member (tectocilicates) which also more readily accepts substitution of Si by Al in Si-O links.

Ahrens (1952, 1953) employed the ionisation potential of an element as a most important factor controlling its distribution, suggesting that elements of similar ionization potential are diadochic.

Ringwood (1955) explains diadochy from the standpoint of electronegativity and proposes that it is more possible for ion with lower En to be preferentially accepted in the structure since it forms a stronger bond.

Fersman (Saukow, 1950) explained element distributions using the energy of the crystalline lattice which is supposed to be a function of ion charges and their radii. It is measured by the amount of work required for destruction of the ionic bond in the composite ions. For the determination of this energy for any crystalline compound, he calculated EK values (energetic coefficients) of elements.

All the above-mentioned concepts, however, encountered numerous exceptions and contradictions in their application.

The crystallochemical constants of the elements analyzed to which reference has just been made, are listed in Table XVI. They are as follows:

- ionic radii (R) for six-fold coordination given by Rankama and Sahama (1950, Appendix 3)
- ionisation potentials listed by Ahrens (1952)
- electronegativity values (En) after Fyfe (1951)
- lattice energy coefficients given by Saukov (1950)

Since the minerals studied in this work are of metamorphic origin, some other views helpful in an explanation of the structural relations between major and minor elements should be presented.

Graf and Lamar (1955, PP.668, 669) pointed out that having unsaturated ionic bonds and abnormal lattice spacing in the near-surface layer, a crystalline carbonate surface is an abnormal environment allowing increased absorption. Many other minerals have the same properties.

An experimental study of Douglas and Walker (as it is reported by Graf and Lamar, 1955) has shown that there is a negative surface charge on calcite powder resulting from the loss of Ca ions in the surfacial layer after various electrolytic solutions had been passed through it. As a result, a strong adsorption of positive ions (Ba^{++}, Pb^{++}, Mg^{++}) and some negative ions (HCO_3^-, $CO_3^{=}$, $(PO_3^-)_6$) occurred.

These theoretical considerations and experimental results indicate a possible adsorption of positive and negative ions by growing carbonate crystals during metasomatic processes or during processes of material redistribution in situ.

Thus, in our case one can anticipate presence not only of Mg, Fe, and Mn in calcite structures, but also that of larger positive ions such as Sr, Pb and Ba.

The experiments showing adsorption of large anions by carbonate surfaces encourages a suggestion; that analogous adsorption of Al_2O_3, SiO_2, TiO_3 and other anions may have occurred during crystal growth, whether during metamorphic replacement and redistribution or during precipitation and diagenetic recrystallization, assuming that in each case some fluid was present.

TABLE XVI

Crystallo-Chemical Constants of the Elements Analyzed

Element	Co-ord. Number	R (Å)	Ip	En	Ek
B^3	6	0.20	37.9	2.0	6.00
Si^4	6	0.39	45.1	1.8	8.60
Al^3	6	0.57	28.4	1.5	4.95
Cr^3	6	0.64	96.0	1.2	-
Ti^3	6	0.69	-	-	4.65
Ni^2	6	0.78	18.2	1.7	2.18
Mg^2	6	0.78	15.03	1.2	2.10
Fe^2	6	0.83	16.24	1.65	2.12
Mn^2	6	0.91	122.0	1.4	2.00
Ca^2	6	1.06	11.87	1.0	1.75
Sr^2	6	1.27	11.03	1.0	1.50
Pb^2	6	1.32	39.0	1.1	1.65
Ba^2	6	1.43	10.0	0.85	1.35

De Vore (1955) anticipates that direct substitution can be replaced by a process of adsorption. He further suggests that, most of the amount of the minor element in the structure, or at least a portion of it, can be incorporated by the growing crystal surfaces. Part of the minor elements are consequently located not on the structural sites, but rather in the structural defects and dislocations.

Chukhrov (1955) supports the importance of adsorption and believes that: "elements adsorbed by a crystalline substance during its growth do not participate in its structure, but are forming in it solid solutions either true or colloidal. It seems to be that in this particular manner minerals capture admixtures of the elements which cannot be accepted in their crystalline structure". (PP.236-237).

He also advocates that dispersed phase of solid particles in crystalline minerals can be formed in result of either mechanical capture during crystallization or disintegration of isomorphous mixtures at a decreased temperature with a very vague difference between them in most cases. The classification of dispersed systems by their sizes is cited as follows:

(a) coarse dispersed systems with the size of dispersed phase of 1000 Å (visible under microscope).

(b) colloidal dispersed systems with the size of dispersed phase 1000-10 Å (submicroscopic).

(c) molecular and ionic dispersed systems with the size of dispersed phase of 10 Å.

In his opinion, "the abundance of some elements in minerals which could not be included into the lattice in respect to the laws of isomorphism is often explained by the presence of dispersed colloidal particles in it ("anomalous mixed crystals")." (PP.248-250).

One cannot expect, of course, that the abundance of all the minor elements in carbonates will be explained on the basis of the above theories, as De Vore's work is restricted to a few elements in some particular minerals and may not be a general case. But, Chukhrov's views are open to an argument since he admits that: "solid dispersoid minerals are, as yet, studied to an inadequate extent".

However, these theories explain the abundance of the elements which are difficultly accepted into the structure and therefore may be helpful for location of Al, Ti and Si in carbonates. How they occur, whether as submicroscopic inclusions, colloidal or molecular dispersed plases is difficult to anticipate, but in agreement with these theories they should not occur on the structural sites of carbonates.

Geochemistry of the Elements Sought.

In the following discussion of the geochemical properties and relations of the elements sought in the carbonates, these elements are subdivided into groups in accordance with their ability to substitute into the carbonate structure.

The first group comprises Mg, Mn, and Fe which having ionic radii most similar to calcium readily substitute for it in the calcite structure to a considerable degree.

The second group includes Sr, Ba, and Pb which by reason of their ionic sizes preferably substitute for Ca in the aragonite structure although they can substitute to a smaller extent in the calcite structure.

The third group consists of Al, Si, and Ti which probably cannot substitute on the Ca structural sites in the carbonates.

The fourth group includes B, Cr, and Ni, one of which (B) is present in all the carbonate groups, and the others only in sedimentary carbonates. Probably the last two can be partly related with the other minor elements in the carbonates.

Magnesium

The average magnesium concentrations in different carbonate groups show large variations.

The abundance of Mg in sedimentary carbonates is 7850 ppm. with considerable variations within the sub-groups (see Table VII); the marble carbonates show the highest Mg abundance - approximately 35100 ppm., while the Lens and Vein carbonates the lowest - 4440 ppm.

The abundance of Mg in the limestones shown in Table VIII, unfortunately, cannot be compared with the results of the present investigation (Table VI) since dolomite limestones were included in the averages reported by the other authors. In this work high Mg concentration (72.0%) was found in three samples of sedimentary carbonates (in two of precipitated and in one of skeletal type, Table VI).

2%.

Mineralogical study (Shaw, 1956) of the Grenville rocks from which the investigated metamorphic carbonates were extracted did not reveal any dolomite in the marbles and "skarn series". Consequently, the magnesium detected should be located within the calcite structure. In present work most of high Mg concentrations were estimated semi-qualitatively. Therefore it is difficult to decide whether magnesium occurs in an exsolution of dolomite and magnesian calcite or in the latter only.

An experimental study of dolomite - magnesian calcite relations by Graf and Goldsmith (1955) showed that at elevated temperatures and Co_2 pressures calcites contain Mg in solid solution in equilibrium with dolomite or periclase. The exsolution curve revealed that field of unmixed magnesian calcite containing 6 mol. per cent of $MgCO_3$

starts at 500° C. and at the temperature of 800° C. the amount of $MgCO_3$ in magnesian calcite increases to 22 mol per cent.

Most of Mg enriched metamorphic carbonates of present work occur in the group of Precambrian marbles. The amount of $MgCO_3$ in them (recalculated from Mg concentrations) is approximately 3.5% to 26%.

If one assumes that Grenville marbles are of the same metamorphic facies, then for the same temperature the above variation in Mg concentrations suggests presence of dolomite - magnesian calcite exsolution in the samples of higher Mg concentration.

Goldsmith, Graf and Joensuu (1955) reported 2.2 to 6.6 mol. per cent of $MgCO_3$ in natural magnesian calcites or calcite marbles (with no dolomite present). This supports presence of dolomite - magnesian calcite exsolution in the carbonates of Precambrian marbles.

However, possibility of big analytical error for semi-qualitative estimation in spectrographic analysis makes this conclusion doubtful.

Manganese

Manganese is closely related to iron in respect to its chemical properties. Its natural occurrence is similar to that of iron also, though they are more or less separated during processes of sedimentation.

Although most manganese in the sea precipitates in the form of Mn^4 , it can also precipitate as Mn^2 in the form of carbonates when pretective organic colloids are removed from manganese bicarbonate. Thus, $MnCO_3$ is common in deep-sea sediments.

From hydrothermal solutions manganese and iron can be deposited together forming Fe-Mn carbonate (Manganosiderite).

In calcite Mn^2 readily substitutes at the structural sites of calcium having preference in respect to iron since its ionic size is more similar. (See Table XVI)

In natural carbonates up to 42 per cent of Ca sites can be replaced by Mn^2 (Kreiger, 1930) while in synthetic calcites, only up to 15 per cent (Vengard, 1947).

Distribution of manganese in various groups of sedimentary carbonates investigated is more uneven than that of any other element. For this group of carbonates the ratio Fe:Mn in different age subgroups changes as follows: 4.64 in Ordovician, 16.94 in Devonian, 26.68 in Mississipian, and 6.20 as the average value of all the sedimentary groups. For the marbles the ratio is 6.72 and for the Lens and Vein carbonates it is 2.62.

The average manganese content in the various genetic groups (Table XV) increases simultaneously with iron from the sedimentary carbonates through the marble variety to the Lens and Vein carbonates. (See plate, Appendix III, Fig. 1).

The manganese content in the last group is close to that reported by Moxham for Grenville metamorphic pyroxenes average of 1350 ppm. (range from 600 to 2500 ppm.) and amphiboles average of 1280 ppm.

In Table XVII Mn content found in carbonates is compared with that in various rocks.

TABLE XVII

Manganese Content in Carbonates Compared with other Rocks

		Min.	Max.	Aver.
Carbonates from Paleozoic Limestones		17	620	147
Carbonates from Precambrian Marbles		66	610	191
Lens and Vein Carbonates		380	3000	1492
Limestones (composite)	Rankama & Sahama (1950) Table 31.4			385
Oolites, Scania, Sweden	Rankama & Sahama (1950) Table 31.4			1800
Ultra basic rocks	Rankama & Sahama (1950) Table 31.3			1120
Granites	Rankama & Sahama (1950) Table 31.3			965
Limestone (Paleozoic from Illinois)	Ostrom (1957)	400	3700	1400
Limestones (Paleozoic from Kansas)	Runnels & Schleicher (1956)	20	6000	850

Iron

The abundance of iron shows a gradual increase from less to more metamorphosed carbonates investigated. The averages are: 911 ppm. in Palaezoic carbonates, 1680 ppm. in Precambrian marble carbonates, and 3910 ppm. in Grenville Lens and Vein carbonates.

The average iron content in various rocks is as follows (Rankama and Sahama, 1952, P. 668): Igneous rocks - 7.15 per cent, Shales - 6.73 per cent, Sandstones - 1.41 per cent, and Limestones - 0.54 per cent.

Ferrous iron precipitated in the carbonate form is common and important in sediments. Its precipitation and acceptance in carbonates is analogous to manganese with the maximum Fe ^{2} content for carbonates of 48.2 per cent in siderite.

In the substitution into calcite structure, iron shares cationic sites with other bivalent elements where its proportion can be, to a certain extent, evaluated by the ratio to corresponding elements. In the case of carbonates studied the Fe:Mg ratio for sedimentary group is 0.116, for marble group is 0.048, and for Lens and Vein carbonate group is 0.881.

Strontium

The abundance of strontium in the various groups of carbonates compared with that of some rocks is shown in Table XVIII.

The size of strontium ionic radius (Table XVI) and other chemical properties are similar to those of calcium. Therefore, strontium is closely associated with it in sedimentary and igneous rocks.

Turebian and Kulp (1956) reported strontium crustal abundance of 450 ppm., while its abundance in limestones of 610 ppm. and in shales of 245 ppm.

Shaw (1954) found average Sr content of 710 ppm. in pelitic metamorphosed rocks of New Hampshire region in the Appalachians.

The highest Sr content in rocks is reported for nepheline syenites, although it is relatively evenly distributed among other igneous rocks.

In sedimentary rocks Sr is most abundant in limestones into which Sr can precipitate from sea water.

The results of analysis by Nall (1934) show 5-1400 ppm. (mean 702 ppm.) of Sr in sedimentary calcites and 4800 ppm. in magmatic calcite from the Fen area of Norway (Graf and Lamar, 1955, P.666). The increase in Sr content of magmatic calcite is 6.9 fold, while the increase in Sr of Lens and Vein carbonates compared to its concentration in sedimentaty carbonates investigated is 7.5 fold.

The incfease in Sr content of calcite formed at high temperatures is explained by a thermal effect on the structure which leads to more ready substitution of Sr into Ca sites. (Rankama and Sahama, 1950).

If this conception of Sr abundance is true, then the enrichment in Sr of Lens and Vein carbonates should have been completed at elevated temperatures.

Two more factors are in support of this view: (a) considerable amounts of Sr which enter postmagmatic solution; (b) inability of strontium to form minerals during metamorphism. (Rankama and Sahama, 1950, P. 482.)

The location of Sr in carbonates was discussed earlier; it enters into the calcite structure substituting for Ca.

TABLE XVIII

Strontium Content of Carbonates Compared with Other Rocks

Analyzed Sample	Reference	Strontium		
		Min.	Max.	Aver.
Carbonates of Palaeozoic Limestones		110	490	312
Carbonates of Precambrian Marbles		45	930	296
Lens and Vein Carbonates		530	6600	2345
Limestones (average)	Rankama & Sahama (1950) Table 15.4	425	765	
Carbonate Rocks, Southern Lapland	Rankama & Sahama (1950) Table 15.4			850
Nepheline Syenites	Goldschmidt (1954, P.245)			1400
Nepheline Syenites	Rankama & Sahama (1950) Table 15.4			1200
Basement Complex of So. Lapland	Rankama & Sahama (1950) Table 15.4			
Ultrabasics				9
Gabbros and Dolerites				80
Hetta Granites				250
Youngest Granites				90
Syenites				570
Syenites	Goldschmidt (1954, P.245)			700

Barium

The values of Ba concentration in various carbonate groups in this work are compared with the barium content in other rocks in Table XIX.

The Ba results of this study are much lower than those listed in Table XIX for corresponding material. However, the values given by Moxham for pyroxenes and amphiboles from the same Grenville area show relatively similar low content of Ba.

Although the chemical properties of barium are similar to those of calcium, its large ionic radius prevents a great amount of substitution in the calcite structure. It is generally accepted that Ba (as well as Sr) more readily substitutes into the aragonite structure.

TABLE XIX

Barium Content of Carbonate Compared with Other Rocks

Analyzed Sample	Reference	Barium		
		Min.	Max.	Aver.
Carbonates of Palaeozoic Limestones		2	10	4
Carbonates of Precambrian Marbles		7	200	42.4
Lens and Vein Carbonates		6	100	52.5
Crustal Abundance	Green (1953)			250
Limestones	Rankama & Sahama (1950) Table 15.4			120
Carbonate Rocks, So. Lapland	Rankama & Sahama (1950) Table 15.4			270
Syenites and Trachytes	Rankama & Sahama (1950) Table 15.3			1600
Nepheline Syenites	Rankama & Sahama (1950) Table 15.3			520
Rocks of Basement Complex of Southern Lapland	Rankama & Sahama (1950)			
Ultrabasics				18
Gabbros and Dolerites				45
Hetta Granites				670
Youngest Granites				630
Syenites				620
Grenville Pyroxenes	Moxham (1958)			11
Grenville Amphibles	Moxham (1958)			15

Lead

In this work only traces of Pb were detected in sedimentary carbonates. The amount is considerably lower than the limestone average reported by Rankama and Sahama (1950), although its content is gradually increased to an average of 2.4 ppm. in the marble carbonates and to an average of 22 ppm. in the Lens and Vein varieties.

Lead abundance in the pyroxenese of the same area of up to 49.8 ppm. is reported by Moxham (1958).

In pelitic rocks of New Hampshire (Shaw, 1954) lead content increases from the low-grade metamorphic rocks (16.1 ppm.) through the medium grade (23.3 ppm.) to the high-grade (27.3 ppm.) with the final average for all the rocks of Devonian Littleton formation of 24 ppm.

For comparison the lead content of some igneous rocks is shown in Table XX.

The ionic size of lead is slightly larger than that of calcium, indicating that it is more readily acceptable in aragonite structure (see Table XVI). Considering this commonly accepted view, one can anticipate occurrence of lead in carbonates investigated as a direct replacement of Ca sites in the calcite structure (to a small degree), in this way causing some imperfection in calcite structure.

The possible proportional increase of Pb and Sr was investigated by plotting Pb content vs. Sr content, but no linear correlation was found.

TABLE XX

Lead Content of Carbonates Compared with Other Rocks

Analyzed Sample	Reference	Lead		
		Min.	Max.	Aver.
Carbonates of Palaeozoic Limestones		ND	tr	ND
Carbonates of Precambrian Marbles		ND	12	2.4
Lens and Vein Carbonates		4	60	22
Limestones (average)	Rankama & Sahama (1950) Table 5.52			5-10
Gabbros and related Rocks (average)	Rankama & Sahama (1950) Table 41.4			5
Granitic Rocks (average)	Rankana & Sahama (1950) Table 41.4			9
Granities, Southern Lapland (average)	Rankama & Sahama (1950) Table 41.4			30

Aluminum and Silicon

Average aluminum and silicon contents in limestones of 4300 ppm. and 24200 ppm. respectively (Rankama and Sahama, 1950, Table 5.52) are most probably present in the form of Al-Si clay minerals and SiO_2 which are included into limestones during sedimentation.

Part of this material, having smaller size, may be included in carbonate grains. Thus, 735 ppm. of Al and 3450 ppm. of Si in the purified sedimentary carbonates may represent inclusions of various sizes corresponding to solid dispersoids discussed elsewhere in this paper.

Assuming that during metamorphic and particularly metasomatic redistribution of material, that fluids are present, one can expect migration of these elements in anionic or molecular form and consequently, in metamorphic carbonates they should occur also in this form.

The sizes of this dispersed phase (following terminology of Chukhrov) remain unknown and the possibility, therefore, of Al and Si presence in cationic form could not be excluded. But, in case disintegration of anions occurred and small Al and Si cations enter carbonates, they probably would be located in the interstructural voids.

In both cases, then, Al and Si probably will not substitute on the cationic sites in the structure of metamorphic carbonates.

The averages of Al 387 ppm. and Si 3410 in marble carbonates and respectively 400 ppm and 2470 ppm. in Lens and Vein carbonates are smaller (except Si in marbles) than the corresponding figures for sedimentary carbonates.

The various genetic carbonate groups show a different proportion of Al and Si present. The Si:Al ration of average concentrations is 4.7 in sedimentary, 8.8 in marble and 6.2 in Lens and Vein carbonates.

The plot of Al vs. Si concentrations in the samples (Appendix IV, Fig. 3) shows that Al content increases proportionally to that of Si in all the carbonate groups.

Titanium

Average titanium content in the studied sedimentary carbonates is 41 ppm. (range from 9 to 82 ppm.); it decreases in Precambrian marble carbonates to 15 ppm. (range from 6 to 37 ppm.) and in Lens and Vein carbonates to the average of 21 ppm. (range from 7 to 46 ppm.).

Titanium is a minor element in most rocks. Its average content in igneous rocks is 4400 ppm. It is closely related to silicon and usually occurs in the silicate or oxide phase.

The following titanium contents in some sedimentary and metamorphic rocks are listed by Rankama and Sahama (1950, Table 21.2): Shales - 4300 ppm., Sandstones - 4400 ppm., aluminum-rich schists - 6300 ppm., and quartzites - 960 ppm.

The abundance of Ti in limestones given by Ostrom (1957) is an average of 400 ppm. for Pennsylvanian limestones from Illinois and given by Runnels and Schleicher (1956) is an average of 200 ppm. for Palaeozoic limestones from Kansas.

Comparing these figures with values obtained for carbonates, it should be considered that in both of these cases alumo-siliceous material incorporated in limestones was included in analysis and therefore the lower figures of Ti content in purified sedimentary carbonates appears to be reasonable.

The decrease in Ti content found in both groups of metamorphic carbonates may be connected to the relation of titanium to the silicate and oxide phases.

For instance, part of the Ti in carbonates could have migrated as a result of material redistribution to sphene or pyroxenes which are present in the same assemblage.

Some evidence for this suggestion can be found in Moxham's

(1958) thesis where average Ti value is 330 ppm. with range of 150-1000 ppm. in the metamorphic pyroxenes of the Grenville formation. He had suggested that titanium would substitute for ferric iron, magnesium, and aluminum in the pyroxene structure.

Boron

Goldschmidt and Peters considered that boron is more abundant in the sedimentary cycle than in the average igneous rock. They report a concentration of 30 ppm. in sandstones and up to 300 ppm. in shales.

The values of boron in the carbonates studied compared with those in various rocks are given in Table XXI. There is a definite increase in concentration from Palaeozoic sedimentary carbonates through Precambrian marbles to the Lens and Vein carbonates.

During magmatic crystallization, boron is partly included in rock forming minerals and in part enters emanations and mineral waters of the areas with volcanic activity. The enrichment of boron occurs in postmagmatic processes where it forms tourmaline and other boron bearing minerals.

Evaluating the increase in boron concentration of metamorphosed carbonates, the following factors should be taken into account: The small size of boron and its high mobility, a possibility that primary boron in sediments could remain in them or could be removed while the secondary boron could be introduced by metasomatic processes. A mobilization of boron by an intrusive process (as described by Góldschmidt, 1954, P.247) with later redistribution by post-magmatic and metamorphic processes could also occur.

Presence of submicroscopic inclusion of tourmaline is also possible.

TABLE XXI

Boron Content of the Analyzed Carbonates Compared with Other Rocks

Analyzed Sample	Reference	Boron		
		Min.	Max.	Aver.
Carbonates of Palaeozoic Limestones		Nd	16	8
Carbonates of Precambrian Marbles		4	36	18
Lens and Vein Carbonates		6	48	21
Calcitic and Dolomitic Limestones	Rankama & Sahama (1950) Table 16.3			3
Carbonate Rocks, Southern Lapland	Rankama & Sahama (1950) Table 16.3			9
Nepheline Syenites	Rankama & Sahama (1950) Table 16.2			3
Rocks of the Basement Complex of Southern Lapland				
Ultrabasics	Rankama & Sahama (1950) Table 16.2			31
Gabbros and Dolerites	Rankama & Sahama (1950) Table 16.2			9
Granites	Rankama & Sahama (1950) Table 16.2	0.9	3	
Syenites	Rankama & Sahama (1950) Table 16.2			9
Pennsylvanian Limestones from Ostrom, Illinois		1	200	18
Palaeozic Limestones from Kansas	Runnels & Schleicher	0.5	300	6.9

Chromium

Detectable amounts of chromium averaging 2 ppm. have been found only in the carbonates of sedimentary limestones. The limit for visual detectibility (tr) for chromium is 1-2 ppm.

In Table XXII the results of this work are compared with the abundance of chromium in various rocks.

The ionic size and charge of chromium as well as other chemical properties closely correspond to those of Fe^{+++} and Al^{+++}, therefore the abundance of Cr should be related to that of those elements.

The effect of alumo-silicious impurities in limestones on the concentration of Cr and some other elements was already discussed in the chapter of analytical method.

The presence of Fe and Al bearing minerals together with carbonates in the same metamorphic assemblage can provide more suitable emplacement for Cr in their structure than in carbonates.

TABLE XXII

Chromium Content of Carbonates Compared with Other Rocks

Analyzed Sample	Reference	Chromium		
		Min.	Max.	Aver.
Carbonates of Palaeozoic Limestones		ND	6	2
Carbonates of Precambrian Marbles		ND	ND	ND
Lens and Vein Carbonates		ND	ND	ND
Limestones (average)	Rankama & Sahama (1950) Table 5.52			2
Carbonate Rocks, Southern Lapland	Rankama & Sahama (1950) Table 28.3			2
Nepheline Syenite	Rankama & Sahama (1950) Table 28.2			0.7
Basement Complex of Southern Lapland	Rankama & Sahama (1950)			
Ultrabasics				2000
Gabbros and Dolerites				410
Granites				2-6.8
Syenites				200

Nickel

Crustal abundance of Ni reported by Rankama and Sahama (1950, Table 2.3) is 80 ppm., while its average in limestones is 3-10 ppm. and it is absent in carbonate rocks from Southern Lapland.

Results of the present investigation show traces of Ni only in sedimentary carbonates, with the value of tr being slightly below 3 ppm. corresponding with the values reported for similar rocks (Table XXIII).

TABLE XXIII

Nickel Content of Carbonates Compared with Other Rocks

Sample Analyzed	Reference	Nickel		
		Min.	Max.	Aver.
Carbonates of Palaeozoic Limestones		ND	tr	tr
Carbonates of Precambrian Marbles		ND	ND	ND
Lens and Vein Carbonates		ND	tr	tr
Limestones (average)	Rankama & Sahama (1950) Table 5.52			0
Limestones, Vastergotland, Sweden.	Rankama & Sahama (1950) Table 34.3			3-10
Carbonate Rocks, Southern Lapland	Rankama & Sahama (1950) Table 34.3			0
Nepheline Syenite	Rankama & Sahama (1950) Table 34.2			2.4
Basement Complex, Southern Lapland				
Ultrabasics	Rankama & Sahama (1950) Table 34.2			790
Gabbros and Dolerites	Rankama & Sahama (1950) Table 34.2			47
Granites	Rankama & Sahama (1950) Table 34.2			2-8
Syenites	Rankama & Sahama (1950) Table 34.2			8

VIII CONCLUSION

1. The spectrographic method developed for anarysis of carbonates provides satisfactory accuracy and precision for the interpretation of results.

2 Three genetic groups of carbonates studied show an increase in Mn, Fe, Sr, Ba, B, and Pb and a decrease in Al and Si from Palaeozoic limestones through Precambrian marbles to Grenville Lens and Vein carbonates. The highest average value of Mg concentration is found in carbonates of Precambrian marbles, while the average value of Ti decreases from limestones to marbles and then slightly increases in Lens and Vein carbonates. Small amounts of Cr and Ni are detected in sedimentary carbonates, while they are absent or present in the amounts below the limit of calculation of the method in metamorphic carbonates. No detectable amounts of V and values of Ag below the limit of calculation are detected in all the carbonates studied.

3. Most of the minor elements found in the carbonates (Mg, Mn, Fe, Sr, Ba, Pb) appear to be present in the lattice structure of the carbonates substituting on the calcium sites. Al, B, Si, and Ti are probably located in interstructural space of the carbonate lattice either as ions in structural voids or as a dispersed phase of their components placed in structural imperfection. Distribution of Cr and Ni is probably connected with the impurities in sedimentary carbonates.

APPENDIX I

WORKING CURVES

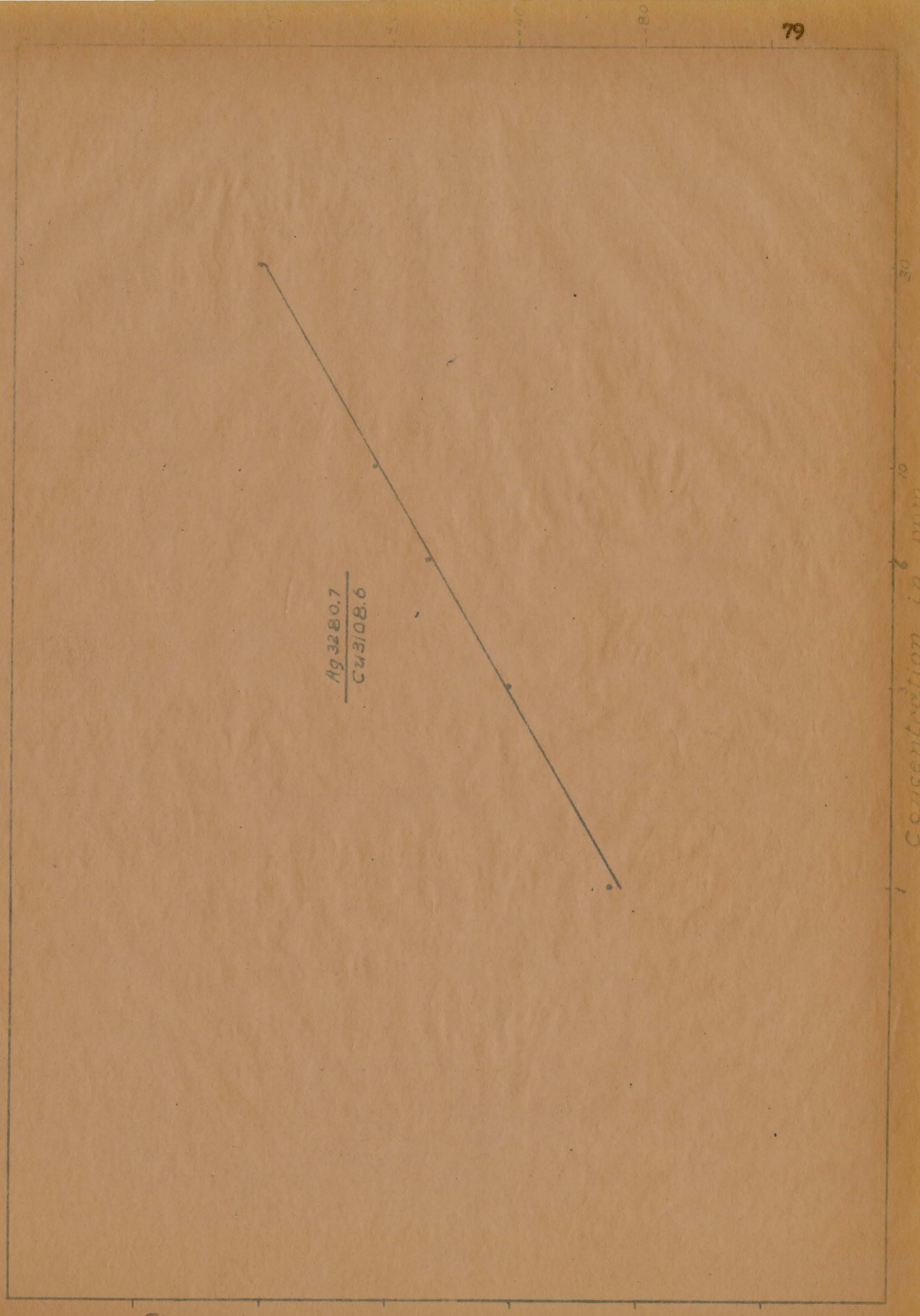


Fig. 1 Working Curve for Ag.

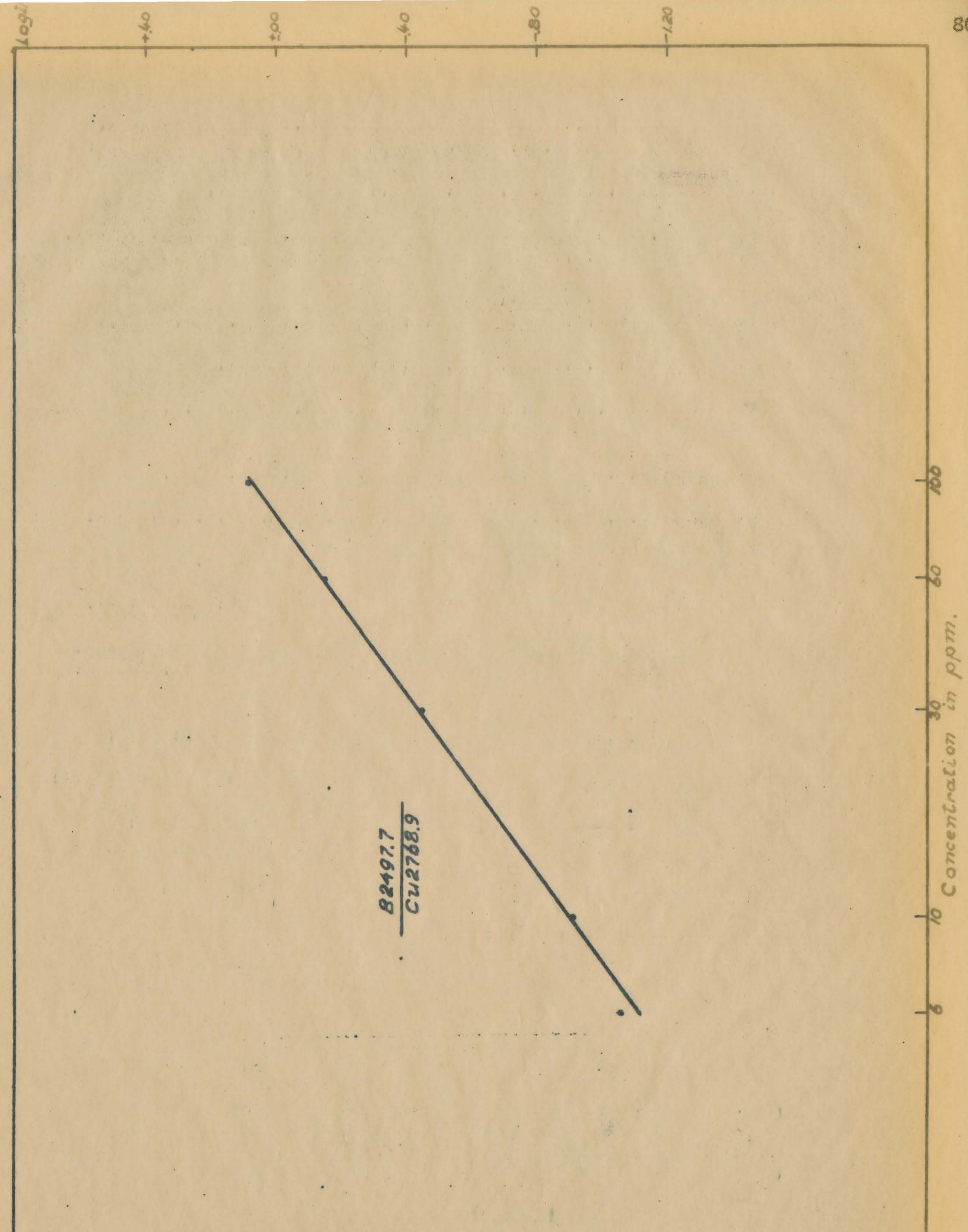


Fig.2 Working curve for B.

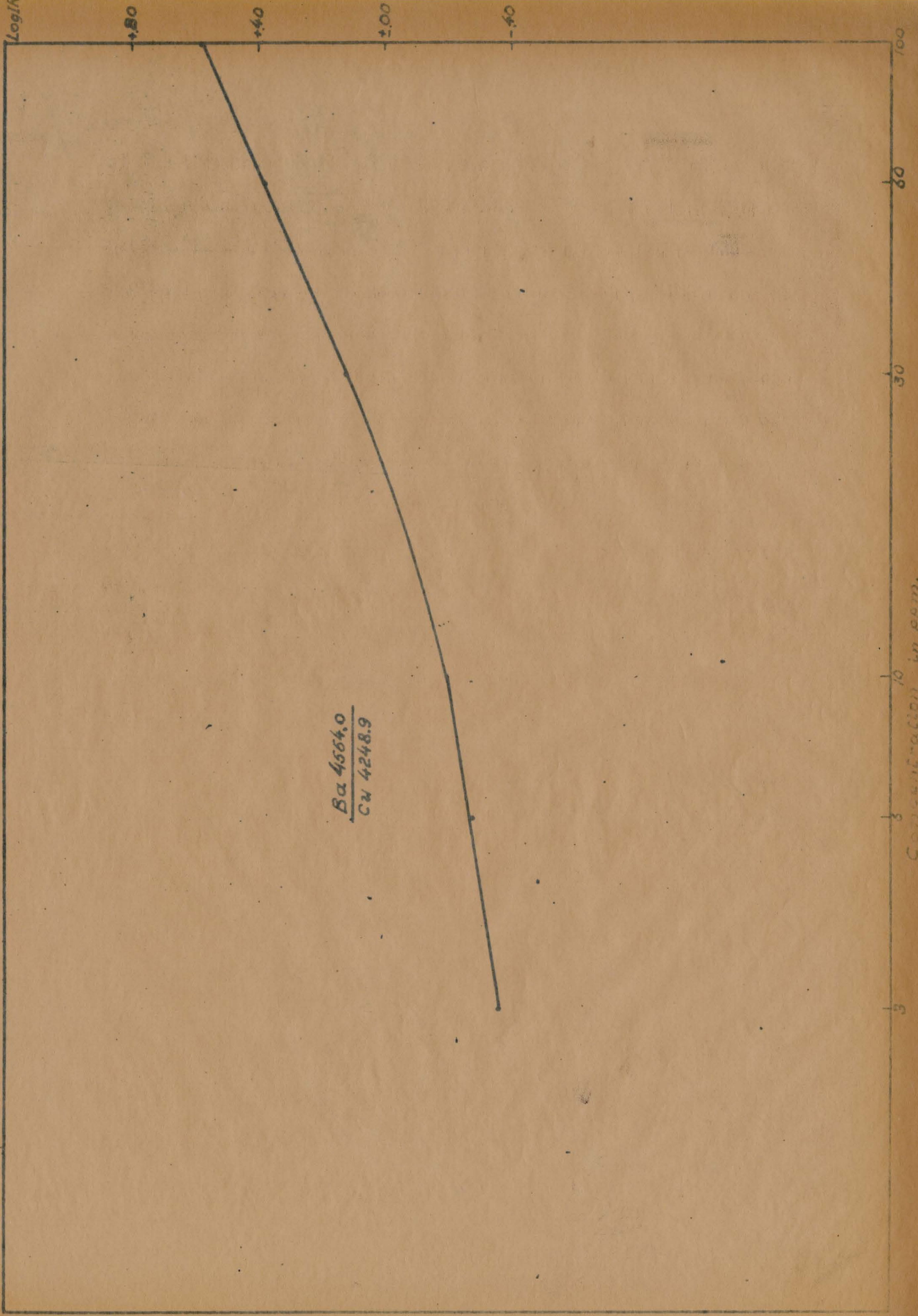


Fig. 3 Working Curve for Ba.

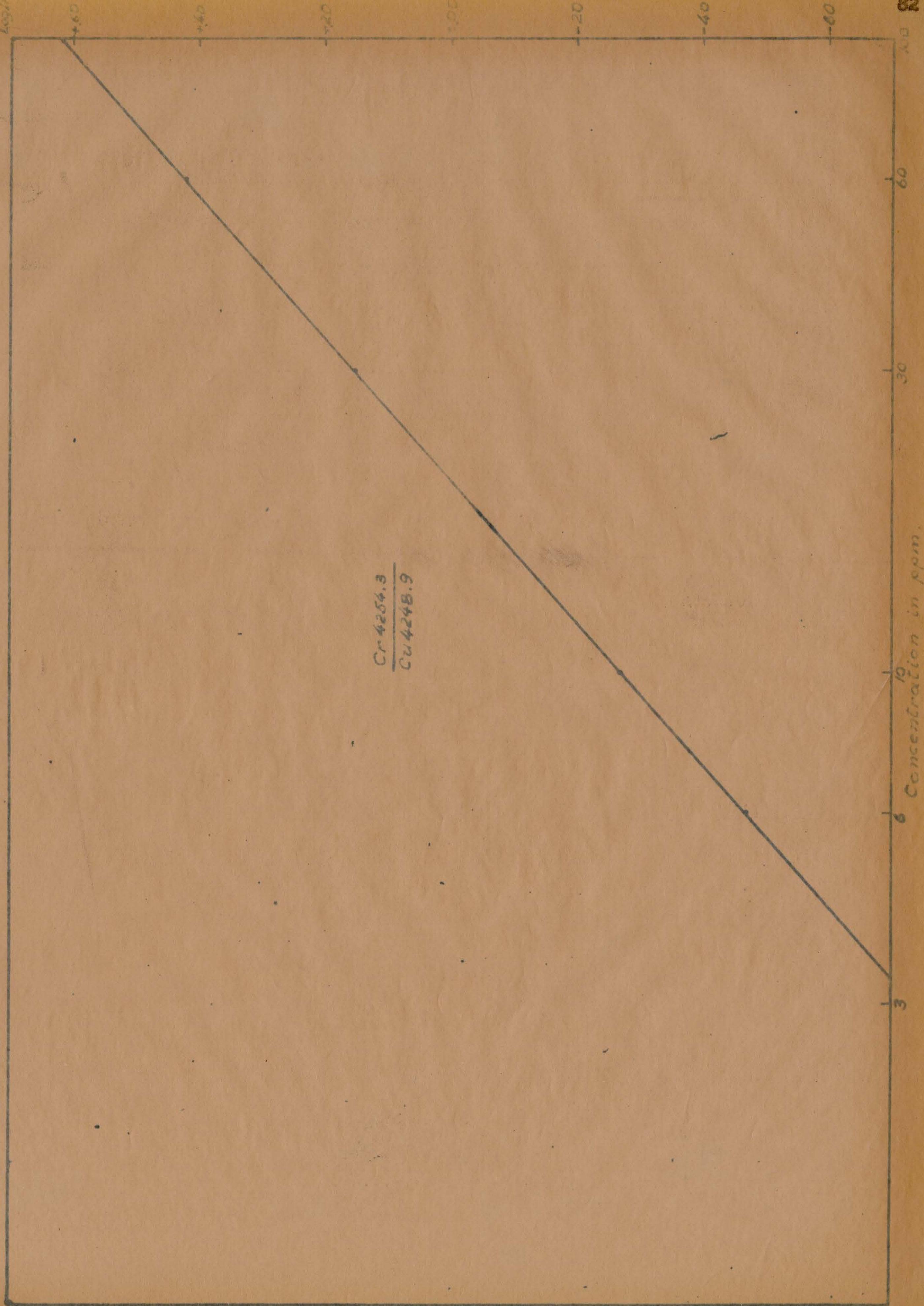


Fig. 4 Working Curve for Cr.

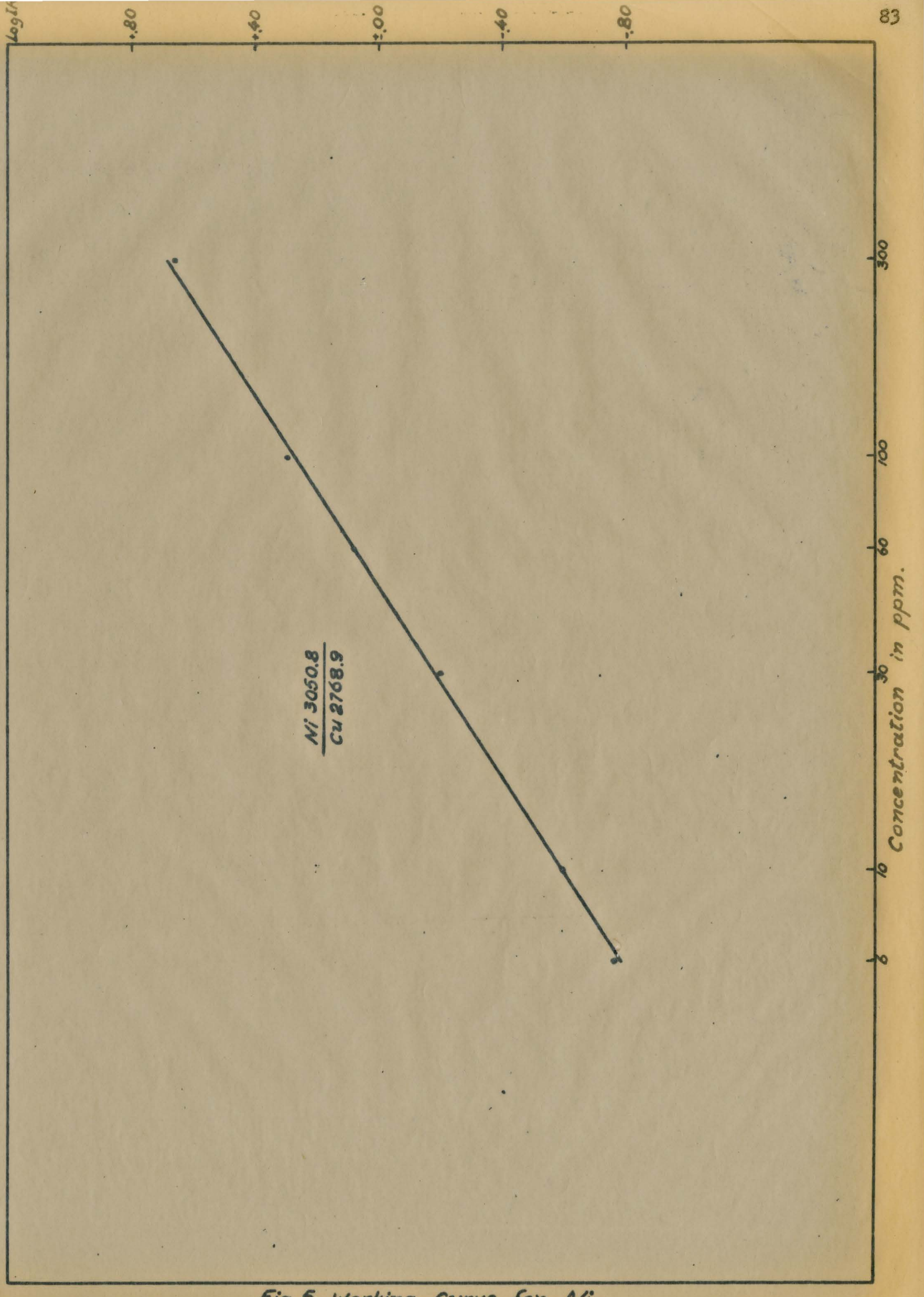


Fig.5 Working Curve for Ni.

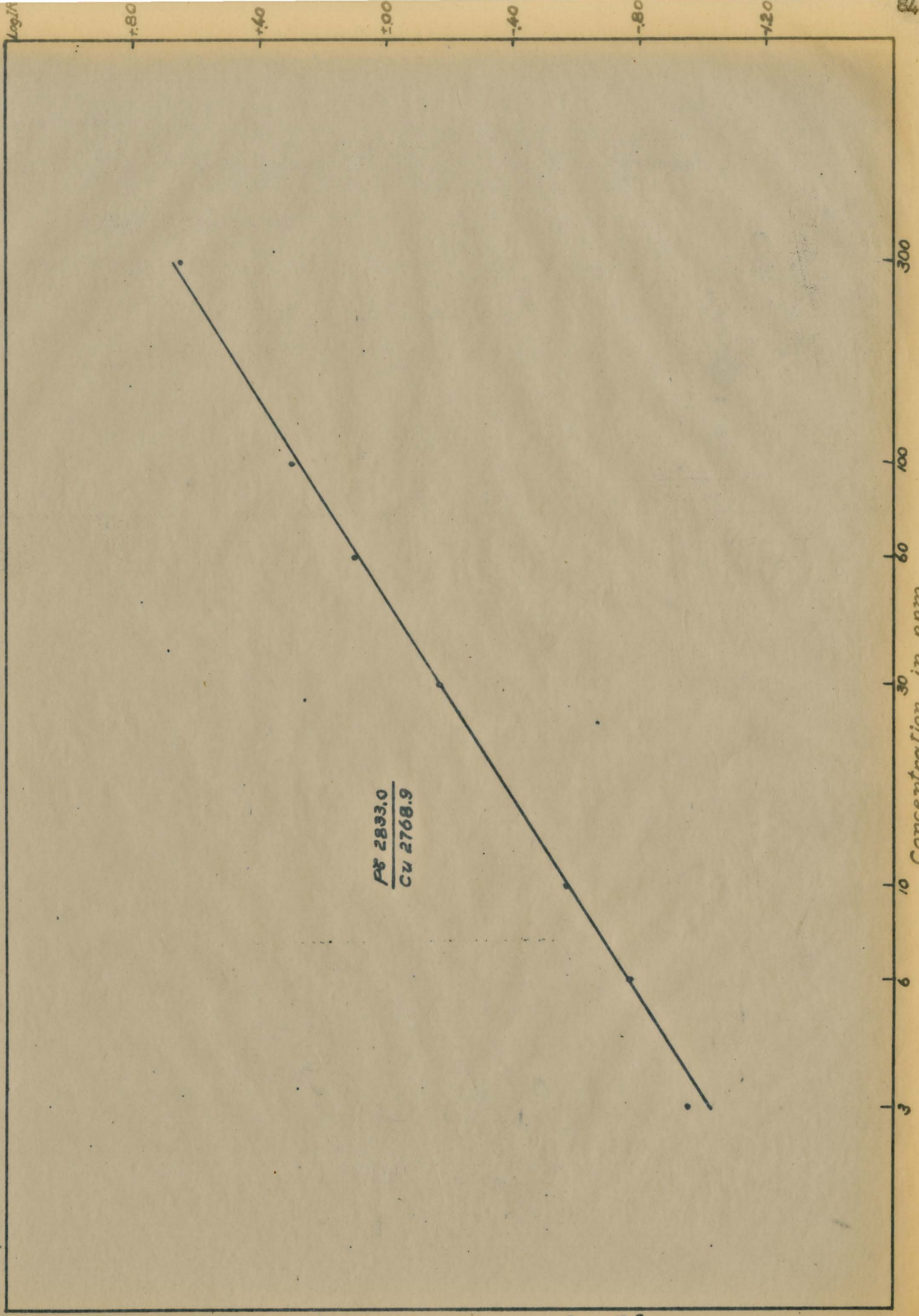


Fig.6 Working Curve for Pb.

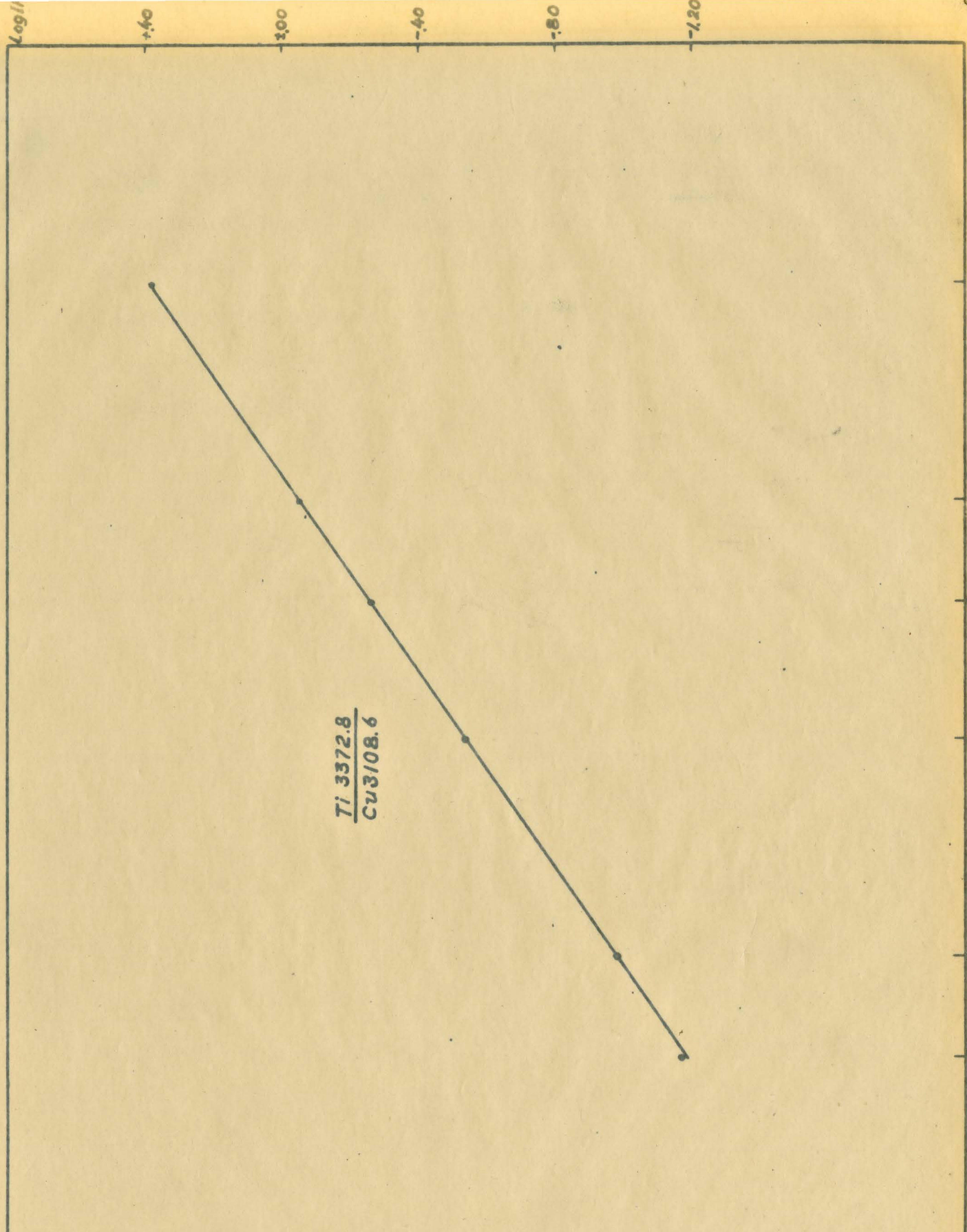


Fig.7 Working Curve for Tl.

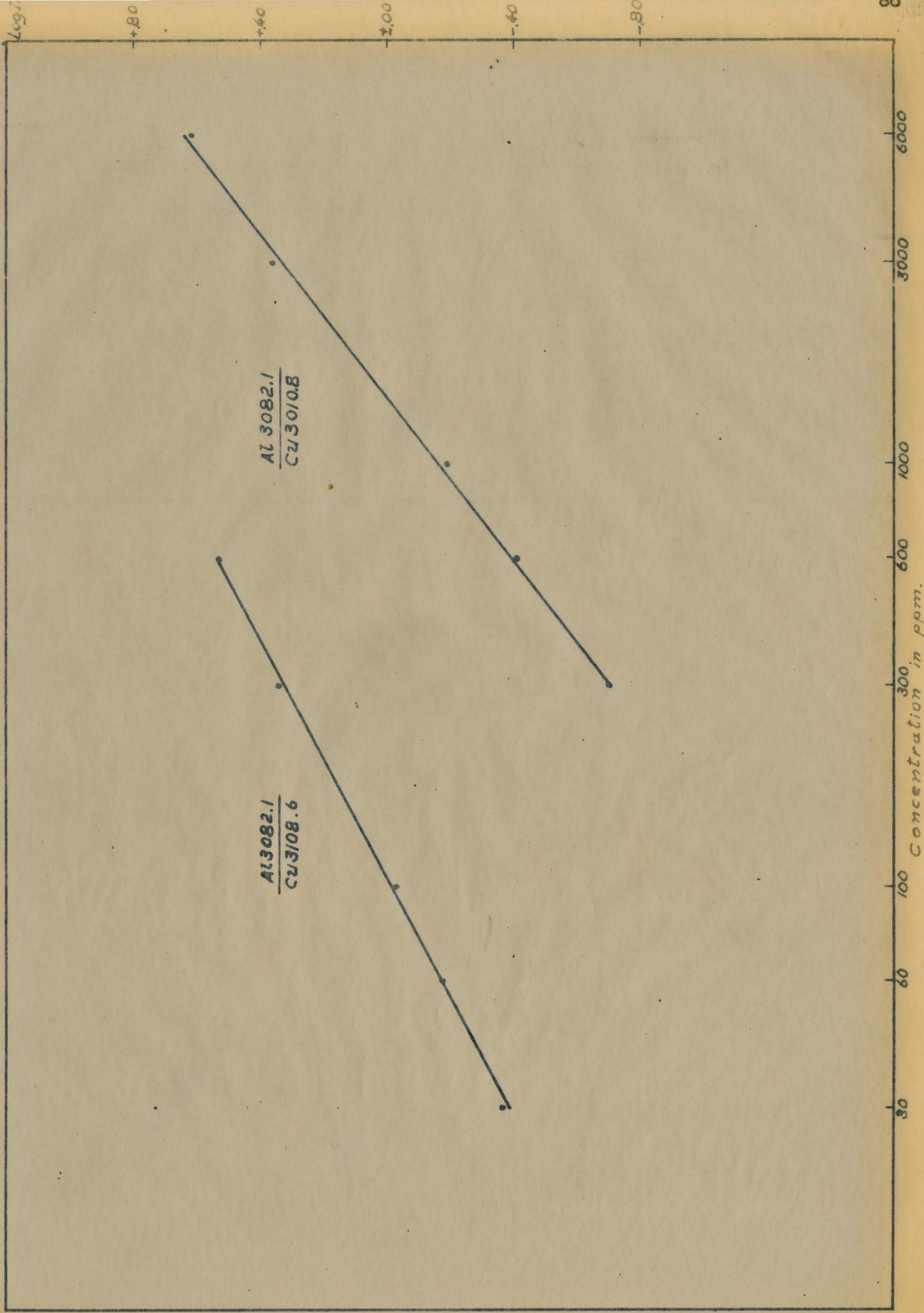


Fig. 8 Working Curves for Al.

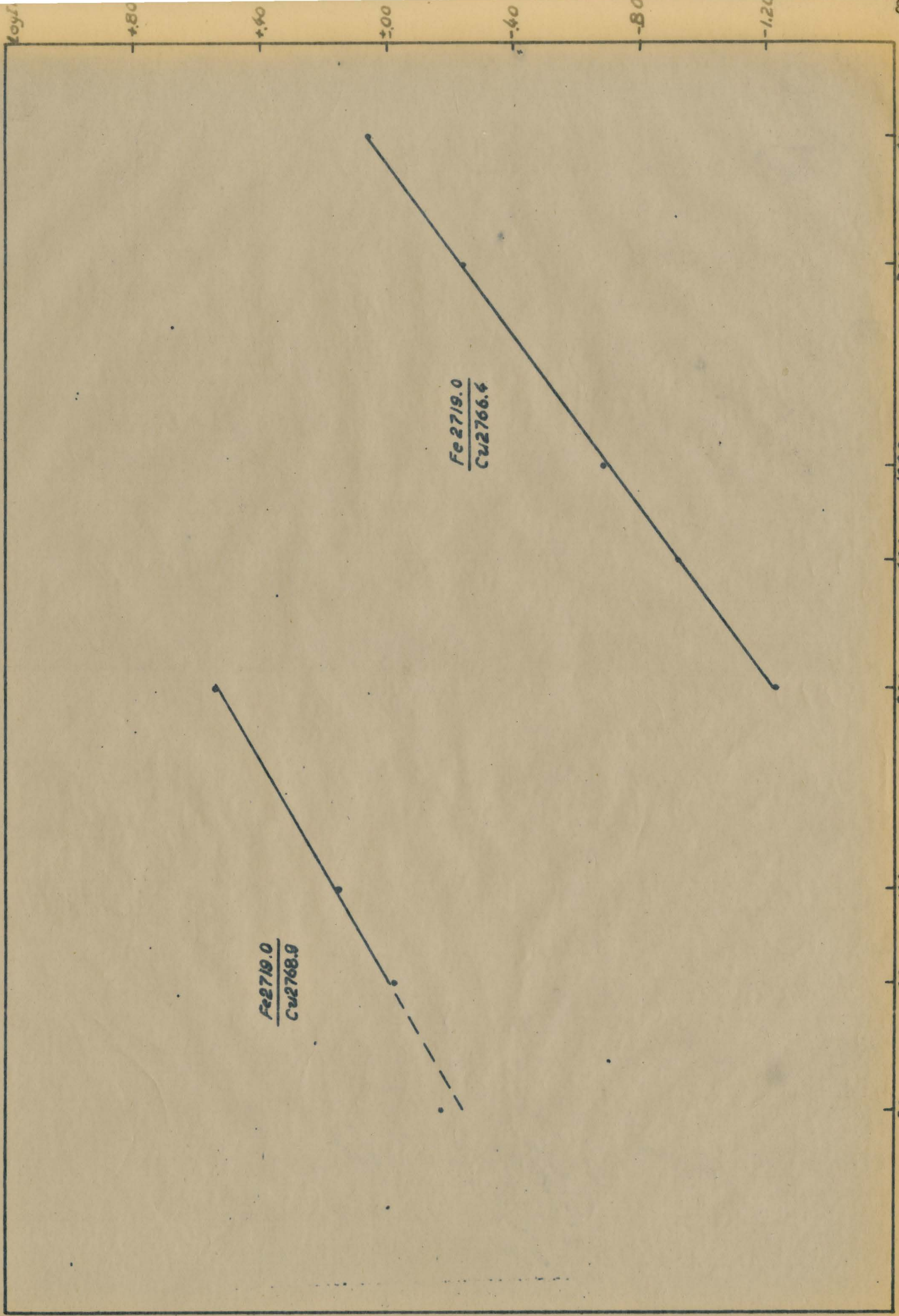


Fig. 9 Working Curves for Fe.

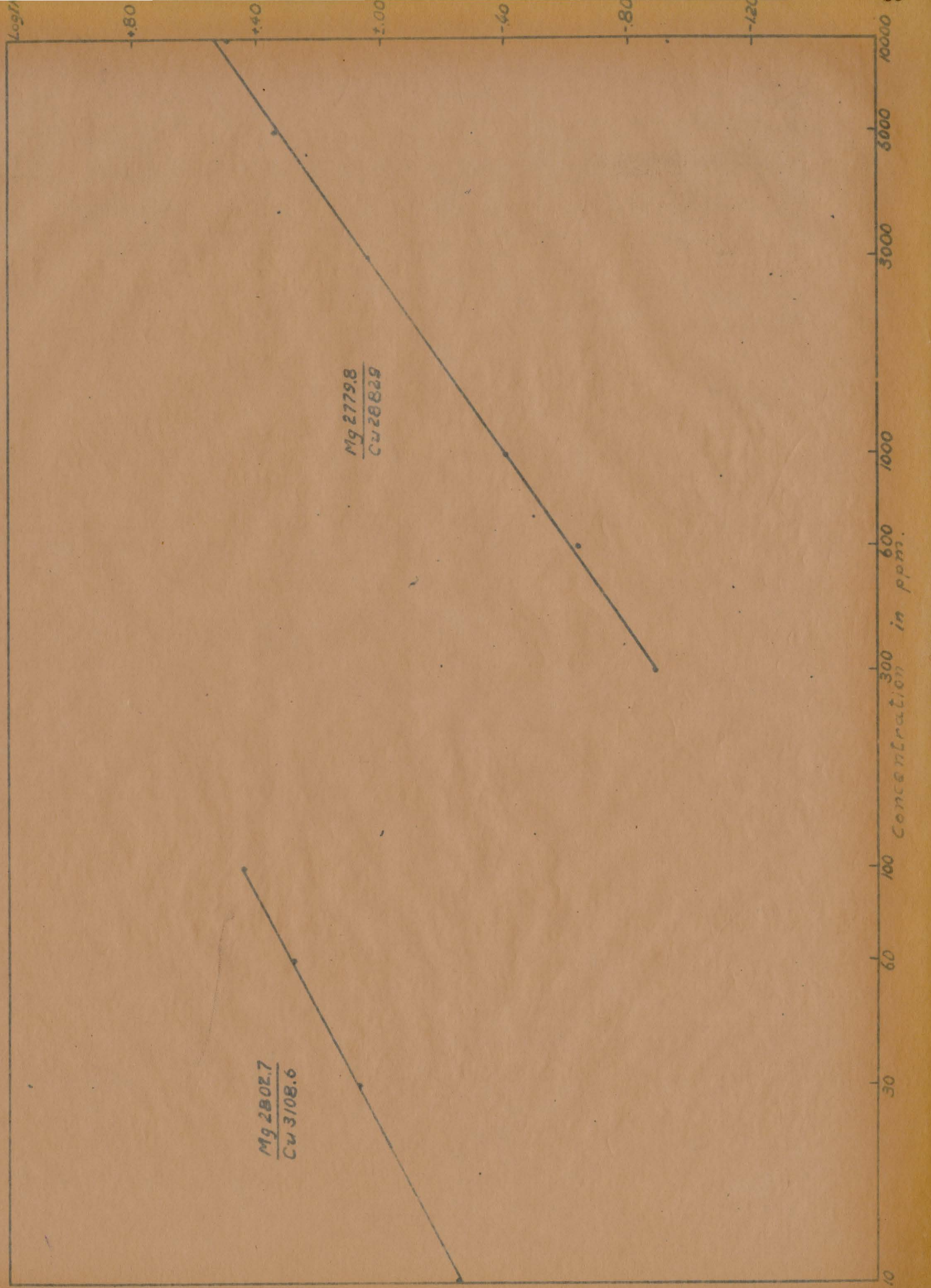


Fig.10 Working Curves for Mg.

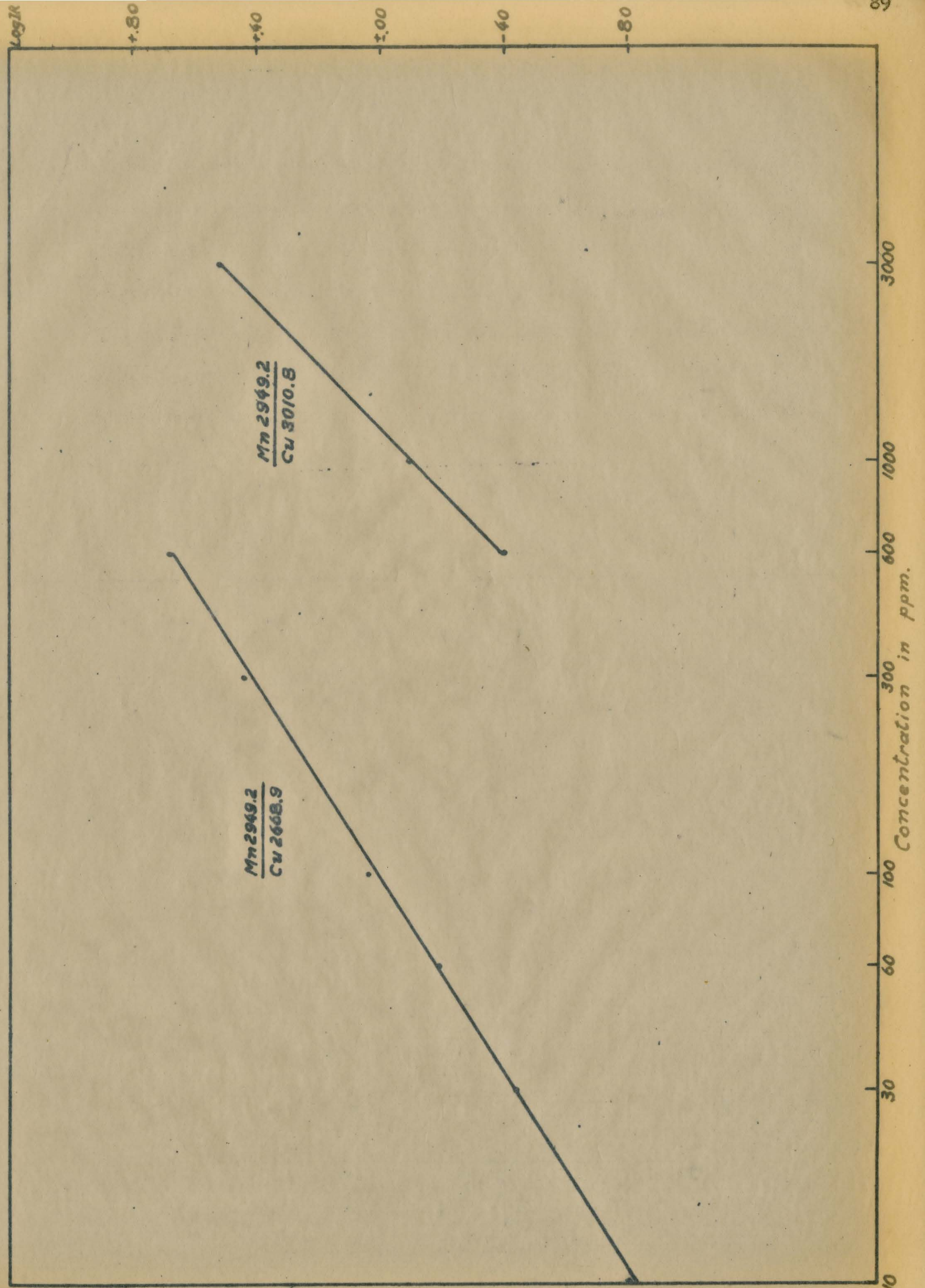


Fig.11 Working Curves for Mn.

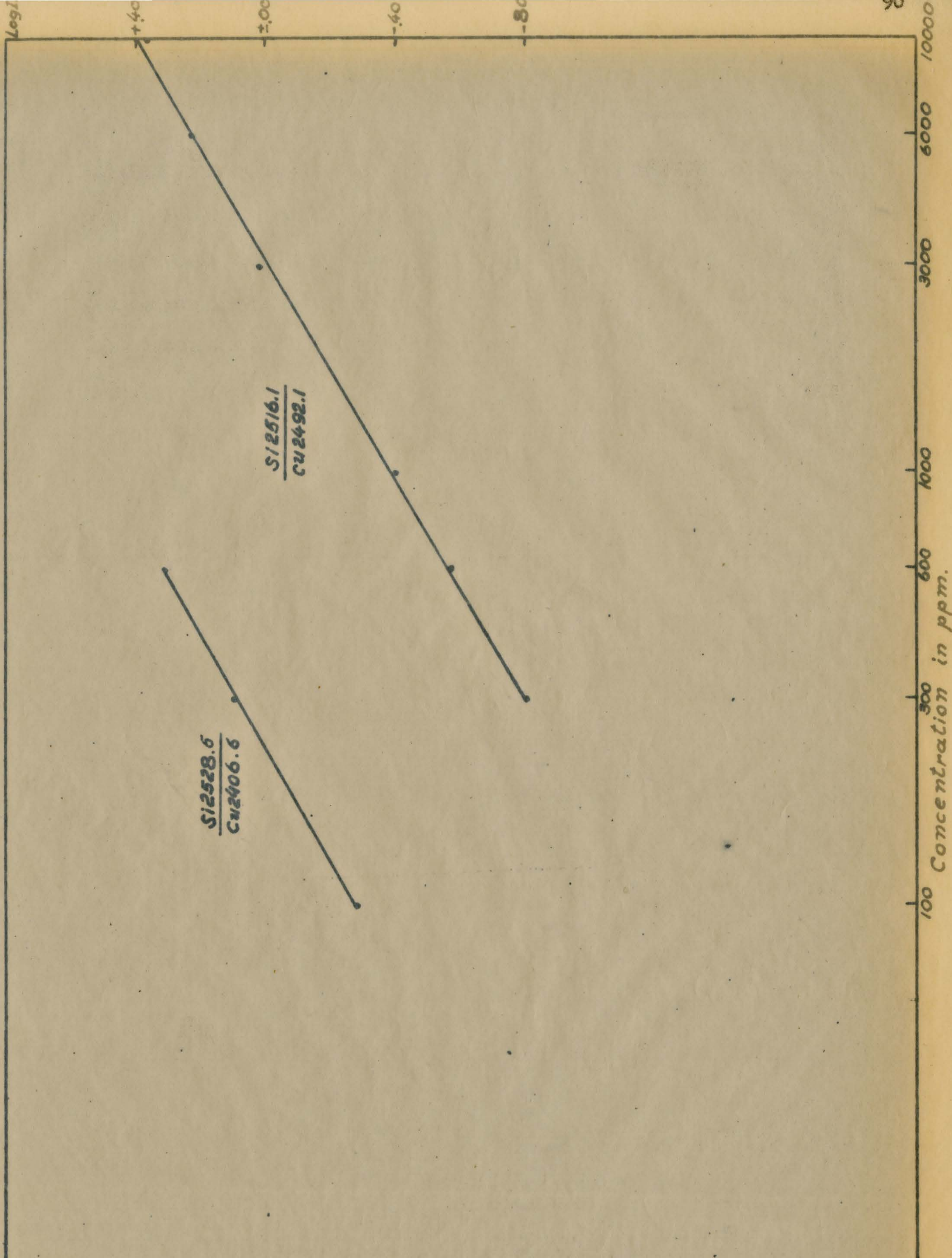


Fig.12 Working Curves for Si.

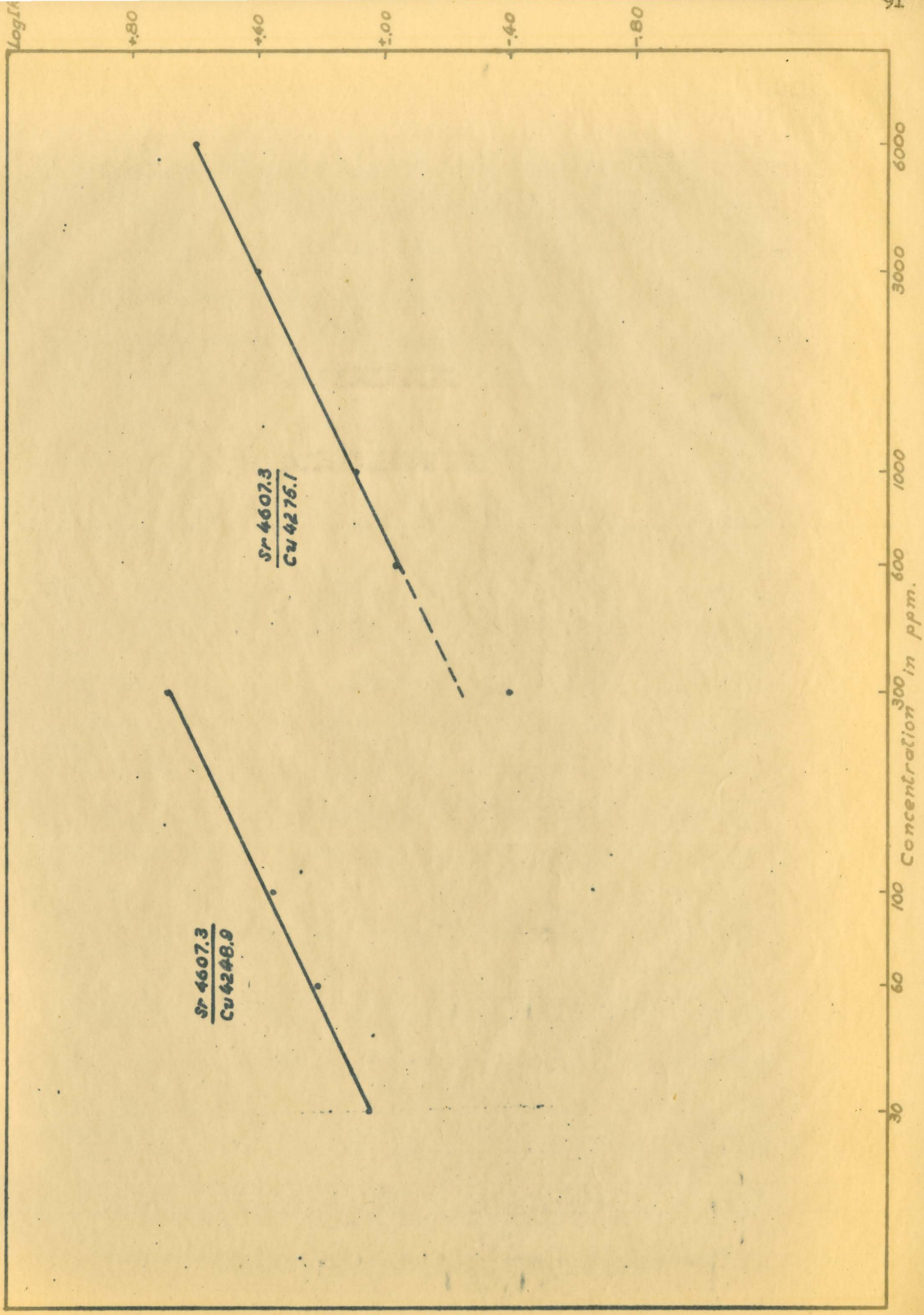


Fig.13 Working Curves for Sr.

APPENDIX II

SAMPLES LOCALITIES

APPENDIX II

SAMPLES LOCALITIES

Number	Rock Description	Age	Locality	Collector
H-30	Calcilutite with lesser fine calcarenite	Ordovician Black River Group	Southern Ontario	F.W.Beals
H-33	Fine calcarenite	"	"	"
U-6-2	Crinoidal/Brahiopod calcarenite	"	"	"
U-6-9		"	"	"
U-6-16-6	Crinoidal/Brahiopod calcarenite	"	"	"
Girvanella	Part of Girvanella skeleton	"	"	"
P-1735	Calciculite	Devonian,Palliser formation	South-western Alberta	"
W-690	Calcirudite	"	"	"
P-1550	Calcilutite with fine skeletal debris mainly crinoidal	"	"	"
JR-6 0	Fine calcarenite	Mississipian, Rundle Group	"	"
JR-530	" "	"	"	"
JR-100	Crinoidal coarse calcarenite	"	"	"
78	Medium-grained oolite with moderate amount of skeletal grains and skeletal nuclei	"	"	"

Samples Locality (contd.)

Number	Rock Description	Age	Locality	Collector
Miami Oolite	Medium-grained oolite with quartz grain nuclei	Recent	Miami, Florida, U.S.A.	F.W.Beals
P-1A	Spirifer	Devonian	Arcona, Ontario	D.M.Shaw
P-2A	Crystalline calcite from Vog in dolomitic Limestone	Silurian, Irondequait	Clappison Cut, Hamilton, Ontario	R.V.Best
CA-103	Graphitic marble	Precambrian, Grenville	Lot, Range IX, Grand Calumet Twp.,Quebec	D.M.Shaw
M-16	Chandrodite marble	"	Boundary between Lots 13-14,Con.XIV,Monmouth Twp.,Ont.	H.S.Armstrong
M-6116a	Marble containing pyrito headra	"	Road cut near Wilbermere Lake,Lot28,Con.XI,Monmouth Twp.,Ontario.	"
PC-187	White marble	"	Lot 31,Con.XI, Cardiff Twp., Ont.	J.Satterley
PC-189	" "	"	Boleurder Quarry, Lot 22, Con.IV,Guilford Twp., Ont.	"
44-1941	Crystalline limestone	"	Seuguin River, Lot 9, Con.XI, Christie Twp. Ont.	"
807	Forsterite-chondrodite marble	"	Lot 9, Con.XI, Christie Twp. Ont.	"
FR-5	Silicate marble	"	Farmers Rapids, Hull Twp. Quebec	D.M.Shaw

Samples Locality (contd.)

Number	Rock Description	Age	Locality	Collector
CA-43	Chondrodite marble	Precambrian Grenville	Lot 28,Range VII, Grand Calumet Twp. Quebec	D.M.Shaw
CA-84	Graphitic marble	"	Lot 31 Range 1, Litchfield Twp., Quebec	"
A-1	Pink Carbonate Lens	"	Magnetite pit, Lot 27-28,Con. XV,Glamorgan Twp., Ont.	"
A-2	Pink carbonate lens with apatite	"	Brauwer pits, Lot 17,Con.XII Monmouth Twp. Ont.	"
A-3	Pink carbonate lens with quartz	"	McDonald Quarry Monteagle Twp. Ont.	"
A-4	Pink carbonate with large crystal of magnetite	"	Magnetite pit, Lot 27-28,Con. XV, Glamorgan Twp.,Ont.	H.S.Armstrong
A-5a A-5b A-5c	Pink ct. Grey ct. White ct. from carbonate mass in hybrid gneiss	"	New road cut at Beaver Pond, Glamorgan Twp., Ont.	"
A-6a A-6b	Pink ct. White ct. from carbonate mass in hybrid rocks	"	Highway west of Gooderham, Lot 22,Con.VI, Glamorgan Twp., Ont.	"
CA-105	Pink calcite in diopside marble with Thorianite	"	Lot 22,Range V, Huddersfield Twp.,Quebec	D. M. Shaw
Q-67	White calcite from calcite-quartz vein	"	Mercier dam, Gatineau river, Mitchell Twp. Quebec.	"

Samples Locality (contd.)

Number	Rock Description	Age	Locality	Collector
ON-6	Pink calcite	Precambrian Grenville	Lot 13,Con.XVI Monmouth Twp. Ont.	D.M.Shaw
ON-15	Pink calcite	"	Lot 34,Con.XIV Monmouth Twp. Ont.	"
ON-26	Pink calcite	"	Pits in Essonville granite,Lot 17 Con.XII Monmouth Twp. Ont.	"
ON-30A	Coarse grain	"	Richardson (Fussion) Mine,Lot 4-6 Con.XXI, Cardiff Twp. Ont.	"
ON-30B	Medium grain			
ON-30C	Fine grain White calcite from calcite-fluorite-apatite gneiss			
ON-31	Pink calcite and apatite	"	Lot 17,Con.VI, Glamorgan Twp. Ont.	"
ON-39	Pink calcite	"	Camex radioactive property, Lot 6,Con. IX,Monmouth Twp. Ont.	"

APPENDIX III

DIAGRAMS OF ELEMENT DISTRIBUTION

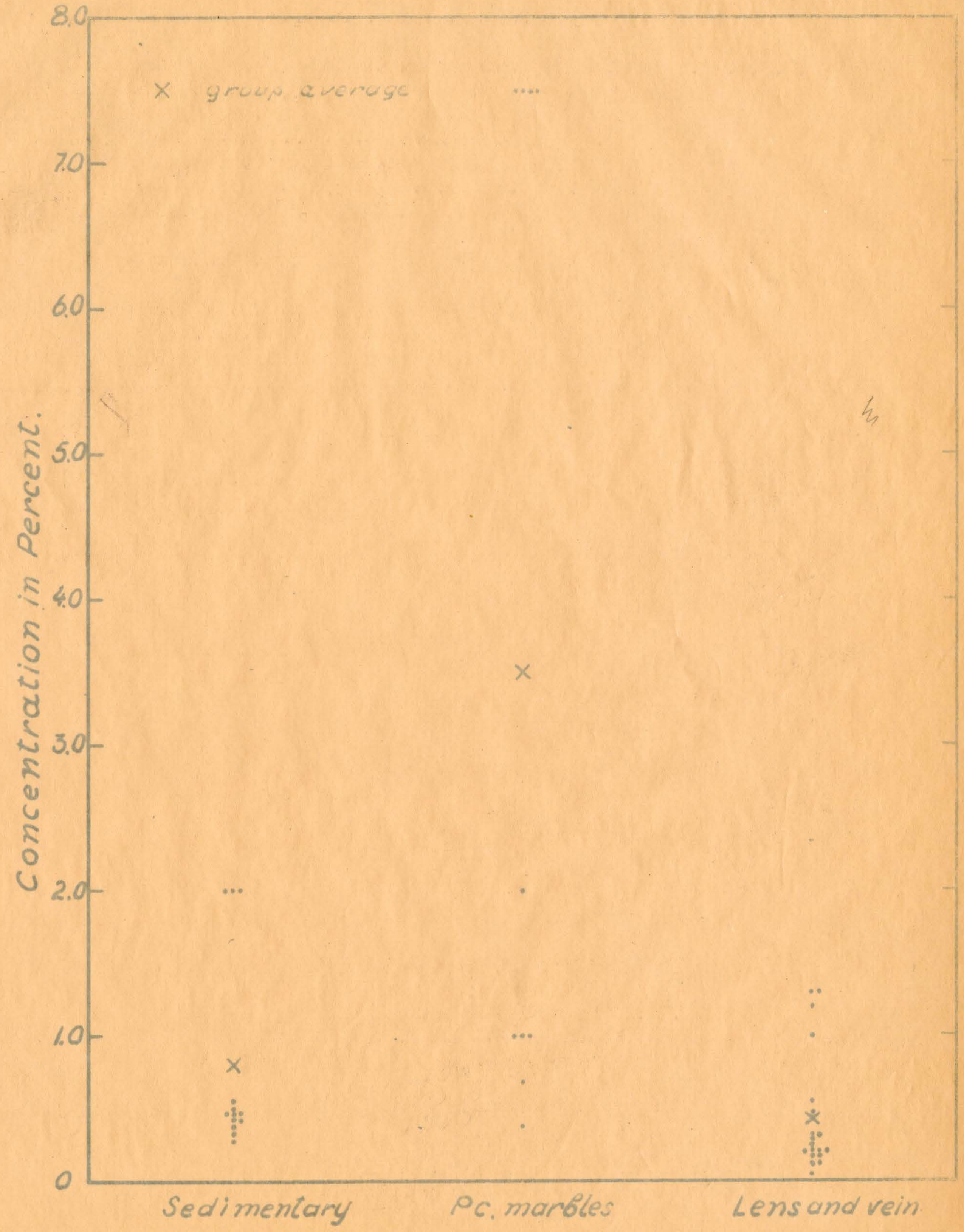


Fig. 1. Distribution of Mg. in various carbonat

Fig. 2. Distribution of Mn in various carbonates.

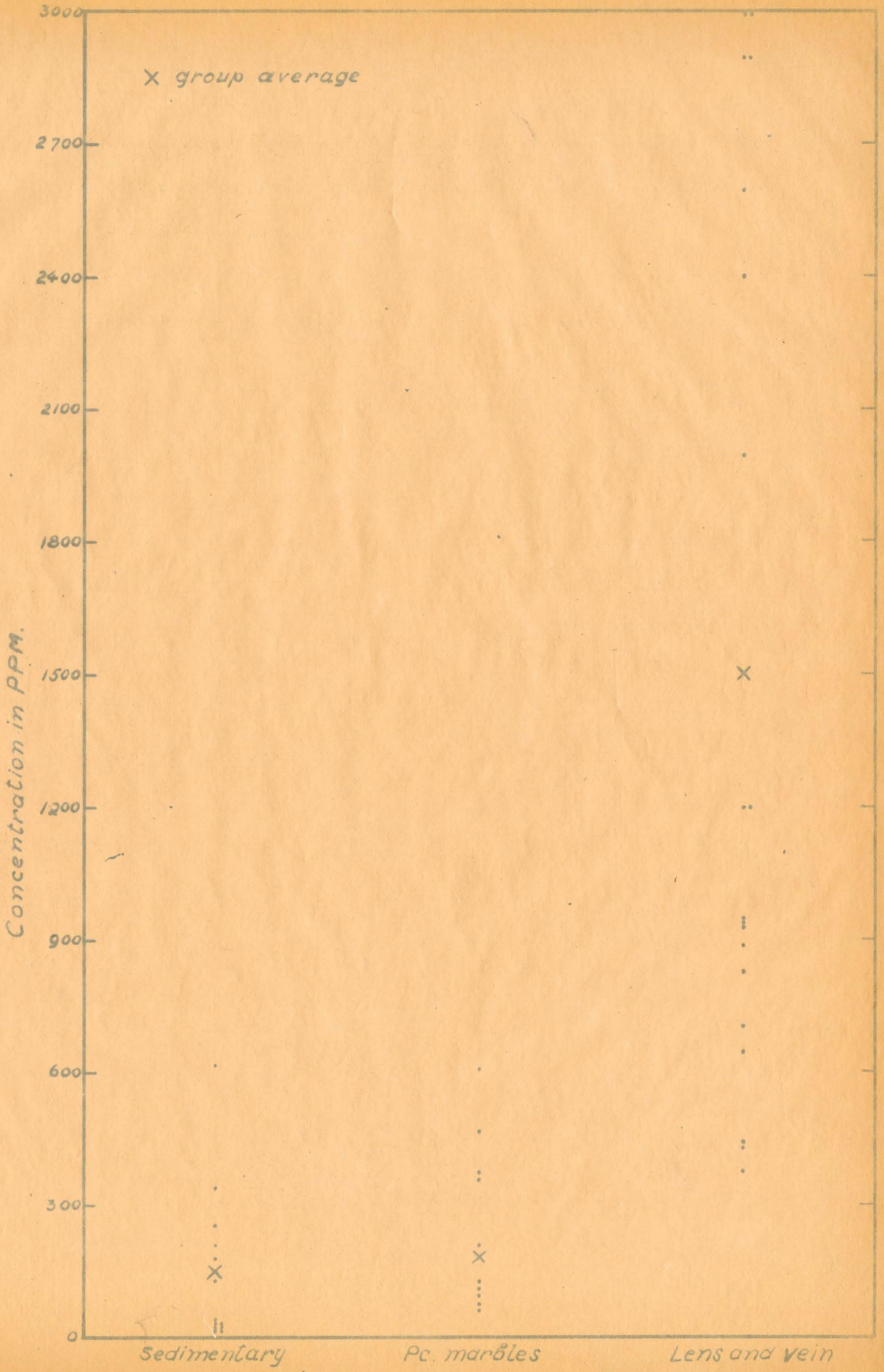


Fig. 3. Distribution of Fe in various carbonates.

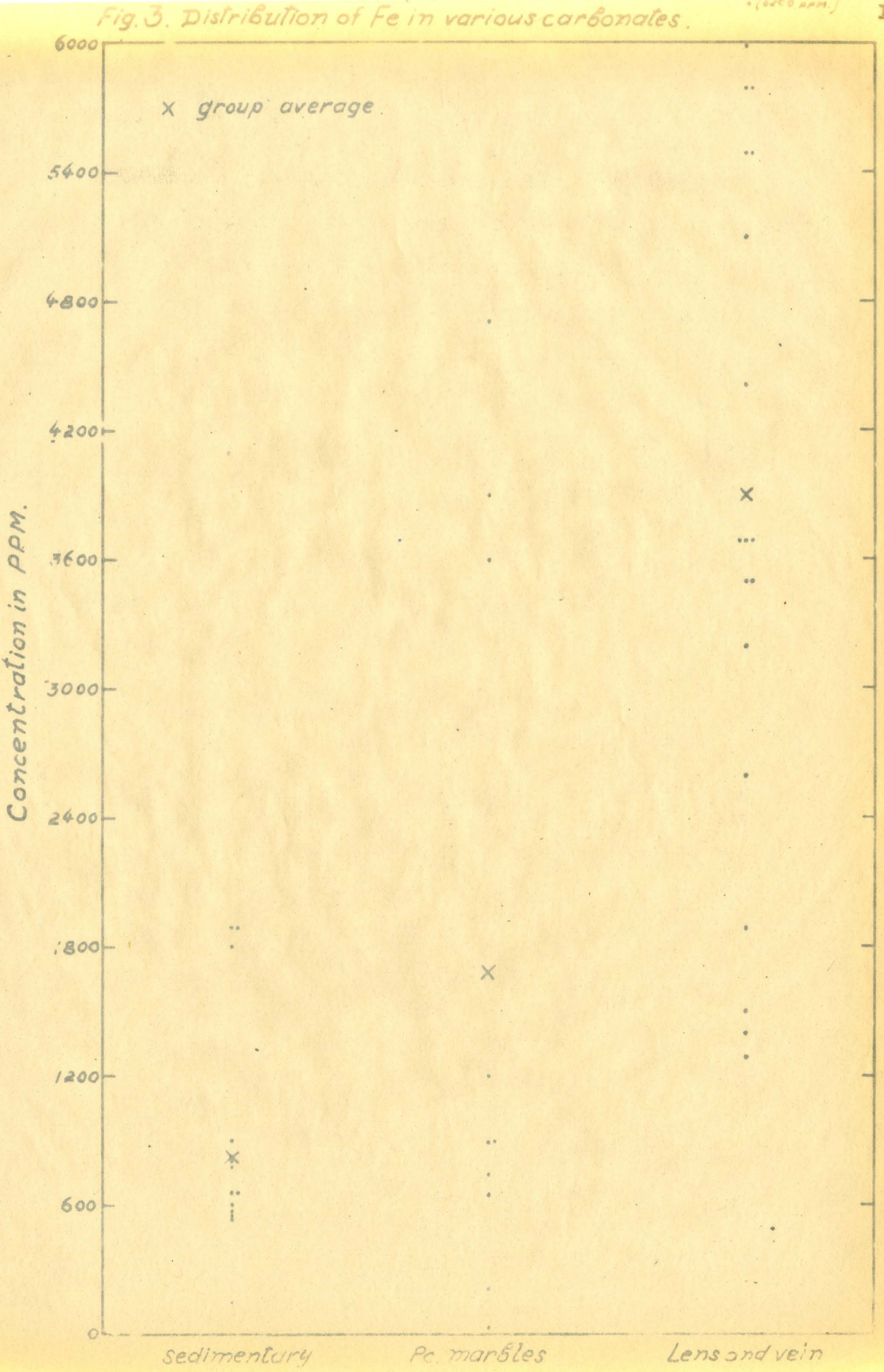


Fig. 4 Distribution of Sr in various carbonates.

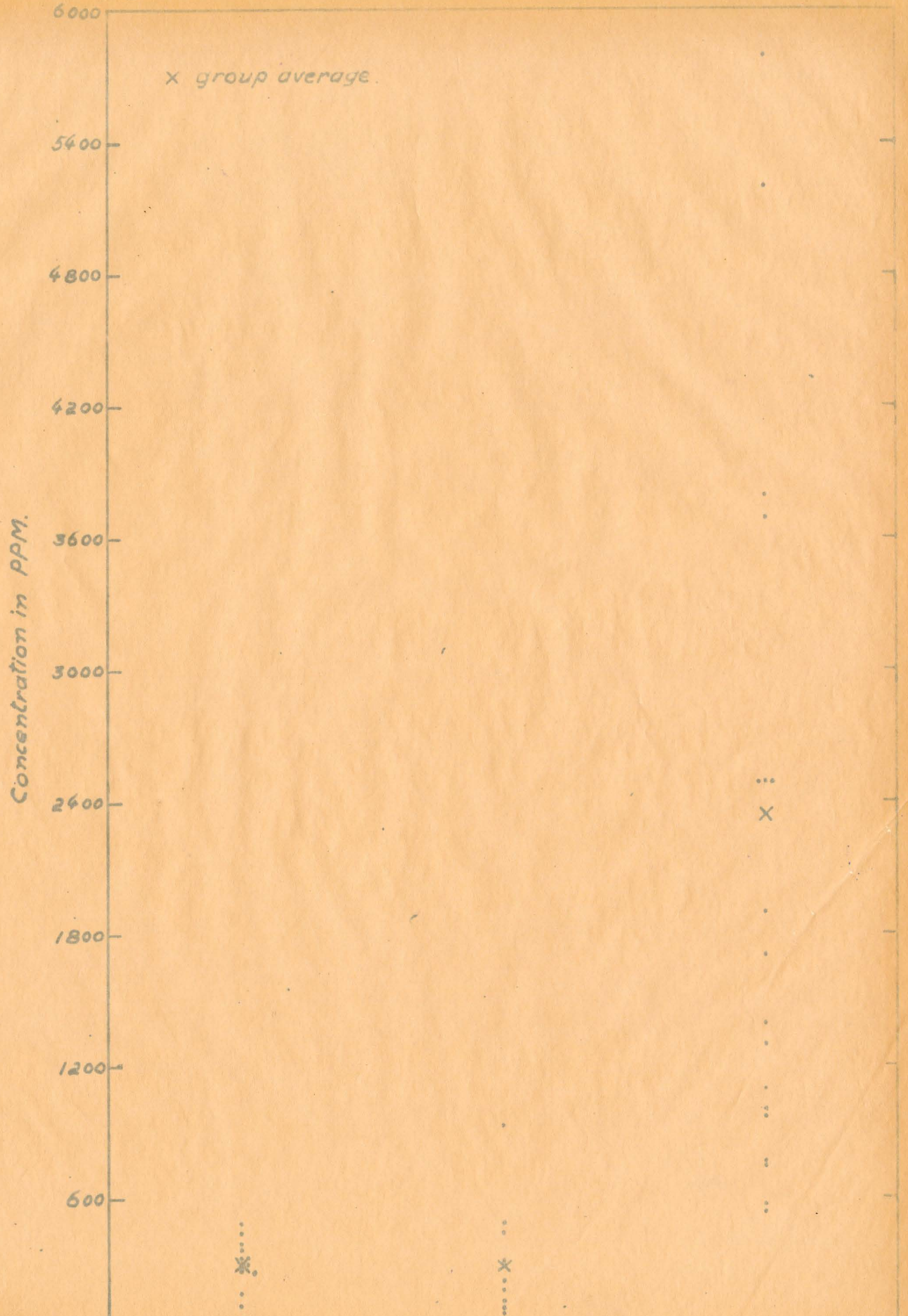


Fig. 5. Distribution of Ba and Pb in various carbonates.
(x - group average)

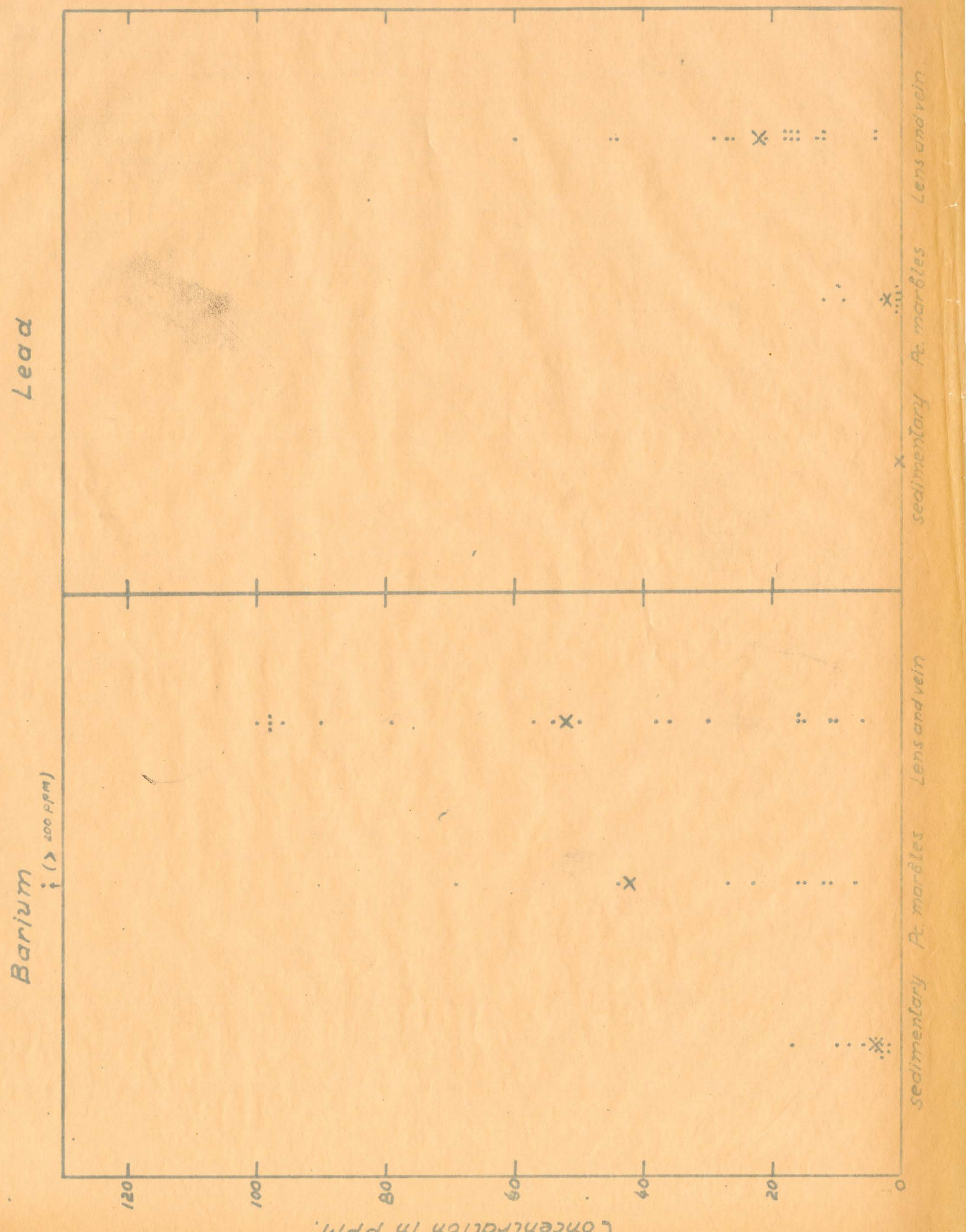


Fig. 6. Distribution of Al in various carbonates.
(x - group average)

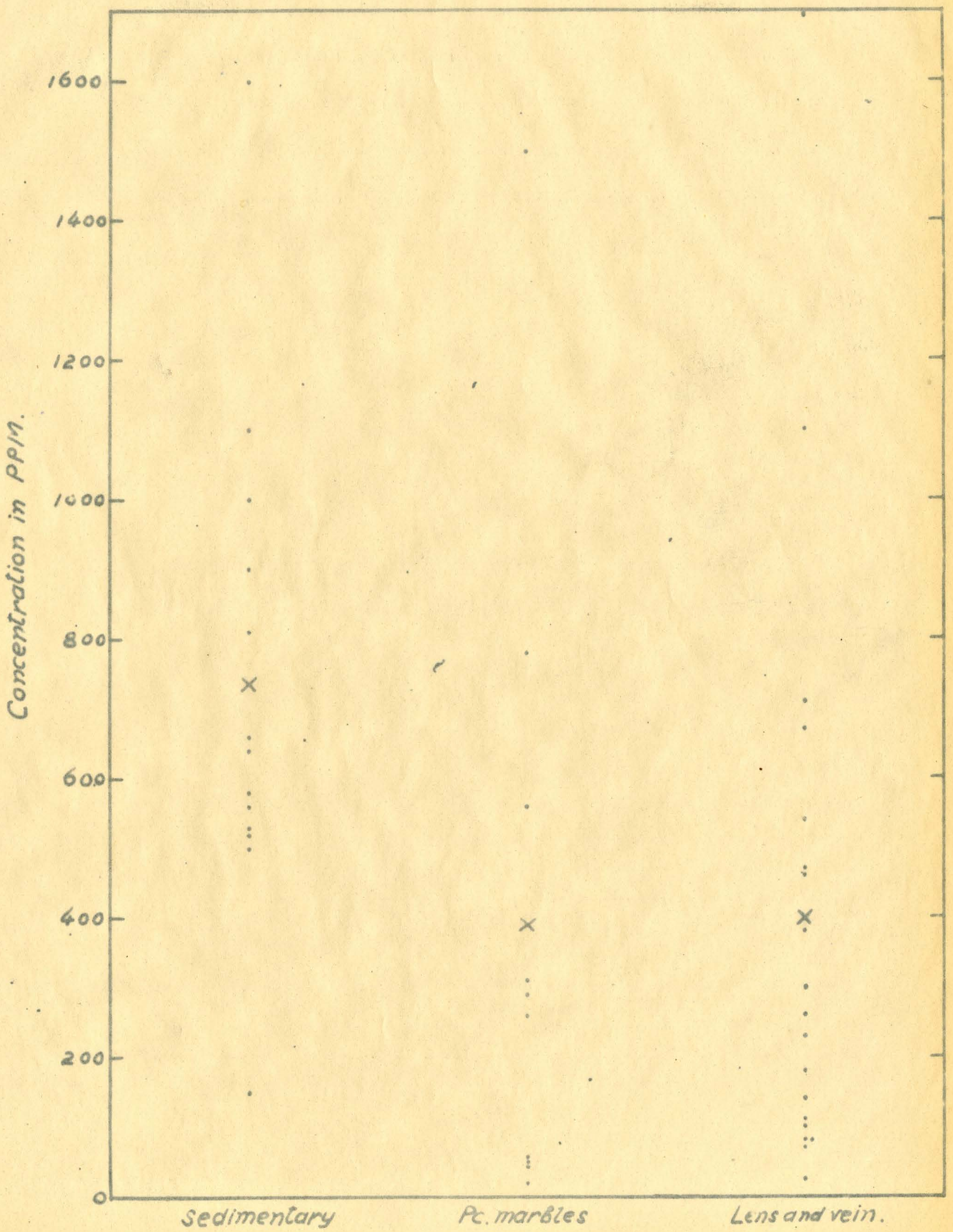


Fig. 7. Distribution of Si in various carbonates.

(x - group average)

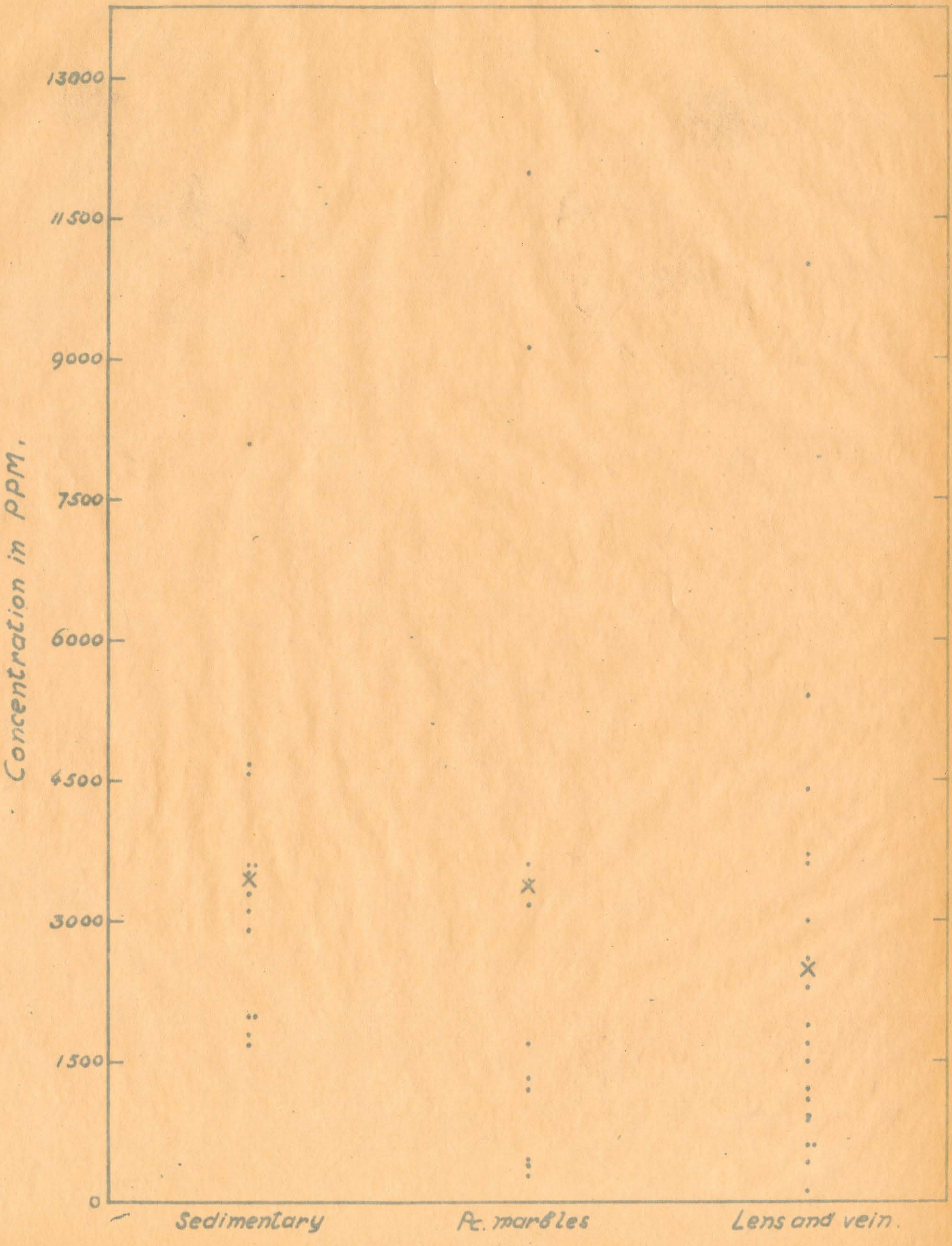
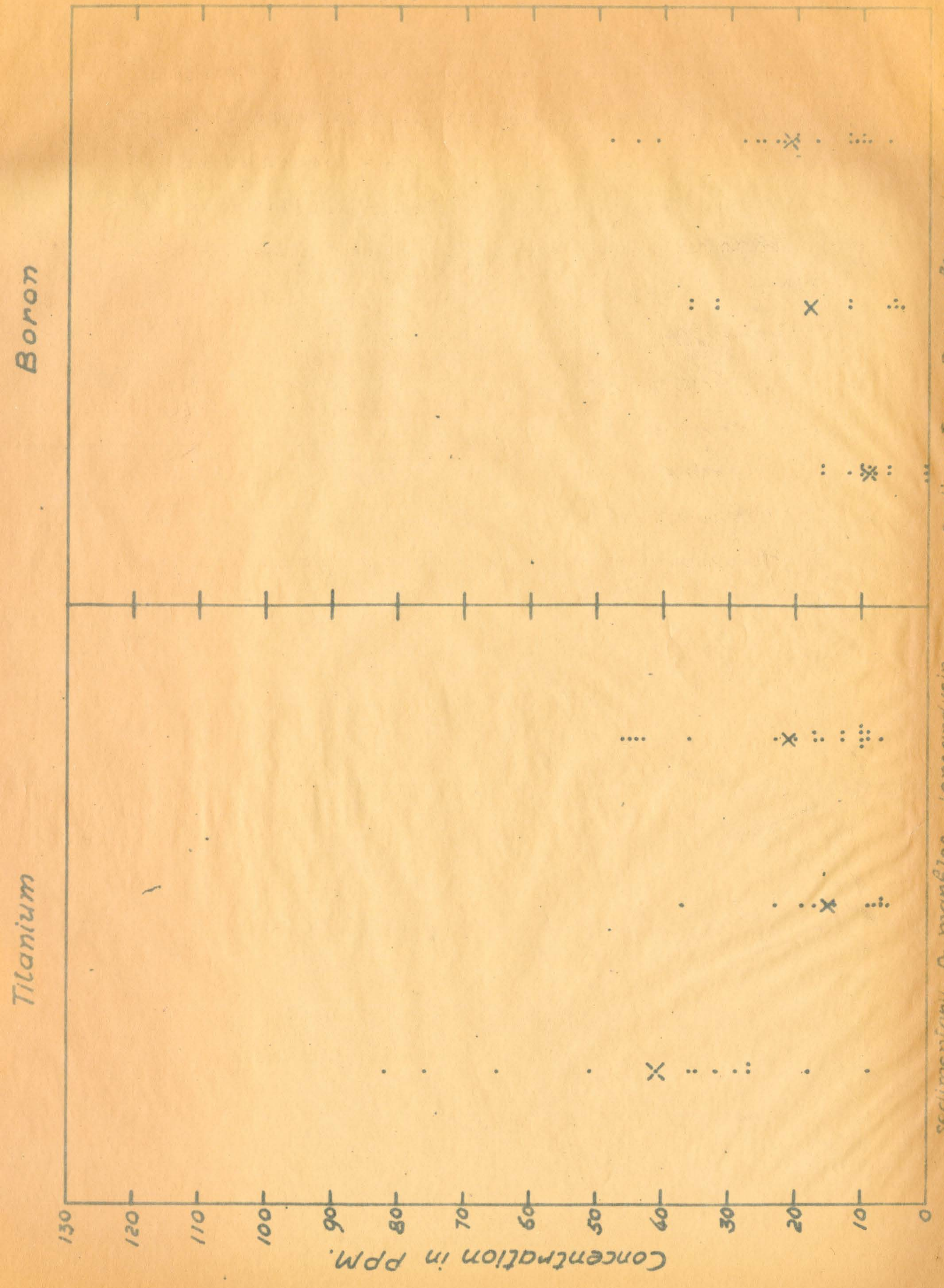


Fig. B. Distribution of Ti and B in various carbonates.
(x - group average)



APPENDIX IV

CORRELATION OF SOME ELEMENTS
DISTRIBUTION IN VARIOUS
CARBONATES

Fig. 1. Plote of Mn vs. Fe concentrations in various carbonates ; (x)- sedimentary , (·)-Pc. marbles , (⊙)Lens and vein carbonates.

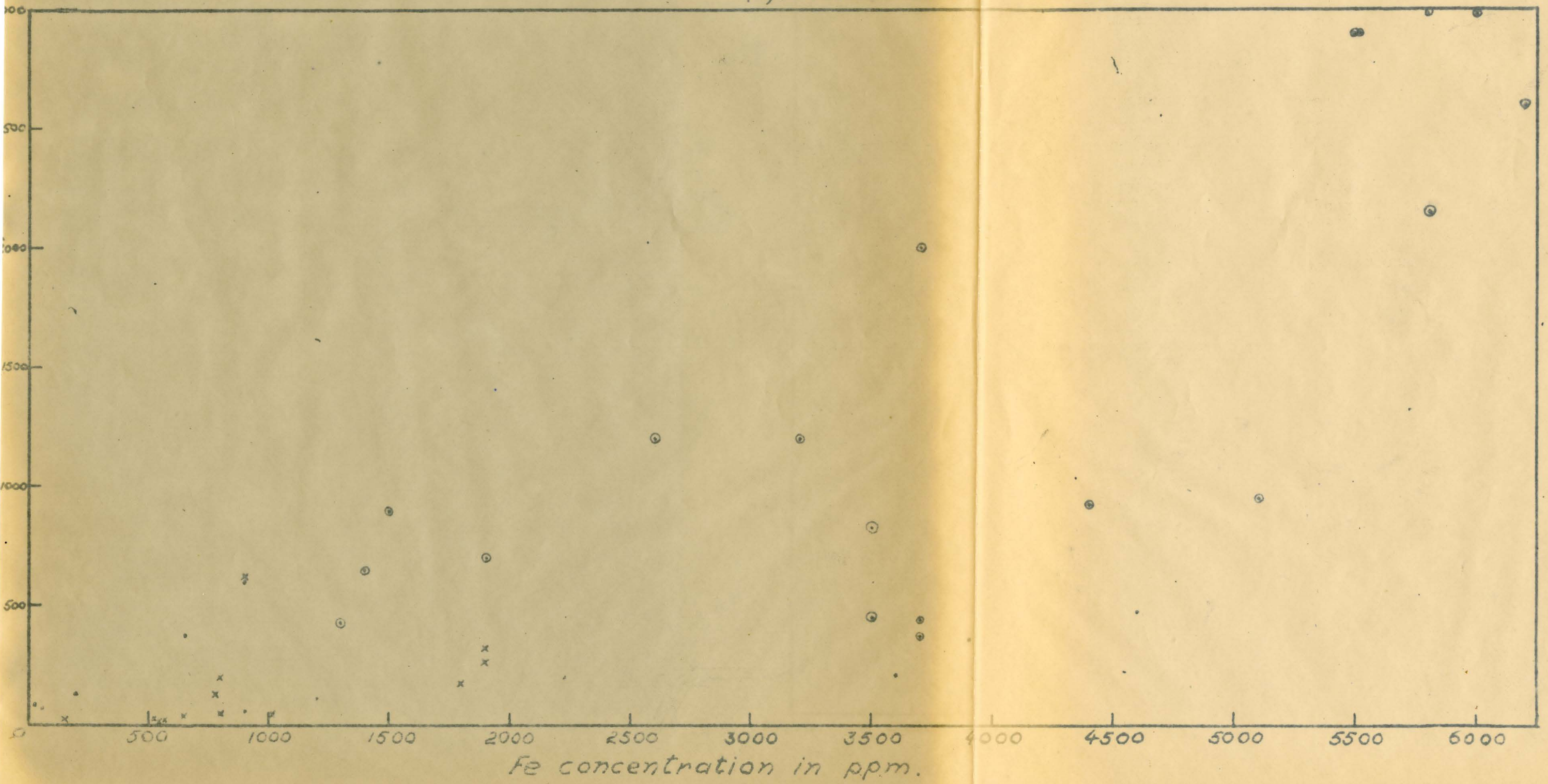


Fig.2. Plote of Ba vs. Sr in various carbonates; (x)-sedimentary, (·)-Pc.marbles, (◎)-Lens and vein carbonates.

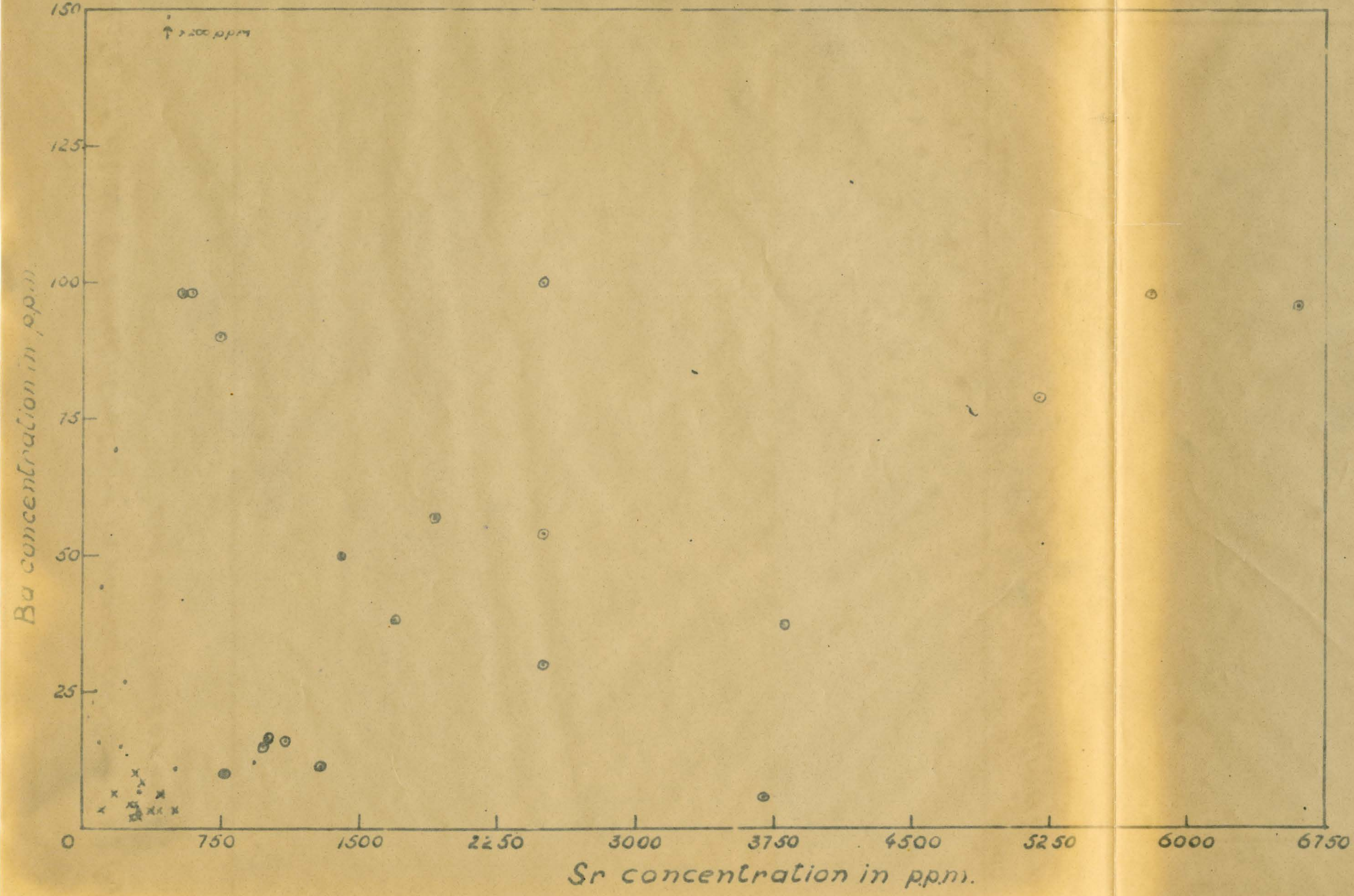
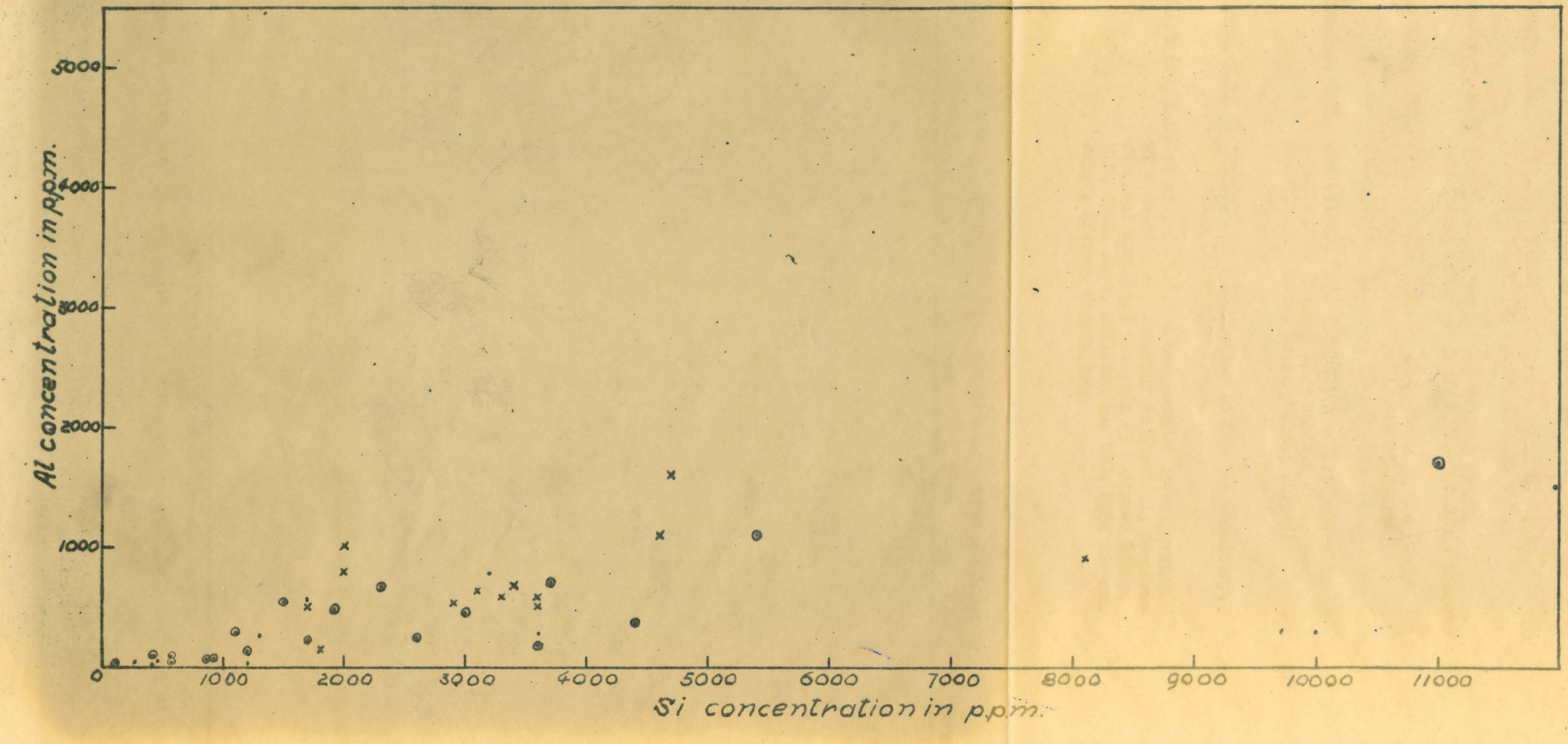


Fig.3. Plote of Al vs. Si concentrations in variou carbonates; (x)-sedimentary, (·)-Pc. marbles, (⊙)-Lens and vein carbonates.



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