

DISTRIBUTION OF SULPHUR, IRON, COPPER AND ZINC  
IN MODERN MARINE SEDIMENTS OF MUD BAY,  
CRESCENT BEACH, B.C.

by

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## ABSTRACT

The purpose of this thesis was to investigate the pattern of distribution of some elements in the tidal flat environment at Mud Bay near Crescent Beach, B.C. Samples of sediment were collected in a regular pattern over the bay. Quantitative chemical analyses of the samples were made for acid-soluble copper, zinc, lead, and molybdenum. The same samples were analysed spectrochemically for iron and sulphur. The results of the analyses were plotted on base maps and contoured. It was found that there was a definite pattern of sedimentation. Because of the shallow depth of water at high tide and the bay's sheltered aspect, deposition of finer-grained material occurred near shore. In slightly deeper and more exposed parts of the bay fine-grained material was winnowed leaving coarse-grained sediment. Most of the elements showed a definite pattern of distribution. Sulphur, copper, and zinc showed a tendency to concentrate in finer-grained materials. Iron, in the form of magnetite, was deposited with coarser-grained materials near river mouths and exposed parts of the bay. Lead values were too low to permit conclusions regarding its distribution. Molybdenum concentrations were below the detection level of the method of chemical analysis. No attempt was made to determine the form in which the elements were present nor to determine the reason for their concentration other than to suggest the most obvious possibilities.

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# TABLE OF CONTENTS

	Page
CHAPTER I. STATEMENT OF THE PROBLEM . . . . .	1
CHAPTER II. PHYSIOGRAPHY AND GEOLOGY . . . . .	3
<u>GENERAL CONDITIONS</u> . . . . .	3
<u>PHYSIOGRAPHY AND GEOLOGY OF CRESCENT BEACH AREA</u> . .	4
Surface Geology . . . . .	5
Source of Metals and Sulphur . . . . .	7
CHAPTER III. SAMPLING PROCEDURE . . . . .	9
CHAPTER IV. SEDIMENTATION . . . . .	11
<u>DISTRIBUTION</u> . . . . .	11
<u>COMPOSITION OF THE SEDIMENTS OF MUD BAY</u> . . . . .	14
CHAPTER V. ANALYTICAL PROCEDURE . . . . .	15
<u>PROBLEMS OF CONTAMINATION</u> . . . . .	15
Contamination in the Laboratory . . . . .	15
Inter-sample Contamination . . . . .	15
<u>SULPHUR ANALYSIS</u> . . . . .	16
Accuracy of Sulphur Analyses . . . . .	18
Reproducibility of Sulphur Analysis . . . . .	18
<u>IRON ANALYSIS</u> . . . . .	20
Reproducibility of Iron Analysis . . . . .	21
<u>COPPER ANALYSIS</u> . . . . .	21
Reproducibility of Copper Analysis . . . . .	22
<u>ZINC ANALYSIS</u> . . . . .	23
Reproducibility of Zinc Analysis . . . . .	24
<u>LEAD ANALYSIS</u> . . . . .	24
<u>MOLYBDENUM ANALYSIS</u> . . . . .	25
CHAPTER VI. RESULTS . . . . .	26
<u>SULPHUR</u> . . . . .	26
<u>IRON</u> . . . . .	27
<u>COPPER</u> . . . . .	28
<u>ZINC</u> . . . . .	29
<u>LEAD</u> . . . . .	30
<u>MOLYBDENUM</u> . . . . .	30
<u>ORGANIC MATERIAL</u> . . . . .	31
CHAPTER VII. DISCUSSION . . . . .	32
<u>SEDIMENTATION</u> . . . . .	32
<u>SULPHUR</u> . . . . .	32
<u>IRON</u> . . . . .	33
<u>COPPER</u> . . . . .	34
<u>ZINC</u> . . . . .	36
<u>LEAD</u> . . . . .	37
CHAPTER VIII. CONCLUSIONS . . . . .	38

## TABLE OF CONTENTS

	Page
SELECTED BIBLIOGRAPHY . . . . .	39
APPENDICES	
APPENDIX A. <u>SAMPLE ANALYSES</u> . . . . .	40
APPENDIX B. <u>MEAN VARIATION OF ANALYSES</u> . . . . .	43
APPENDIX C. <u>TABLE OF FORMATIONS</u> . . . . .	44

## CHAPTER I. STATEMENT OF THE PROBLEM

There has been much discussion and speculation during the past few years concerning the apparent concentration and orderly zoning, with respect to the former shorelines, exhibited by certain elements in some ore deposits that may be of syngenetic origin (Garlick, 1953; White, 1954). The purpose of this thesis was to determine if copper, zinc, lead, molybdenum, iron and sulphur had a random or zonal distribution with respect to shorelines or river mouths in recent sediments of a littoral, tidal flat environment of deposition. The reasons for any such concentrations and the form in which the elements occur lies beyond the scope of this thesis.

Mud Bay, at Crescent Beach, B.C., is the site of present-day tidal flat deposition of unconsolidated, interbedded, and intermixed mud, silt, and sand. There is no obvious source of heavy metals and sulphur to cause their deposition in large amounts in the sediments of Mud Bay. It was suggested that if favourable conditions exist at Mud Bay that would produce large concentrations of heavy metals and sulphur from a source rich in these elements then a smaller concentration might occur from a source poorer in these same elements. There would have to be, however, a sufficient concentration of metals being transported into the bay to allow a "saturation" and deposition under favorable conditions. A method of analysis is required of sufficient sensitivity to

measure copper, zinc, sulphur, iron, lead, and molybdenum in their small background concentrations. Significant increases in concentration would then be detected. Mud Bay was chosen as a model for this type of research because of its ready accessibility and because it exhibits the desired environment of deposition. The bottom sediments were easily sampled because of the shallow depth of water at high tide.



## CHAPTER II. PHYSIOGRAPHY AND GEOLOGY

### GENERAL CONDITIONS

Mud Bay, on the east side of Boundary Bay, is 4 miles north of the British Columbia - Washington border,  $1\frac{1}{2}$  miles west of Highway #99 and immediately north of the village of Crescent Beach, B.C.

Access to the north, or Colebrook, side of Mud Bay was gained by access roads through private property to a dyke at the edge of the bay. On the south side, access was gained to the bay from Blackie Spit at Crescent Beach.

Mud Bay consists of approximately four square miles of mud flats of very low relief, cut only by the meandering river channels of the Serpentine and Nicomekl Rivers and a small stream which enters the bay from the north. The mud flats slope gently seaward to a depth of about 12 feet below high water level at the junction of the Nicomekl and Serpentine Rivers. Mud Bay becomes completely submerged by a 10-foot tide, and it is possible to row a small boat back and forth across the bay on an 11-foot to 12-foot tide. The marshy areas at the edges of the bay are completely covered during the high winter tides in excess of 13 feet.

The Serpentine and Nicomekl Rivers enter Mud Bay at its northeast and southeast sides, respectively. The Nicomekl River has a yearly average discharge of 115 cfs.

A maximum of 985 cfs. was recorded December 9th, 1956 and a minimum of 5 cfs on November 16, 1955 and February 3, 1956.<sup>1</sup> No data were available for the rate of flow of the Serpentine River but it appears to be somewhat less than from the Nicomekl River. During an incoming high winter tide the flow of river water is reversed for at least a mile-and-a-half up the rivers and during outgoing tides the Nicomekl River flows seaward with sufficient velocity to make rowing against it difficult in the narrow reaches.

#### PHYSIOGRAPHY AND GEOLOGY OF CRESCENT BEACH AREA

Department of Mines and Technical Surveys Paper #57-5 entitled "Surficial Geology of the New Westminster Map Area, British Columbia" by J.E. Armstrong is the only source of good published information pertaining to the geology of the area surrounding Mud Bay.

Mud Bay, and the area adjacent, forms a small part of the Coastal Trough which is called the Fraser Lowland (Armstrong, 1957, p.2). The Mud Bay area includes part of the broad Fraser Valley delta to the north and low hills of 300 to 350 feet elevation to the northeast, east, and south between which lie the valleys of the Serpentine and Nicomekl Rivers.

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<sup>1</sup> Data were obtained from B.C. Game Commission, Fisheries Research group. Measurements were made at the edge of the tidal influence.

The headwaters of the Nicomekl River arise on Fern Ridge and flow northerly to the vicinity of Langley where the river changes its direction to westerly and flows to the southeast side of Mud Bay. The headwaters of the Serpentine River arise between the Surrey and North Langley Highlands and flow in a southerly direction. At a point about 4 miles upstream from the river mouth, direction of flow changes to westerly to the northeast side of Mud Bay. The lower portion of the Nicomekl and Serpentine Rivers occupy the north and south sides, respectively, of the same broad valley. The valleys occupied by the Nicomekl and Serpentine river are not believed to be formed by stream erosion but are thought to be former embayments of the sea (Armstrong, 1957, p.3).

#### Surface Geology

The exposed sediments of the Mud Bay area are all of Pleistocene and Recent age. The broad, flatter portions of the Nicomekl-Serpentine Valley and that part of the Fraser Delta lying to the north of Mud Bay consist of part of the Salish group of Post-Glacial sediments composed of:

- (1) Fraser Floodplain deposits and
- (2) Richmond Delta deposits.

Here the Salish group is composed of lowland peat and variable thicknesses of silty clay, clayey silt, and sandy silt. The Salish group is still in the process of formation.

The uplands of Surrey, North Langley, and Crescent Beach expose on their flanks the following formations (Armstrong, 1957,):<sup>2</sup>

- (3) Nicomekl "silt"; of deltaic and floodplain origin consisting of sand, silt, and gravel.
- (4) Colebrook gravel; of deltaic, channel and floodplain origin, composed of gravel and sand.
- (5) Surrey till; of glacial origin, composed of sandy to silty till and minor stratified drift.
- (6) Cloverdale sediments; of marine origin, composed of silty clay, clayey silt, silt and clay with minor sand and gravel.
- (7) Sunnyside sand; of littoral and beach origin, composed of medium to coarse sand resting on Cloverdale sediments.

The tops of the Surrey, North Langley and Crescent Beach uplands consist primarily of:

- (8) Newton Stony clay; of glacio-marine origin, composed of stony, clayey silt, poorly sorted till-like mixtures, minor clayey silt, silty clay and sand.

Fern Ridge, lying to the south and southeast of Langley, exposes Cloverdale and Sunnyside sands on its flanks as do the

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<sup>2</sup> See Appendix C, Table of Formations.

uplands of Surrey, North Langley and Crescent Beach. Fern Ridge, however, exposes sediments on its top which differ from those of the other uplands and are described as follows (Armstrong, 1957, figure 1):

- (9) Whatcom deposits; of glacio-marine origin, approximating the Newton stony clay in composition.
- (10) Abbotsford outwash; composed of glacio-fluvial deposits which consist of recessional outwash sand and gravel.

The source of the bulk of the sediments deposited in Mud Bay are from within the drainage area of the Serpentine and Nicomekl Rivers and from fine detritus carried by long-shore drift, at periods of high tide and favourable wind direction, from the more exposed portion of Boundary Bay to the west. Minor amounts of detritus are contributed by the small stream entering the north side of Mud Bay and relatively insignificant amounts by material washed off the banks of the bay. The material making up the sediments of Mud Bay is probably almost entirely composed of debris derived from the formations of Pleistocene and Recent age listed above and in the Table of Formations of Appendix C.

#### Source of Metals and Sulphur

Possible sources of metals and sulphur are as follows,

the first two probably being the most important:

- (1) Surficial sedimentary deposits.
- (2) Ocean water and ocean borne sediments.
- (3) Cultural sources, on Serpentine-Nicomekl  
Valley farms.

### CHAPTER III. SAMPLING PROCEDURE

A grid was set up by locating azimuth lines about 1000 feet apart and by collecting samples along these lines at intervals of approximately 1000 feet. Sampling was done from a row boat which was kept on the north-south line by a line of sight and by signals from an assistant on shore. When the location of the station was in doubt checks were made by compass resection. The distance from shore was measured with an artillery range finder. Such sample locations are not precise but are believed to be accurate within 50 yards. It was not always possible to row precisely on the north-south line. The accuracy of the range finder decreases with the square of the distance so that the location of stations farther from shore may be in greater error. However, for purposes of this thesis, it is felt that the stations were located with sufficient accuracy (see Map #1, Sample Locations).

Sampling was done during the period from September 16th to December 5th, 1960 by means of a corer 8 feet in length. The corer consists of an aluminum tube of 1 inch inside diameter fitted with a steel cutting edge and a graduated wooden dowel plunger with a leather and aluminum packer to draw in and eject the core. Duplicate samples were taken at each station. The cores were ejected from the corer into separate polyethylene bags and labelled.

The samples were then taken to the laboratory, transferred to clean aluminum plates and dried in a Fisher electric oven at 105°C. During the drying process portions of the samples, especially the finer fractions, consolidated. The lumps of sample were broken up and the grains separated in an agate mortar, care being taken not to crush the constituent grains. The samples were then passed through a 200 mesh screen. The +200 and -200 fractions were weighed and stored separately in labelled polyethelene bags. The -200 fraction (less than 0.74 mm) represents a grain size slightly larger than the upper size limit of silt (E.W. Lane, 1947, p.937). The coarse fraction was not used for analysis.

The fine fraction of each sample was analysed for extractable copper, zinc, lead and molybdenum using quantitative methods of chemical analysis. An X-ray spectrochemical analysis of the fine fraction was made to determine the total amount of iron and sulphur.

The results of the chemical and X-ray spectrochemical analyses were then plotted on base maps of scale 1 inch to 1000 feet and were contoured at appropriate intervals.



## CHAPTER IV. SEDIMENTATION

### DISTRIBUTION

Map #2 shows a marked concentration of finer sediment, of 75 and 80% -200 mesh size, around most of the shoreline of Mud Bay. To the southwest, in the more exposed and deeper portions of the bay, the concentration of fine-grained material decreases to less than 20%. At the mouth of the Nicomekl River, and at the north flank of Blackie Spit, at Crescent Beach, the concentration of sediment of -200 mesh size may be as low as 1 to 3%. Several "ridges" of coarse material are evident crossing the mud flats in east and/or northeast directions. The most conspicuous "ridge", in two branches, leads to the mouth of the Serpentine River. Others may represent former channels crossing the mud flats.

The mud flats have very slight relief, the maximum being only 3 or 4 feet with the exception of the deeper river channels. The slope from the shore to the edge of the mud flats is very gentle but steepens at its outer edge. The bottom depths, at high tide, vary along the north-south lines from 1 or 2 feet at the north shore to a maximum of 6 feet, with the exception of river channels, at the south ends of the lines.

The area adjacent to the shoreline of Mud Bay is one of little deposition and reworking of the sediments.

Evidence for this was found when tracks made from an initial attempt to walk across the flats were still visible two weeks later. The tracks had been covered by tides at least once a day. The near-shore portions of Mud Bay are covered with water only during periods of flood tides in excess of 9 feet, thus making possible only intermittent deposition near shore. The small flow of water from the Serpentine and Nicomekl Rivers suggest a relatively small amount of material is brought into the bay from the land. Probably of greater significance would be the amount of material that is moved along the shore at periods of high tide by restricted current and wave action with deposition of fine material occurring in the very sheltered and shallow waters of Mud Bay.

Mud Bay is sheltered from the direction of the prevailing winds that veer from southeast to southwest. Because of its sheltered condition and very shallow depth even at high tide, there is little opportunity for near-shore wave action to rework the sediments. The finer-grained fraction is not differentially removed, leaving coarser-grained materials behind as has happened in the deeper and more exposed part of the mud flats farther from shore. To seaward the sediments are submerged for longer periods of time to sufficient depth for wave action to become effective as a sorting agent. Map #2 shows the distribution of sediments that occurs under the conditions outlined above.

It should be noted that Map #2 gives only an approximation of the size- distribution of sediment in Mud Bay. It was obvious that there is some interbedding of coarse-grained and fine-grained sediments in parts of the bay. The sampling corer passed much more easily through the finer-grained than coarser-grained material. A casual inspection of the core for interbedding was often misleading because the fine-grained material tended to smear over the coarser-grained. The percent fine-grained versus coarse-grained material is dependent on the length of core where interbedding occurs. It was not possible to sample to exactly the same depth at every station. The lengths of the core recovered ranged from 2 inches to greater than 18 inches, the average length being 8 inches. When about 8 inches of core was drawn into the core barrel the friction of the core against the inside of the barrel was sufficient to cause further sediment to be pushed aside as the barrel was forced downwards.

The concentration of finer-grained material would be slightly greater than shown on the map because of a tendency to lose finer material during the sieving process. As no estimates were made of the relative losses of fine-grained and coarse-grained material, the resulting percent -200 mesh size probably is somewhat low.

COMPOSITION OF THE SEDIMENTS OF MUD BAY

A binocular microscopic examination of the 200 mesh fraction of a few of the samples indicates they consist chiefly of angular quartz grains, and some feldspar fragments that show cleavage and multiple twinning. Fragments of plutonic rock, scattered grains of altered mica, (muscovite), and magnetite are also present. Shell fragments of present-day molluscs and crustaceans occur in many samples. The fine-grained fraction appears to contain the same minerals. No clay minerals were recognized and if present must be in very small amounts. The bulk of the clay-size materials probably consists of rock flour of glacial origin.

Microscopic examination of grain thin sections prepared from the coarse fraction of a few samples were made to confirm the binocular microscopic examination. The samples were found to consist chiefly of angular quartz grains and fragments of plutonic rock. Smaller amounts of multiple-twinned and untwinned feldspar were present. The rock fragments were composed mainly of feldspar and quartz with muscovite, (sericite), epidote, and chlorite (chloritized biotite). Composite fragments also present are composed chiefly of minute grains of quartz. Some composite fragments are composed of feldspar with sericite and chlorite.

## CHAPTER V. ANALYTICAL PROCEDURE

### PROBLEMS OF CONTAMINATION

#### Contamination in the Laboratory

The main source of contamination is laboratory equipment, particularly the set of screens used on this project. These screens were used by a number of other students for projects including sieving sediment from other areas and for sizing samples of high-grade ore. There are also other sources of contamination in the laboratory such as paint particles, tap water, and dust. With care these can be controlled. Samples were re-analysed when contamination was suspected and/or when values were anomalously high. Laboratory contamination could be almost eliminated if a complete set of laboratory equipment, including stainless steel screens, were used exclusively for the project.

#### Inter-sample Contamination

Inter-sample contamination could occur during the coring process by incomplete cleaning of the core barrel between samples. The core barrel was cleaned thoroughly between each station and the first core cut at each station was discarded. The second and third cores at each station were retained for analysis.

Inter-sample contamination may occur also during the sieving process. The same screens were used for all samples, screens being carefully cleaned before each sample was sieved. It is not possible to get the screens absolutely clean as there will always be some extremely small grains adhering to the screen and rim as well as larger fragments stuck in the screen openings. Some contamination from this source was unavoidable and is recognized as contributing to error in the final analytical results. However, if one considers the relatively large quantity of material that passes through the screen for each sample (15 to 50 grams); the small concentrations of the elements present in even the richest sample; and the rather small difference in concentration between them, this source of error becomes practically negligible.

#### SULPHUR ANALYSIS

The fine-grained fraction of each sample was analysed for sulphur spectrochemically using an X-ray fluorescent spectrometer with special adaptations for elements of low atomic number. These special adaptations include (Molloy, Kerr, 1960):

- (1) ammonium dihydrogen phosphate crystal,
- (2) helium gas for the instrument path,
- (3) methane-argon gas (P 10) and a
- (4) linear amplifier for the flow proportional counter.

The instrument settings were as follows:

X-ray unit 50 KV and 20 ma

Flow proportional counter 1400 V

Baseline 10 V

Window 4 V

Time constant 4 sec

Scale factor 100

Count duration 30 sec

Sulphur was determined using a peak-to-background count method and a calibration curve prepared from synthetic standards. At least two counts were taken for peak and background with their average value being used. The standards were prepared by adding native sulphur in increments of 0.5% to one of the samples until counts were obtained for  $x$  plus 0% to  $x$  plus 3% sulphur, where " $x$ " is the amount of sulphur originally present in the sample. A calibration chart was prepared by plotting sulphur content as the ordinates and number of counts peak-to-background in 30 seconds as abscissa. The increase in the number of counts for a given increase in sulphur content is linear. It was possible, therefore, to project the calibration curve back to the ordinate for zero counts peak-to-background corresponding to 0% total sulphur and recalibrate the ordinate for percent total sulphur. Figure #1 is the resulting calibration curve for sulphur. Values were then obtained for the percent total sulphur for each sample from this calibration curve. Percent sulphur content was plotted

and contoured on Map #3. This shows the sulphur distribution in Mud Bay and represents total sulphur less that lost in the form of  $H_2S$  gas.

### Accuracy of the Sulphur Analysis

Sulphur in the form of  $H_2S$  gas is not included in the analysis because it is lost from the samples during coring and during their preparation for analysis. The spectrochemical analyses for sulphur, because of the loss of  $H_2S$ , do not represent the total sulphur content of the sediments.

The method of comparing the relative number of counts from peak-to-background is not as accurate as the method of comparison of the areas which lie under the  $K\alpha$  peak for sulphur. More accurate, but more time consuming, methods could have been used, but were not warranted because of the unknown amount of loss of  $H_2S$  gas.

### Reproducibility of the Sulphur Analysis

Figure #2 (a), (b), and (c) shows graphically the reproducibility of the X-Ray spectrochemical method for sulphur. Figure #2(a) is the sulphur  $K\alpha$  curve for sample #31. Figure #2(b) is the same curve for a different portion of sample #31 and Figure #2(c) is a re-run of #2(b). The results indicate that the reproducibility of separate portions of the same



sample falls within the statistical variation obtained by rerunning the same portion of a sample. However if many such tests were made the above statement might not be proven valid. It was found also that the difference in the number of counts obtained from a crushed and uncrushed sample appear to fall within the variation of the number of counts obtained for a given sample and would not appreciably affect the overall pattern of concentration. A crushed portion of sample #43 gave a decrease in the number of peak-to-background counts as compared to the uncrushed sample. The difference between the two peak-to-background counts was 235 for the crushed and 250 for the uncrushed sample. A difference in background counts caused the discrepancy. The peak counts for both were approximately the same,<sup>3</sup> the difference in the two readings represent about 0.05% sulphur. However, if a great number of samples were tested in the above manner it might be found that crushing could significantly alter the value of the peak counts.

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3	Sample	Background counts	Peak counts	Difference
	#43 uncrushed	177	427	250
	#43 crushed	196	235	<u>235</u>
			Discrepancy	15 counts

### IRON ANALYSIS

The samples were analysed for iron by using an X-Ray fluorescent spectrometer with a lithium fluoride crystal. A similar procedure to that of sulphur was used. The iron content is proportional to the difference in the number of counts in a 15-second period between the iron K $\alpha$  peak and the background. A calibration curve was made from standards. These standards were prepared by taking a sample low in iron and adding Fe<sub>2</sub>O<sub>3</sub> to it in 0.5% Fe increments from x plus 0% to x plus 2.5% Fe; where "x" is the amount of Fe present in the original sample. There is a linear relationship between the iron concentration and the number of counts obtained. As for sulphur, it was possible to calibrate the ordinate for total iron content by projecting the calibration curve back to the ordinate for zero counts. Figure #3 is the resulting calibration curve for iron. Instrumentation was as follows:

X-Ray unit 40 MV and 20 ma

Threshold 15.5 V

Flow proportional counter 900V

Time constant 2 sec

Scale factor 12800

Li F analysing crystal

The values plotted and contoured on Map #4 represent the total concentration of iron at each station.

## Reproducibility of Iron Analysis

Figure #4(a) and (b) illustrates graphically the excellent reproducibility of results for iron by using different portions of the same sample. This test was repeated several times with excellent reproducibility. Figure #4(a) and (c) shows graphically the increase in the peak height observed when the sample is finely crushed in an agate mortar. Using the method of the difference in the number of counts peak-to-background, it was found that the peak counts were substantially increased by grinding the coarser-grained samples thus making a significant increase in the total iron detected in the coarser samples. For this reason all the samples were finely ground in an agate mortar before analysis.

## COPPER ANALYSIS

The fine-grained fraction of each sample was analysed for copper by the quantitative method devised by R.E. Delavault (Warren and Delavault, 1949). The procedure is briefly as follows:

Two grams of minus 200 mesh sample, previously heated for 3 hours at 1150° F in a Heavy Duty Electric Furnace, were digested at boiling point for thirty minutes in 30 ml 1 N H<sub>2</sub>SO<sub>4</sub> then made up to 40 mls with distilled water (Warren, Delavault, 1956). A 5 ml aliquot of the clear fluid was evaporated to dryness after 1 ml of 20% hydroxylamine hydro-

chloride solution was added. Two drops of 3 N HCL were added to the residue and the residue was washed into a "shaking cylinder" with distilled  $H_2O$  and made up to 10 ml. Approximately 5 mg of ascorbic acid added and after checking the acidity, the solution was titrated to a greyend point with "dithizone" dissolved in  $CCl_4$  (60 mg/l). The results of the analyses were plotted and contoured on Map #5. The values plotted on Map #5 represent the amount of copper which was soluble in  $H_2SO_4$  and is a fraction of the total amount of copper present.

#### Reproducibility of Copper Analysis

The first thirty analyses for copper are likely to be less accurate than the remainder because the author was unfamiliar with the analytical method. For this reason the first thirty samples were re-analysed for copper and zinc. The results of the analyses are listed in Appendix B. At first glance these results are extremely discouraging. The mean variation for copper content is 12 ppm which is higher than was expected. The variation of low values, of course, is much less than 12 ppm, whereas, with higher concentrations the variations are much higher than 12 ppm. It is worthy of note that the repeat analyses for copper gave consistently higher values. If the second set of analyses were plotted on the map instead of the first the observed concentrations on Map #5 would be more pronounced. Therefore, in spite of the

fact that the variation in results is larger than desired, the overall pattern obtained for the distribution of copper is considered valid.

### ZINC ANALYSIS

The samples were also analysed chemically for zinc according to the procedure devised by R.E.Delavault, (Warren, Delavault, 1949).

A 1 ml aliquot of the clear solution from the "shaking cylinder" used in the copper analysis was transferred to a second "shaking cylinder". One ml of 20% hydroxylamine hydrochloride solution and 0.5 ml of acetate buffer were added. The pH of the solution was checked with congo red paper to ensure the solution was basic. The solution was then titrated to a grey end point with "dithizone" dissolved in  $\text{CCl}_4$  as for the copper determination. A standard of known zinc content prepared and titrated to an end point was used in calculating the amount of zinc in the samples. The results of the analyses were plotted on Map #6. The value plotted for zinc represents the amount of zinc which was soluble in  $\text{H}_2\text{SO}_4$  and is only a fraction of the total amount of zinc.

## Reproducibility of Zinc Analysis

The first thirty samples, which are likely to be greatest in error, were re-analysed for zinc to check the reproducibility of the laboratory technique and the method of analysis. The results are tabulated in Appendix B. The mean variation is about 13 ppm with the variations in the lower concentrations somewhat less and in higher concentrations somewhat more. Most of the repeat analyses are lower than the initial analyses. The reproducibility of the analyses was much poorer than was hoped. However, the variation obtained does not appear to be sufficient to alter appreciably the overall pattern of the zinc concentrations shown on Map #6.

## LEAD ANALYSIS

The fine-grained fraction of each sample was analysed for lead using the quantitative chemical method developed by R.E. Delavault (Warren, Delavault, 1961 in press).

A 5 ml aliquot of the clear fluid from the 40 ml  $\text{H}_2\text{SO}_4$  digested sample was transferred to a "shaking cylinder". Approximately 5 mg of ascorbic acid was added with 1 ml citrate solution and a sufficient number of drops of ammonia to ensure a pH of 8.5 - 9.0. Then 0.5 ml of cyanide solution was added and, using a burette, 0.5 ml of dithizone dissolved in chloroform was added and colors compared to a set of standards. Samples higher in lead required addition of more

dithizone until they could be matched to one of the standards. The results of the lead analyses are listed in Appendix A. Lead values were too low and the range too small to warrant plotting and contouring on a map. The value listed in Appendix A for lead represents the amount of lead soluble in  $H_2SO_4$ , which is an unknown fraction of the total lead content.

### MOLYBDENUM ANALYSIS

The samples were analysed for molybdenum using another method of analysis devised by R.E.Delavault (Warren, Delavault, 1953).

Another 5 ml aliquot from the 40 ml  $H_2SO_4$  digested sample for each station was transferred to a test tube where 1.5 mls of the cyanate solution and 1 ml of stannous chloride were added then 0.5 ml of isopropyl ether was added then polyethylene corks were inserted. The test tubes were inverted and shaken vigorously then allowed to set with cork end up. The presence of molybdenum causes an amber coloration in the ether.

The concentration of molybdenum was below the level of detection in the sediments of Mud Bay.

## CHAPTER VI. RESULTS

The results of the analyses show a definite pattern of sedimentation and an orderly distribution of sulphur, iron, copper, and zinc in Mud Bay. No conclusions could be drawn regarding distribution of lead and molybdenum. The pattern of sedimentation and the distribution of metals and sulphur are discussed in the following sections.

### SULPHUR

The sulphur content of the sediments of Mud Bay range from less than 0.5% to greater than 2.0%, with most values falling between 0.5% and 1.0%. Map #3 shows that the higher concentrations of sulphur occur near the shoreline especially in the east and northeast sides of the bay. The values decrease with distance from shore, the lowest values occurring in the areas showing the highest percentage of coarser-grained materials. In general, the distribution of sulphur reflects fairly closely the size distribution of the sediments. A close comparison of Map #2 and #3 reveals many places where fine-grained sediments have lower values than those which are slightly coarser-grained.

The form of the sulphur in the Mud Bay sediments is not known. The sulphur determined does not include the  $H_2S$  gas lost during the process of sampling, drying, and sieving.



The smell of  $H_2S$  was comparatively strong in the finer-grained sediments or muds near shore. The total sulphur content of all samples is probably somewhat higher as a result of loss of  $H_2S$  gas, such loss being greater near shore where the smell of  $H_2S$  was most noticeable. Therefore the contrast between sulphur values near shore and off shore would be even more pronounced than appears on Map #3.

### IRON

Map #4 gives the results of the sample analyses for iron. The values for iron range between 1.5% and 3.8%, with most of the values falling between 2 and 3%. Unlike the distribution of sulphur, iron shows no marked concentration along the shoreline. If Map #4, Percent Iron, is compared to Map #2, Percent Sediment Less than 200 Mesh, it is apparent that iron is relatively concentrated in the coarser-grained sediment.

Magnetite is present in the samples, which probably accounts for most of the iron. Magnetite, deposited at the river mouths with the relatively coarse-grained material, as a result of decrease of current velocity, probably accounts for the main iron pattern on Map #4. The high iron content at station #81 also could be explained in part in the same way because this station is approximately at the point where the Serpentine River enters the bay at periods of low tide.

The concentration at station #81 and at station #60 at the northwest side of the bay may be the result of winnowing action of waves and currents removing finer-grained material leaving coarser-grained material relatively rich in magnetite. These stations are beyond the approximate edge of the sheltered and shallower part of the bay where finer-grained material is relatively abundant. It is not possible to explain, in this way, the high iron content at stations #11 and #106, at the north side of the bay. Sample #106 appeared to be streaked with reddish-brown iron oxide, possibly oxidized rubbish discarded in the bay. The high concentration of iron at station #11 remains unexplained. It should be noted that the total range in iron content is comparatively small.

#### COPPER

Map #5, Concentration of Copper in Parts Per Million, shows extremely well-marked concentrations of copper in the finer-grained sediments and near the mouths of the rivers. Values of copper greater than 20 ppm are considered anomalous. Higher concentrations of copper are not restricted to the finer-grained sediments but occur even in the area of coarsest grain-size at the mouth of the Nicomekl River. Scattered, anomalous values occur in oyster beds near the center of the bay. The distribution of copper may depend to some extent upon the ratio of salt and fresh water in and near the river mouths. Again, the presence of bacteria that can precipitate

copper might affect the copper pattern. Thus, it cannot be concluded that grain-size of sediment, proximity to shores and river mouths, organic content, or sulphur content are the only factors affecting the distribution of copper.

### ZINC

Map #6, Zinc Concentration in Parts Per Million, has values ranging from as low as 18 ppm to a high of 109 ppm. Zinc values greater than 60 ppm are considered anomalous. The highest values show some tendency to concentrate close to the shoreline. An exception is the isolated high value at station #56 near the middle of the west side of Mud Bay. As both samples taken at this station gave high zinc values the anomaly is apparently valid. A second and larger zone of anomalous values occurs in the vicinity of station #3 north of the center of the bay. Three stations located on this anomaly suggest that it too is valid. Comparing Map #5 for copper with Map #6 for zinc it will be apparent that the highest copper value is a few ppm higher than the highest zinc value. The lowest zinc value is a few ppm higher than the lowest copper value. The overall concentration of zinc in Mud Bay is somewhat higher than the overall concentration of copper. The higher zinc values extend farther out into the bay. Possibly this reflects the greater solubility of zinc. Copper, on the other hand, appears to be much more concentrated near

shore. The ratio copper:zinc are shown on Map #7. Most of the stations have ratio less than unity. The ratio show a tendency to increase shoreward. An exception is the area of slightly higher copper in the center of the bay where there are oyster beds.

### LEAD

Lead content of Mud Bay is small, generally less than 1 or 2 ppm. Stations #44 and #45, however, give values of 20 and 7 ppm, respectively. These values are difficult to explain by contamination because two sets of samples were processed separately, the second a few weeks after the first.

The overall concentration of lead is so low that valid conclusions cannot be made regarding its distribution in Mud Bay. The slightly higher values occur with finer-grained sediments whereas values less than 1 ppm show some tendency to occur where the sediment is coarser-grained.

### MOLYBDENUM

Molybdenum concentrations were below the level of detection in Mud Bay.

ORGANIC MATERIAL

The distribution of organic material in the sediments of Mud Bay was not determined. However, it is probable that non-living organic material, because of its low specific gravity, would tend to accumulate with the finer-grained sediments.

## CHAPTER VII. DISCUSSION

### SEDIMENTATION

Mud Bay is an environment of slow, tidal flat deposition. Deposition of sediment can take place only at the time of high tide when the bottom is covered for only short periods of time. The sources of sediment are formations of Pleistocene and Recent Age in the drainage areas of the Serpentine and Nicomekl Rivers and, because of the bay's sheltered aspect, sediment may be brought from the west by longshore currents.

The pattern of sedimentation in Mud Bay is the reverse of the normal pattern of coarse-grained materials near shore and finer-grained farther from shore. The finer-grained material is concentrated near shore in the shallower portion of the bay and coarser material is deposited farther away from shore and in more exposed parts of the bay where wave action and long shore currents are sufficiently active to winnow the fine-grained material.

### SULPHUR

Sulphur shows a pronounced concentration near shore with the finer-grained sediments and non-living organic material. The odor of  $H_2S$  was most noticeable in the finer-grained sediments, therefore, sulphur probably would show an even more

pronounced concentration in the finer near-shore sediments had  $H_2S$  been included in the analyses.

The source of the sulphur in the sediments of Mud Bay is probably from ocean water and partly from sulphur in organic material which derived its sulphur from the ocean. Ocean water contains 0.088% sulphur in the readily accessible form of  $SO_4^{-2}$ , as compared to 0.052% sulphur in magmatic rocks<sup>4</sup> in the less accessible form of sulphide compounds (Goldschmidt, 1954, p. 523-531).

The form in which the sulphur occurs in the sediments is not known.  $H_2S$  can be formed by reduction of sulphate to sulphide by heterotropic bacteria and by decomposition of proteins (Goldschmidt, 1954, p. 529). Sulphur also could be in the form of free sulphur produced by oxidation of  $H_2S$  by sulphur bacteria.<sup>5</sup> Goldschmidt points out that the above process occurs in tidal flats and in shallow bays where water movement is restricted and organic material is abundant. The presence of bacteria also may play an important role in the precipitation of sulphides of various metals.

### IRON

Iron has a tendency to concentrate in the coarser-

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4 V.M. Goldschmidt, 1954, cited from F.W. Clarke and H.S. Washington, 1924.

5 Goldschmidt, V.M., 1954, cited from ZoBell, 1939.

grained sediments near the mouths of rivers and in the more exposed parts of the bay. The samples contain abundant magnetite which probably accounts for most of the iron. It is believed that magnetite, a mineral of high specific gravity, would be concentrated with the coarser-grained materials as indicated by the distribution of iron on Map #3.

The magnetite probably is derived from the formations within the source-area of the sediments of Mud Bay. It seems unlikely that 2 or 3% iron could be derived from ocean water, which has an iron content of only 0.001 ppm (Goldschmidt, 1954, p. 664). Iron, therefore, is considered of allogenic rather than diagenic origin. A small amount of iron in the sediments could be present in the form of hydrotroilite,  $\text{FeS} \cdot n\text{H}_2\text{O}$ , which forms in an environment poor in oxygen and rich in organic material (Goldschmidt, 1954, p. 530). Rankama and Sahama, (1950, p. 672-676), discuss other means of iron deposition in water such as gels of marine oxidates derived from weathering solutions of continental origin. Some of the iron may be concentrated by such processes, but allogenic magnetite appears to be the dominant form of iron in Mud Bay.

#### COPPER

The amount of copper in the sediment of Mud Bay shows a tendency to increase in the area of finer-grained sediments that have a noticeable  $\text{H}_2\text{S}$  odor and in areas adjacent to the mouths of rivers. The copper values on Map #5 are the values



of soluble copper and represent fractions of the total amount of copper present. The form of the copper at Mud Bay is not known.

Goldschmidt suggests that copper ions are carried by mud particles in rivers to the ocean where a number of possibilities arise. He emphasizes the affinity of organic material for copper. Copper may be assimilated by living organisms or the presence of  $\text{SO}_4^{-2}$  and organic matter may lead to bacterial formation of  $\text{H}_2\text{S}$  and the deposition of copper as a sulphide (Goldschmidt, 1954, p. 185, 182-183). The Permian shale at Mansfeld, Kupferschiefer, with a copper content of 2.9%, was cited as an example of marine deposition of copper under reducing conditions in sulphide bearing mud from stagnant, anaerobic, bottom waters (Goldschmidt, 1954, p. 185).

The immediate source of copper could be from river water, ocean water, and/or organic material. G.A.Riley found in the Mississippi estuary that the highest copper values occurred in waters of relatively low salinity. His analyses indicated that copper was speedily removed from sea water, probably by organic material. The range of dissolved copper was 0.001 to 0.015 ppm in fresh water (Goldschmidt, 1954 p.186).

The average copper content of ocean water is a subject of debate. Earlier values given by Sverdrup, Johnson, and Fleming are of the order 0.001 to 0.01 ppm, whereas Wattenburg in 1943 gives much lower values ranging from 0.0002 to 0.001 ppm (Goldschmidt, 1954, p. 186).

## ZINC

Zinc shows a tendency to concentrate in the finer sediment. Higher concentrations of zinc extend farther out into the bay than similar copper concentrations. The zinc values plotted on Map #6 represent soluble zinc extractable by "digestion" in  $H_2SO_4$  and is only a fraction of the total zinc present.

The form of the zinc in the sediments at Mud Bay is unknown. Like copper, zinc may be concentrated in considerable amounts in the form of sulphides under reducing conditions. At Mansfeld, in the Kupferschiefer, the highest zinc values occur where sulphur is present but not in the form of  $H_2S$  produced by decaying organisms. Hence, at Mansfeld, the beds rich in zinc do not coincide with the copper-rich beds (Rankama and Sahama, 1950, p. 713). This peculiarity of zinc could account in part for the differences in the patterns of copper and zinc at Mud Bay.

The average concentration of zinc in sea water has not been definitely established. Analyses prior to 1943 indicated a high concentration of zinc in sea water, but Wattenburg gives an average concentration of only 0.0005 ppm zinc (Goldschmidt, 1954, p 265). Possible sources of zinc at Mud Bay are (1) river waters, (2) ocean water, (3) organic material, and (4) water-borne clay particles. It is not known which possible source contributes the most zinc at Mud Bay.

LEAD

The concentration of lead in the sediments of Mud Bay is much too low to permit conclusions to be drawn regarding its distribution. There is a tendency for the slightly higher values to occur in the finer-grained near shore.

Goldschmidt suggests that lead could be precipitated as a sulphide in a manner similar to copper in a reducing environment in the presence of  $H_2S$  (Goldschmidt, 1954, p.403).

## CHAPTER VIII. CONCLUSIONS

It is concluded from this study that copper, zinc, iron, and sulphur have rational rather than random patterns of distribution in the modern sediment of Mud Bay. The reasons for the existence of such patterns presently are unknown. Many questions remain concerning the form, source, and mode of deposition of these elements.

In view of the modern trend to accept syngenetic hypotheses for many base-metal deposits in sedimentary rocks, it seems imperative that the mechanisms of such genetic theories be rigorously investigated. Further research into such matters would spread widely through fields of geochemistry, bacteriology, and zoology. Among other lines of research it would include study of the following:

- (1) Average and seasonal variation of trace element content of rivers, sediments, and marine waters.
- (2) Methods of analysis that give the total amount of elements that are chemically available for formation of ore minerals.
- (3) Distribution of organic materials in the sediments and their effects on the deposition of trace elements.
- (4) Bacteria and their effects on the deposition of trace elements.

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## APPENDIX A

SAMPLE ANALYSES

No	-200%	Cu ppm	Zn ppm	Cu/Zn	Pb ppm	Mo ppm	S%	Fe%
1	61	56	100	.56	1	<1	1.00	2.47
2	36	19	101	.19	1	<1	.75	1.54
3	34	17	100	.17	1	<1	.85	2.49
4	12	14	51	.28	1	<1	.73	2.67
5	46	27	95	.28	<1	<1	.65	2.49
6	65	48	49	1	1	<1	.80	2.49
7	51	14	69	.20	1	<1	.45	2.50
8	36	15	86	.17	1	<1	.71	2.37
9	23	26	51	.51	1	<1	.76	2.56
10	20	34	52	.66	<1	<1	.85	2.52
11	53	27	52	.52	<1	<1	1.12	2.81
12	49	9	78	.12	2	<1	.66	2.52
13	34	5	43	.22	2	<1	.83	2.55
14	27	9	60	.15	1	<1	.79	2.58
15	27	9	60	.15	1	<1	.56	2.48
16	23	11	43	.26	1	<1	.45	2.52
17	59	11	43	.26	1	<1	.70	2.33
18	66	11	60	.18	1	<1	.62	2.37
19	32	12	60	.20	1	<1	.80	2.78
20	52	29	43	.67	1	<1	.83	2.56
21	60	15	43	.35	1	<1	.87	2.54
22	47	15	52	.29	1	<1	.93	2.59
23	42	33	50 <sup>★</sup>	.66	2	<1	.95	2.81
24	51	41 <sup>★</sup>	81	.51	2	<1	.88	2.56
25	46	24	43	.53		<1	1.00	2.63
26	56	34	60	.57	1	<1	.76	2.70
27	68	35	60	.58	1	<1	.92	2.81
28	61	31	77	.40	2	<1	.73	2.48
29	49	31	52	.60		<1	.70	2.56
30	49	35	77	.45	2	<1	.84	2.50
31	70	82	69	1.20	<1	<1	1.10	2.50
32	44	29	70	.41	2	<1	.89	2.83
33	45	56	104	.54	2	<1	.90	2.56
34	55	11	44	.25	1	<1	.96	2.64
35	70	15	70	.22	2	<1	2.09	3.74
36	72	9	52	.17	2	<1	2.11	2.70
37	50	16	78	.20	2	<1	.99	2.82
38	72	16	70	.23	1	<1	1.24	2.76
39	75	18	56 <sup>★</sup>	.32	2	<1	1.10	2.77
40	69	20	72 <sup>★</sup>	.29	2	<1	1.29	3.25
41	75	24	61	.39	2	<1	.91	2.95
42	32	36	52	.69	1	<1	.59	2.76
43	52	13	52	.25	1	<1	.56	2.58
44	18	15	58 <sup>★</sup>	.26	20 <sup>★</sup>	<1	.63	2.58
45	39	7	52	.13	7 <sup>★</sup>	<1	.66	2.50

★ Indicates a re-analysis using the duplicate set of samples

No	-200%	Cu ppm	Zn ppm	Cu/Zn	Pb ppm	Mo ppm	S%	Fe%
46	20	15	70	.21	3 <sup>☆</sup>	<1	.63	2.51
47	26	7	35	.20	2 <sup>☆</sup>	<1	.71	2.48
48	10	13	35	.37	1 <sup>☆</sup>	<1	.54	2.58
49	71	11	52	.21	3 <sup>☆</sup>	<1	.60	2.57
50	68	24	61	.39	2 <sup>☆</sup>	<1	.91	2.64
51	14	18	52	.35	1	<1	.70	2.83
52	29	16	35	.46	2	<1	.48	2.38
53	12	27	35	.77	1	<1	.83	3.10
54	20	9	35	.26	1	<1	.66	2.58
55	20	16	35	.46	<1	<1	.50	2.58
56	30	29	98 <sup>☆</sup>	.24	1	<1	.66	2.43
57	31	9	35	.39	1	<1	.68	2.61
58	23	13	35	.37	1	<1	.55	2.49
59	23	11	44	.25	1	<1	.83	2.93
60	16	44	52	.85	1	<1	.46	2.93
61	26	20	44	.46	1	<1	.85	2.90
62	63	10	31	.32	1	<1	.87	2.68
63	3	17	24	.71	1	<1	.25	2.73
64	10	17	37	.46	2	<1	.57	2.52
65	14	15	31	.48	<1	<1	.59	2.46
66	21	8	31	.26	<1	<1	.58	2.30
67	12	13	24	.54	1	<1	.57	2.54
68	8	18	31	.58	1	<1	.56	2.82
69	15	14	24	.58	<1	<1	.54	2.73
70	15	23	43	.54	1	<1	.64	2.52
71	14	8	31	.26	<1	<1	.58	2.45
72	6	23 <sup>☆</sup>	39 <sup>☆</sup>	.59	<1	<1	.50	2.75
73	6	33 <sup>☆</sup>	48 <sup>☆</sup>	.69	<1	<1	.62	3.87
74	3	29 <sup>☆</sup>	65 <sup>☆</sup>	.45	1	<1	.92	3.13
75	1	74 <sup>☆</sup>	55	1.34	<1	<1	.36	3.20
76	7	28 <sup>☆</sup>	55	.51	<1	<1	.56	2.81
77	9	31 <sup>☆</sup>	37	.84	<1	<1	.62	2.81
78	7	25 <sup>☆</sup>	39	.64	<1	<1	.56	2.83
79	19	6 <sup>☆</sup>	25	.24	<1	<1	.70	2.60
80	16	10 <sup>☆</sup>	25	.40	<1	<1	.61	2.78
81	11	29 <sup>☆</sup>	48 <sup>☆</sup>	.60	<1	<1	.56	3.01
82	4	40 <sup>☆</sup>	80 <sup>☆</sup>	.50	<1	<1	.31	2.87
83	8	15	31	.50	<1	<1	.48	2.76
84	10	13	25	.52	<1	<1	.34	2.50
85	26	7	18	.39	<1	<1	.75	2.49
86	13	10	18	.56	<1	<1	.41	2.70
87	8	15	18	.83	<1	<1	.40	2.95
88	14	14	31	.45	<1	<1	.47	2.65
89	15	27	56 <sup>☆</sup>	.48	<1	<1	.67	2.66
90	8	21	37	.57	<1	<1	.70	2.77
91	4	29	58	.50	4	<1	.38	2.99

☆ Indicates a re-analysis using the duplicate set of samples

No	-200%	Cu ppm	Zn ppm	Cu/Zn	Pb ppm	Mo ppm	S%	Fe%
92	12	43	75 <sup>*</sup>	.57	2	<1	.33	2.53
93	67	12	51	.24	2	<1	1.16	2.30
94	51	36	87	.41	2	<1	.71	2.88
95	41	15	65	.23	3	<1	.47	2.61
96	18	51	65	.79	2	<1	.72	2.56
97	6	55	65	.85	1	<1	.46	2.96
98	5	38	87	.67	1	<1	.53	2.64
99	13	23	80	.29	2	<1	.38	2.23
100	42	13	94	.14	1	<1	1.14	2.44
101	60	57	80	.71	2	<1	1.15	2.46
102	60	58	80	.73	4	<1	.97	2.46
103	62	40	65	.62	1	<1	1.15	2.44
104	3	51	80	.64	2	<1	.63	2.83
105	54	42	58	.73	2	<1	.78	2.40
106	51	37	72	.51	2	<1	1.18	2.84
107	64	45	80	.56	2	<1	.77	2.19
108	53	70	58	1.21	1	<1	1.45	2.61
109	65	57	80	.71	4	<1	1.35	2.93
110	70	102	65	1.57	1	<1	1.21	2.46
111	77	46	109	.42	2	<1	.88	2.5
112	80	122	101	1.20	4	<1	1.17	2.63
113	58	46	58	.79	1	<1	1.16	2.09

<sup>\*</sup> Indicates a re-analysis using the duplicate set of samples



## APPENDIX B

MEAN VARIATION OF ANALYSES

No.	Cu #1	Cu #2	Vari- tion	Zn #1	Zn #2	Vari- tion
1	56	91	35	100	76	24
2	19	35	16	101	85	16
3	17	31	14	100	59	41
4	14	23	9	51	59	8
5	27	31	4	95	76	19
6			not repeated			
7	14	19	5	69	59	10
8	15	23	8	86	59	17
9	26	35	9	51	50	1
10	34	76	42	52	59	7
11	27	51	24	52	67	15
12	9	12	3	78	59	19
13	5	16	11	43	59	16
14	9	12	4	60	42	18
15	9	14	5	60	50	10
16	11	18	7	43	50	7
17	11	12	1	43	50	7
18	11	14	3	60	42	18
19	12	18	6	60	50	10
20	29	39	10	43	59	16
21	15	23	8	43	42	1
22	15	23	8	52	50	2
23	33	39	6	93	50	43
24	14	41	27	81	50	31
25	24	33	9	43	59	16
26	34	65	31	60	59	1
27	35	49	14	60	59	1
28	31	45	14	77	67	10
29	31	33	2	52	67	15
30	35	39	4	77	59	18
31	82	113	31	69	76	7

Mean Variation 12 ppm

Mean Variation 13 ppm

# APPENDIX C

## TABLE OF FORMATIONS<sup>\*</sup>

GROUP	GLACIAL	GLACIO- FLUVIAL	GLACIO- LACUSTRINE	GLACIO- MARINE	OFF SHORE	SHORE	ESTUARINE AND DELTAIC	CHANNEL AND FLOODPLAIN
SALISH Postglacial recent							Richmond Delta (2)	Fraser Floodplain (1)
SUMAS Post-Vashon glacial-valley ice (CAPILANO)		Abbotsford Outwash (10)		Whatcom Glacio- marine(9)	Cloverdale Sediments (6)	Sunny- side Sand (7)		
VASHON Last ice-sheet glaciation	Surrey till(5)			Newton Stony Clay(8)				
EROSIONAL INTERVAL								
SEMIAMU Glaciation								
EROSIONAL INTERVAL								
QUADRA Intertill							Colebrook Gravel(4) and Nicomekl Silt (3)	
SEYMOUR Glaciation								

<sup>\*</sup> Taken from J.E.Armstrong, 1957, Figure 1 (2) corresponds to number in text

# CALIBRATION CURVE FOR SULPHUR

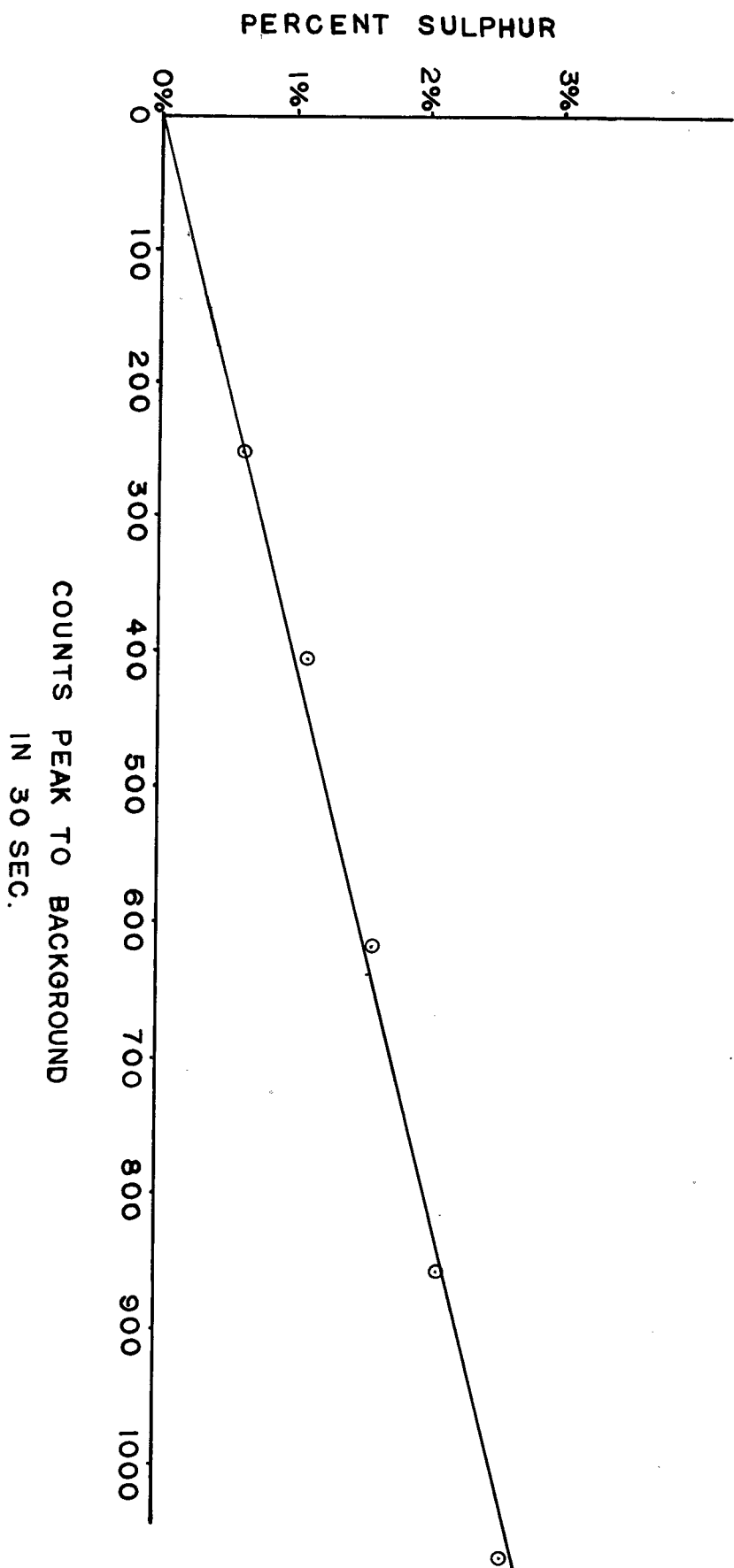


FIGURE 1

# CALIBRATION CURVE FOR IRON

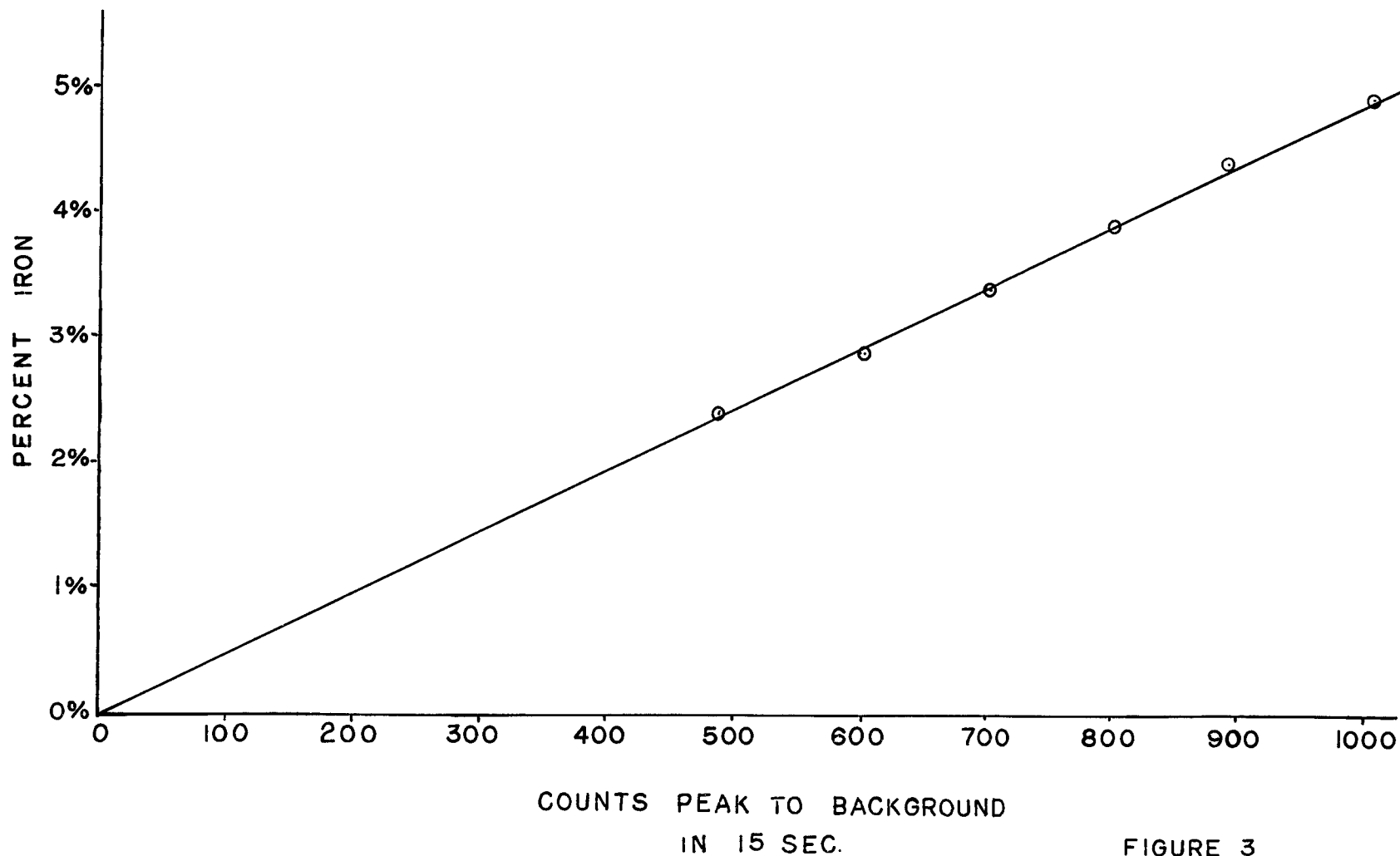
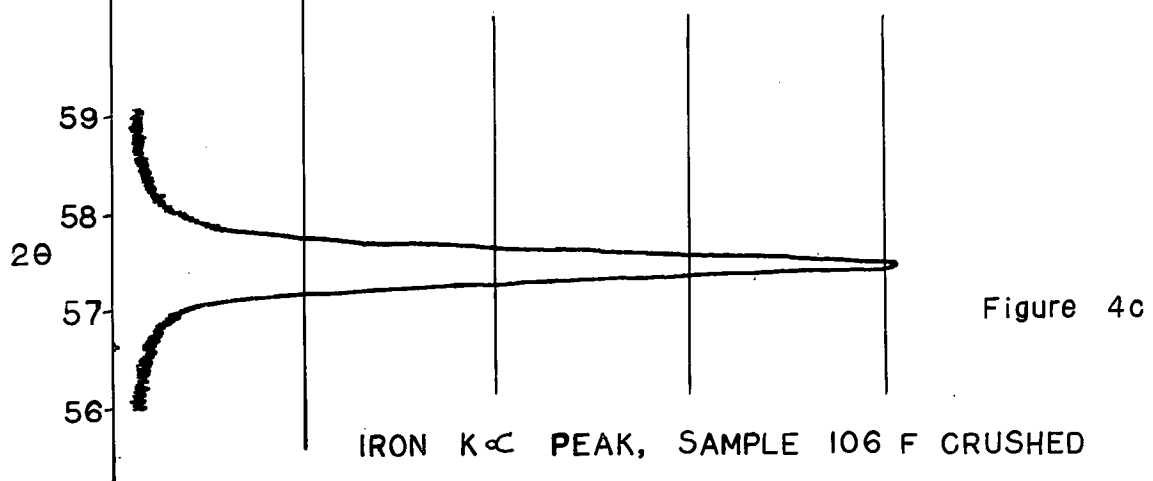
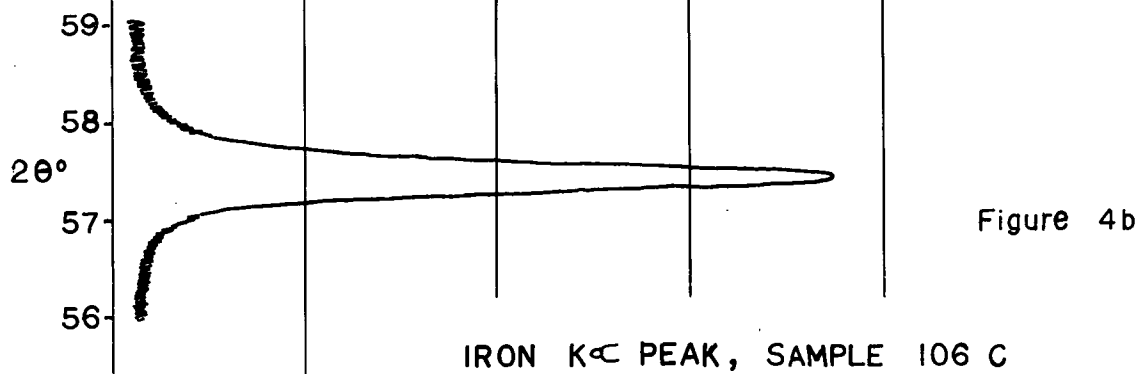
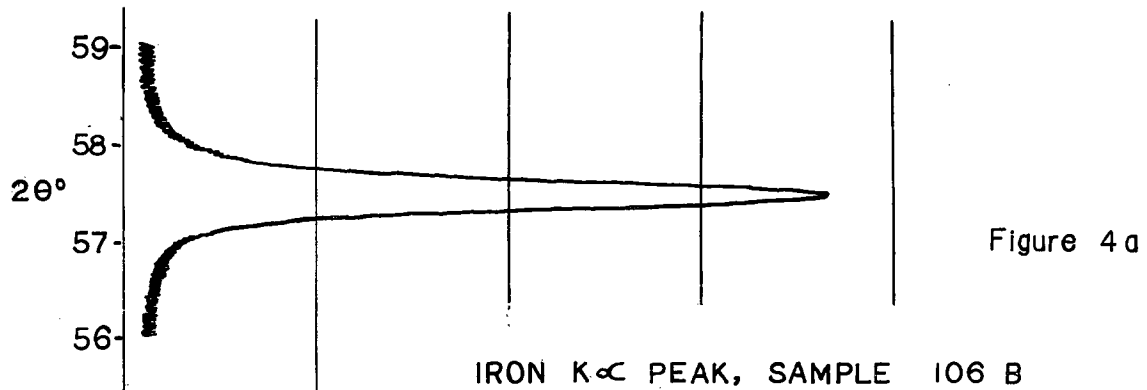


FIGURE 3

LE3 B7  
1961 A67  
N6 D4  
FIG. 3

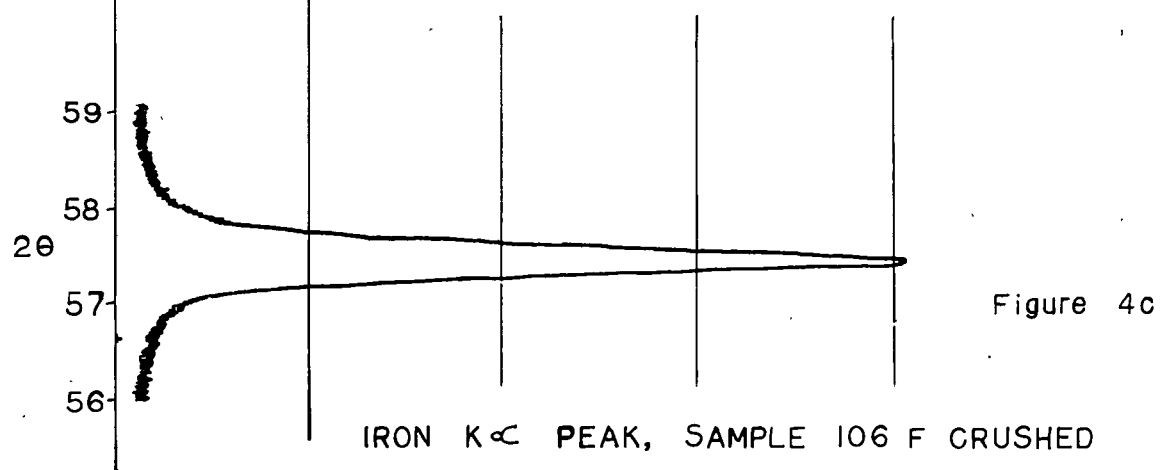
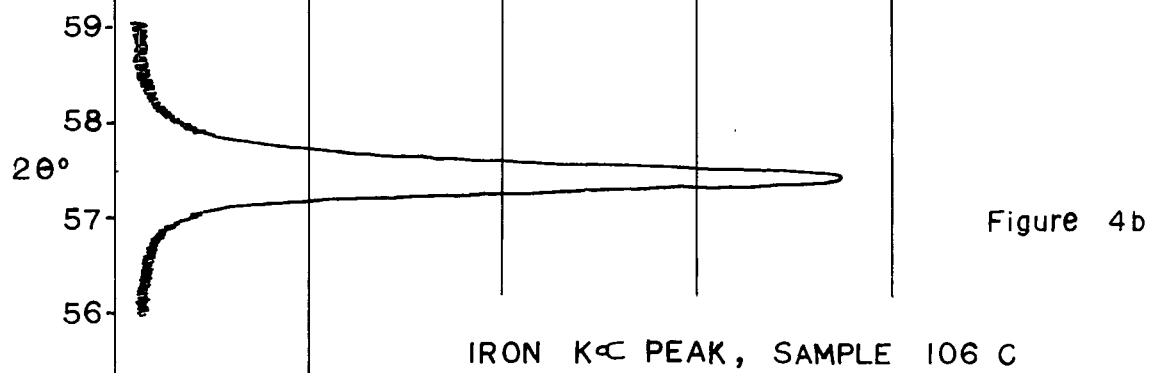
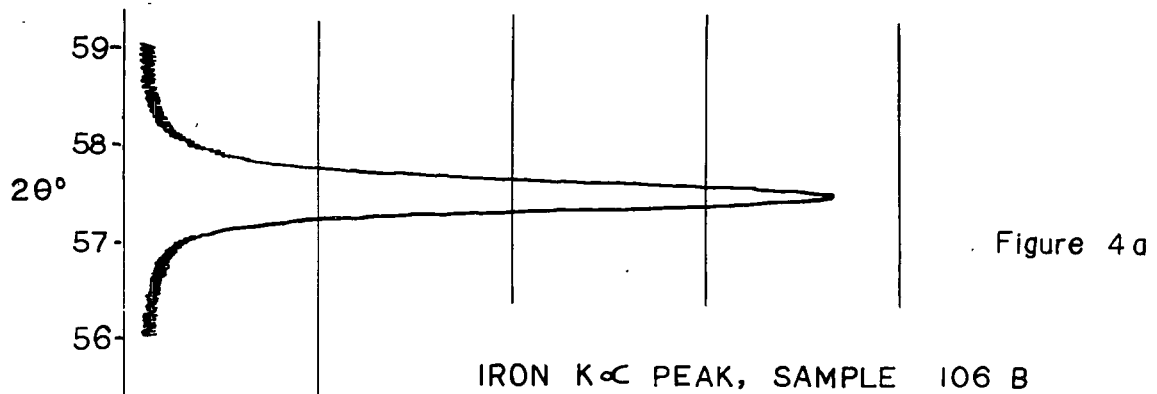
# REPRODUCIBILITY OF IRON ANALYSES



LE3 B7  
1961 A67  
N6 04

FIG. 4

# REPRODUCIBILITY OF IRON ANALYSES



# CALIBRATION CURVE FOR SULPHUR

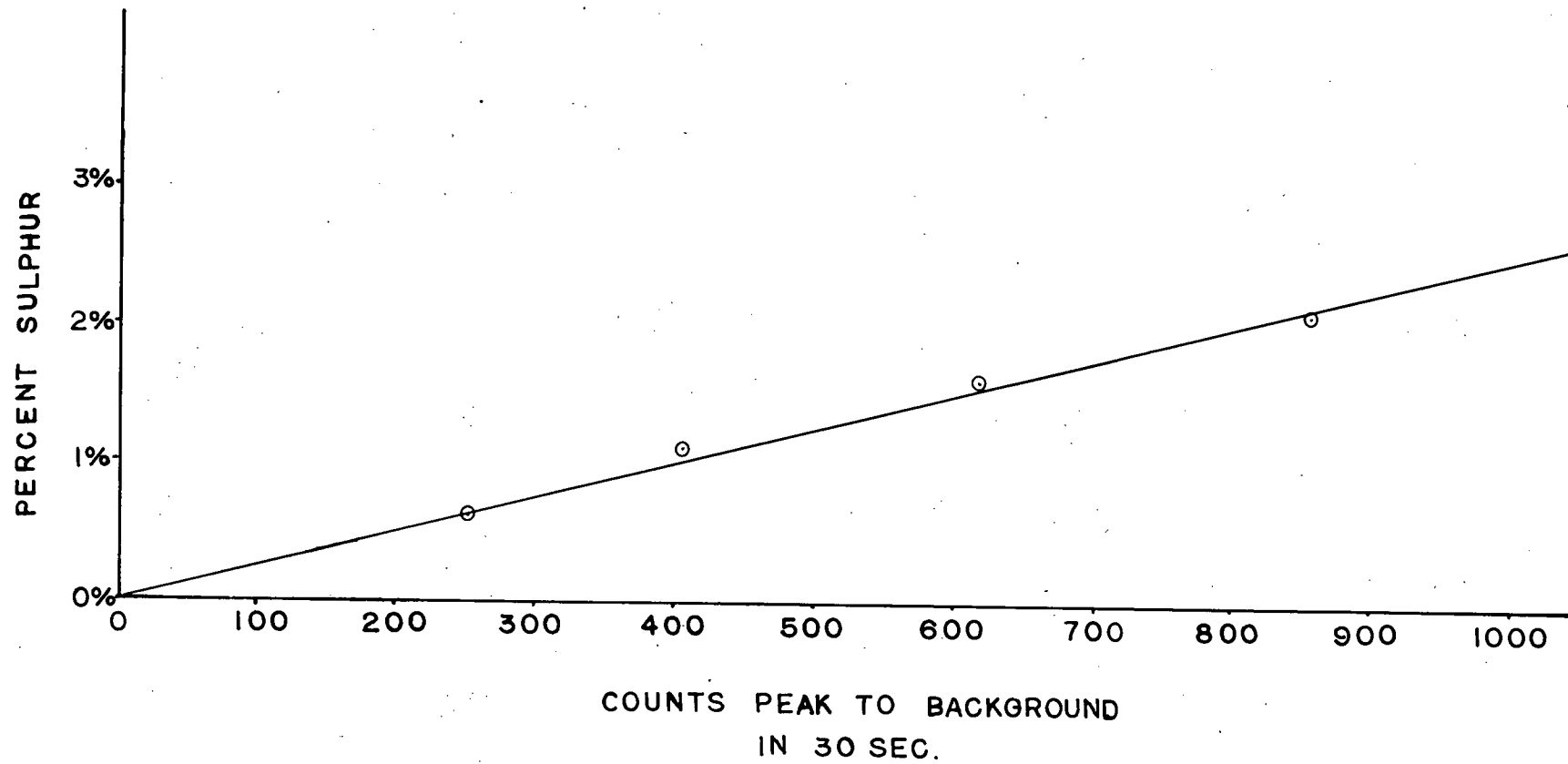


FIGURE 1

# CALIBRATION CURVE FOR IRON

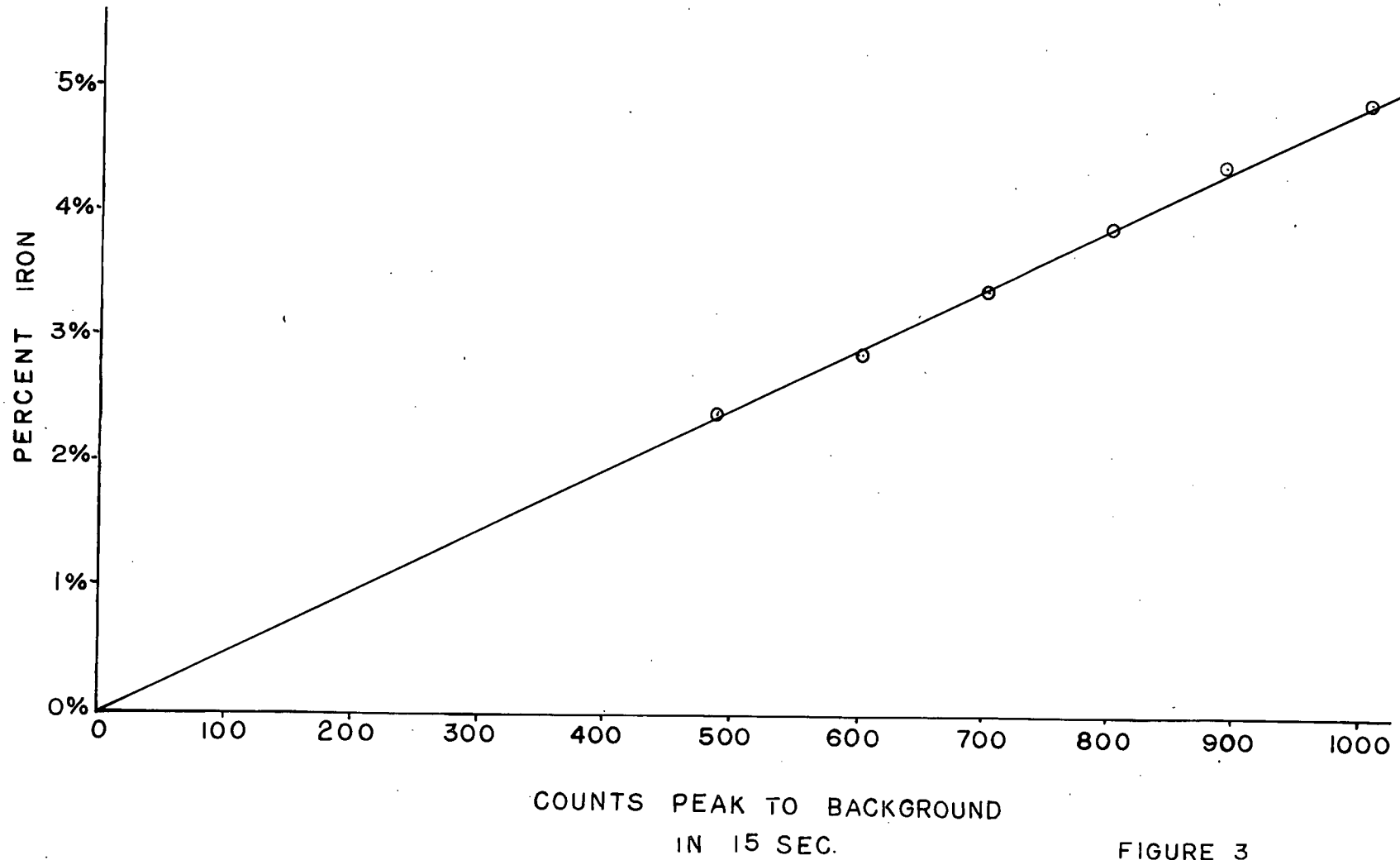


FIGURE 3